THE CHEMISTRY AND STRUCTURE OF LANTHANIDE PHOSPHATES.

A Thesis submitted for the

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by

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ABSTRACT

Tests of sintering reactions of monazite ($LnPO_4$) with sodium carbonate (expected to follow the equation $2LnPO_4 + 3Na_2CO_3 \rightarrow Ln_2O_3 + 2Na_3PO_4 + 3CO_2$) disclosed a much more complex series of products under certain conditions. In order to define these products, several new aspects of lanthanide phosphate chemistry were investigated.

Basic data for X-ray diffraction tests were obtained by preparing the orthophosphates ($LnPO_4$) of most of the individual lanthanides; the majority of them proved to have the monazite structure, for which the lattice constants were determined in each case. The measured unit-cell dimensions have been related to lanthanide cation size, and they show the expected effect of the lanthanide contraction.

Two new types of compound, both entering into the monazite sintering reaction, were characterised; they are a double sodium lanthanide phosphate, $Na_3Ln(PO_4)_2$, and a basic phosphate or "oxide phosphate", $LnPO_4, Ln_2O_3$. The characteristics of these compounds were established by a detailed study of the gadolinium and (in some areas) lanthanum compounds, for which X-ray diffraction data have been obtained. Several methods of preparation of the double phosphates, by both "dry" reactions and precipitation reactions, have been studied.

Clarification of the new intermediates allowed a satisfactory study of the sintering reactions of the phosphates with sodium carbonate, which was carried out with pure lanthanum and gadolinium orthophosphates as well as with monazite, in which the presence of cerium introduces special effects. A possible large-scale process for economic and convenient attack of monazite is proposed on the basis of the result.

Possible participation of pyrophosphates in the reactions led to a short study of gadolinium pyrophosphates. Although X-ray diffraction was mainly relied upon to characterise the compounds obtained, infra-red absorption data were used to confirm the type of phosphate group present.

The existence of an apparently new crystalline form of anhydrous sodium orthophosphate was established.

CONTENTS

DEDICATED

- to -

my husband and children.

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SECTION 1

GENERAL INTRODUCTION

1. General Introduction.

Unpublished work by A. J. E. Welch, carried out some years ago in a study of sinter reactions of minerals, disclosed that monazite (a mineral phosphate of mixed lanthanide elements and thorium) could be decomposed in a convenient and efficient manner by sintering with sodium carbonate. The reaction appeared to offer a technically useful means of recovering the lanthanides as partly separated products, and also of retaining the phosphate content of the ore in a soluble form (i.e., as sodium phosphate). These advantages lent interest to a more detailed study of the reactions involved in sintering monazite with sodium carbonate, a study originally intended to form the main part of the research project described in this thesis.

Further examination of the reaction quickly revealed important complications. In particular, under certain conditions the products included double sodium lanthanide phosphates which could not be identified with compounds described previously; it became essential, in order to clarify the monazite reactions, to prepare these double phosphates by more direct methods and characterise them both chemically and by X-ray diffraction. This essential introductory work led to other sidelines of general importance, including brief studies of certain lanthanide oxide phosphates and of the occasional appearance of pyrophosphates (rather than the better known orthophosphates) in some of the relevant reactions.

This Thesis is mainly devoted to these preliminary investigations, the results of which lead to a relatively simple and clear appreciation of the initial subject of study, namely the reaction of

monazite with sodium carbonate.

The work described falls into four main parts. The first, described in Section 2, is concerned with the preparation and properties (particularly X-ray diffraction properties and structure) of the single phosphates (of both sodium and lanthanides) entering into the subsequent work, and also with some relevant properties and reactions of the lanthanide oxides. Section 3 gives an account of methods by which sodium lanthanide phosphates can be obtained in "dry" reactions at moderately high temperature; Section 4 then introduces precipitation from aqueous solutions as a method of preparation. Throughout this part of the Thesis detailed X-ray powder diffraction data are given for identification of the compounds described. Finally, in Section 5 the sintering of sodium carbonate and monazite is considered, and a possible process for industrial attack of the mineral is proposed.

The previous literature of the focal areas of work now described is extensive, and it is considered appropriate to review it briefly within the appropriate sections rather than begin the Thesis with a lengthy literature survey.

Throughout this Thesis, where nomenclature is complex or ambiguous, individual compounds are referred to by their formulae. The symbol Ln is used to designate any lanthanide element.

SECTION 2

PREPARATION AND STUDY OF SINGLE PHOSPHATES

2. Preparation and study of single phosphates.

2.1. General techniques of X-ray and infra-red examination.

Phase analysis and structural characterisation of the solid systems were carried out by X-ray powder diffraction methods. X-ray fluorescence methods were used to a small extent to assess the proportions of individual lanthanides present in samples in which some separation (e.g. of cerium from other lanthanide elements) had taken place. Infra-red spectroscopy was also employed in some cases as a recognised means of distinguishing different types of phosphates.

X-ray Powder Diffraction Methods

X-ray powder photographs were taken by means of Newton Victor or Philips X-ray source units providing cupper, cobalt or iron $K\alpha$ radiation. Generally a Guinier-type self-focusing camera (Guinier-de Wolff camera No. II), made by Nonius of Delft was used in order to obtain well-resolved diffraction photographs in which absorption errors were minimised. Philips Debye-Scherrer cameras of 57.3 and 114.6 mm diameter were used in some cases, but they were less accurate.

The Guinier diffraction photographs were calibrated by using sodium chloride as an internal standard to avoid errors arising from stretching of the film. Samples were finely crushed and mounted on "Sellotape" attached to the Guinier camera specimen holder; a thin layer of "Vaseline" was spread over the tape to retain a sufficiently thick and even layer of the sample. The specimen was kept very thin for the samples which contained high atomic-number elements, to avoid absorption. Since some of the phosphate and oxide compounds absorbed water during a long exposure, they were covered with a piece of "Mylar" film, which does not interfere with diffraction by the

specimen. The films (Ilford "G" or Gevaert) were processed normally. They were measured by means of a vernier scale allowing line positions to be estimated to plus or minus 0.05 mm. A programmed calculator was used to calculate θ values directly from readings of line positions. The intensities were estimated visually in the usual manner by assigning an arbitrary value of 100 to the strongest line. A Joyce-Loebl double beam recording microdensitometer was also employed in cases where more accurate comparison of intensities was needed. The θ values obtained were converted to d spacings by means of appropriate tables. In appropriate cases the powder data obtained were compared with the A.S.T.M Data File. Space-group details were checked with the "International Tables for X-Ray Crystallography". (1952).

X-ray Fluorescence Methods

Some qualitative and semi quantitative X-ray fluorescence analysis was done (particularly on samples containing mixed lanthanides and thorium) with Philips equipment consisting of a PW 1010/30 X-ray generator, a PW 1520 X-ray spectrograph attachment, a PW 1050 wide-range goniometer and a PW 1051 electronic circuit panel. The samples were ground in an agate mortar to a fine powder and put into the specimen holder over a "Mylar" window. The surface of the powder was made as smooth as possible by applying gentle pressure to the compacted sample. Excitation was effected by the white radiation from a tungsten target tube. A quartz (0111, 2d = 6.6863 A) analyzing crystal was used throughout and a Geiger counter system was employed to measure the intensities of the lines present in the fluorescent radiation. The experimental conditions for qualitative analysis were: tungsten target, tube voltage 40 kV, current 18 milliamp.; goniometer scanning speed $\frac{1}{4}$ °/min.; chart speed 400 mm/hr.; ratemeter time constant 16; ratemeter scale factor 4 x 0.8. Scans were carried out usually

from $2\theta = 15°$ to $49°$; this range of angles included the L lines of the heavy elements of immediate interest, which were identified from reference tables in the usual manner. By comparing charts of several specimens, prepared under the same conditions, some semi quantitative results were obtained also. In such comparisons, individual peak heights, which may not be reproducible under the same conditions owing to instrumental errors, were not so important, because the results depended on the ratios of two or more peak heights on the same chart.

Quantitative analysis was done by counting methods, using fixed time or fixed count techniques. Comparison methods were again employed, because of the work attempt did not justify the labour of preparing special standards. The goniometer angle was preset to a selected line of the element and the counter system was adjusted to give counts in an acceptable range. Since the specimens compared were similar, the matrix effect was largely eliminated. Interference due to nearby peaks was avoided by a suitable choice of the measured lines; inter-element effects were not important in the samples examined. Background correction was applied by deducting the estimated background intensity in the neighbourhood of each peak. Both peak and background counts were taken five times and averages were taken. Duplicate determinations were also made where the concentrations of some elements were nearly identical. The 2θ values below for the peaks and the backgrounds were chosen for counting after appropriate tests.

Peak	Background
Th $L\alpha_1 + L\alpha_2$ (16.26°)	17.60°
La $L\alpha_1 + L\alpha_2$ (47.00°)	
	46.50° ("Acid residue phase")
	46.25° ("Oxide phase")
Ce $L\alpha_1 + L\alpha_2$ (45.01°)	

Measurements from the charts for neodymium and samarium were made on the following peaks:

Nd $L\gamma_1$ (32.63°), Sm $L\beta_1 + L\beta_2$ (34.80°).

Infra-red Methods

The infra-red absorption spectra of solid phosphates were obtained with a Perkin-Elmer 325 grating infra-red spectrophotometer in the 1400-200 $cm.^{-1}$ frequency region in most cases. The 4000-200 $cm.^{-1}$ region was also examined when detection of water was necessary. The potassium bromide disc technique was employed rather than the "Nujol" method because the interference of "Nujol" peaks was troublesome. Very sharp peaks were obtained in the low-frequency region by using this technique. 0.0015 g. of the very finely ground solid was mixed with a 0.15 g. of dried potassium bromide in a specimen tube; an automatic shaker was used in order to obtain a homogeneous sample. The powder was pressed into a pellet of 2 mm. thickness in a 13 mm. die by means of a laboratory hydraulic press. The pressure applied was 100000 lb. per sq. inch. The infra-red absorption spectra obtained were compared with standard data, as described in later sections of this Thesis.

2.2. Preparation and properties of Na_3PO_4, $Na_4P_2O_7$, $Na_2H_2P_2O_7$ and $NaCaPO_4$.

Trisodium Orthophosphate, Na_3PO_4

Preparation of Na_3PO_4 was necessary in order to investigate the solid-state reactions of Na_3PO_4 with $GdPO_4$ and related phosphates, and to establish the nature of intermediate compounds formed during sintering of lanthanide phosphates with sodium carbonate. The complexity of the X-ray patterns obtained showed that full X-ray data for Na_3PO_4 would be necessary for acceptable interpretation. The data originally available in the A.S.T.M. Index (Card 1-1103) were old and incomplete. Data given by Norbert (1966) reproduced more recently in the A.S.T.M. Index (Card 20-1150) appear to refer to a mixture of two different phases of Na_3PO_4. Schroder, Berk and Gabriel (1937) reported that anhydrous Na_3PO_4 has a monoclinic structure. Turkdogan and Maddocks (1952) found two crystal forms: α-Na_3PO_4, the high-temperature form, retained by quenching from 1500°C, is isotropic. Since the rate of quenching was often not rapid enough, they also obtained a β-form of Na_3PO_4 which was claimed to be hexagonal. The crystals obtained by slow cooling from 1474°C. were rather small. The X-ray data were not given, but the hexagonal structure was stated to have similar a and c cell dimensions. Zintl and Morawietz (1940) also reported high- and low-temperature forms of Na_3PO_4 with a transition temperature of 700°C, but again no X-ray data were given.

Anhydrous Na_3PO_4 was prepared by the solid-state reaction:

$$Na_2HPO_4 + \tfrac{1}{2}Na_2CO_3 \rightarrow Na_3PO_4 + \tfrac{1}{2}H_2O + \tfrac{1}{2}CO_2$$

The reaction was first carried out at 500°C. overnight. A 4.3% excess of sodium carbonate was used. The weight loss was slightly (approximately 10%) higher than the theoretical value. The X-ray film of

the reaction products (10054A) showed that Na_3PO_4, Na_2HPO_4 and $Na_4P_2O_7$ were all present, the $Na_4P_2O_7$ evidently as a decomposition product of Na_2HPO_4. The same reaction was therefore repeated at 600°C. overnight; the X-ray pattern (film 10056B) then agreed with the A.S.T.M. Index pattern for Na_3PO_4 (Card 20-1150). When the product obtained at 600°C. was heated at 740°C, a different X-radiogram was obtained (10056C and 10059C) which could be indexed on the basis of an orthorhombic unit-cell with the probable space-group Pnma. (This form of Na_3PO_4, referred to later as the "Y-form", was also shown to be present in the products of sodium carbonate sintering reactions carried out at 700°C).

Attempts were made to obtain the same structure by dehydrating $Na_3PO_4,12H_2O$. $Na_3PO_4,12H_2O$ from B.D.H. Ltd. was dried at 140°C. and its X-ray powder photograph taken (films 10059D and 10080A). The temperature was then gradually increased to 720°C. and held at this value for 12 hours. The weight loss agreed very well with formation of anhydrous Na_3PO_4 (56.4%, to be compared with the theoretical value of 56.8%). The X-ray pattern (10065B) showed lines of the orthorhombic form, together with additional lines.

These lines, which occurred in a number of other photographs with appreciable variations in relative intensities, proved extremely difficult to interpret. Eventually it was found that Palazzi and Remy (1971) had established close similarity between a cubic Y-form of Na_3PO_4 and a cubic Y-form of Na_3AsO_4; they also established the existence of a tetragonal α-form of Na_3PO_4. An orthorhombic β-form of Na_3AsO_4 was established also, but no β-form could be found in Na_3PO_4 by Palazzi and Remy. Close study of the data showed that all the unexplained lines revealed by the present study could be accounted

for on the basis of three forms of Na_3PO_4. These are:

(a) The γ-form referred to above, which proved to be a pseudo-cubic but orthorhombic form corresponding closely with the γ-form of Palazzi and Remy.

(b) An α-form, reported by Palazzi and Remy to be tetragonal, and fully confirmed by the data now presented.

(c) A β-form, not reported at all by Palazzi and Remy, but corresponding closely with the β-form of Na_3AsO_4 reported by them.

Some brief further comments on these phases will help to clarify a difficult set of phase relationships. X-ray photographs showing the presence of γ-Na_3PO_4 could, in some cases, be indexed satisfactorily by assigning a cubic unit-cell closely corresponding with the cubic cell reported by Palazzi and Remy. However, other photographs contained additional lines, superposed on the lines corresponding with cubic indexing, which appeared to result from the same phase and could be accounted for by re-indexing the whole photograph on the basis of the orthorhombic cell. It is evident that the cubic interpretation relates to a pseudo-cell, and that the true cell is slightly distorted from cubic symmetry and requires a modified description in orthorhombic symmetry. Since all the photographs were sharp, with clearly defined lines, it is possible that the difference between the cubic pseudo-cell and the orthorhombic cell represents a true structure distortion, possibly due to analytically undetermined changes in the Na_2O/P_2O_5 ratio in the phosphate. X-ray data for the orthorhombic form are listed in Table 1.

X-ray data for lines assigned to the tetragonal α-form of

Na_3PO_4 are listed in Table 2. They correspond closely with the data reported originally by Hanawalt (1938) and reproduced in A.S.T.M. Card 1-1103. The later results of Norbert (1966), included in A.S.T.M. Card 20-1150, refer to a mixture of the α- and γ-forms.

The β-form of Na_3PO_4 has not been characterised previously; X-ray data for it are shown in Table 3. The β-form appears to be an intermediate in the α→γ and γ→α changes.

Tests showed that the γ-form reverts to the β- and α-forms on keeping. A peculiar (and as yet unexplained) observation is that the γ-form is converted into the α-form on heating at high temperatures (e.g., 950°C).

Later experiments on the sinter reactions confirmed the need to clarify the phase relationships in Na_3PO_4. The γ-form (which could not have been identified without the work just described) was obtained by evaporating the aqueous extract of a monazite and sodium carbonate sinter product, and heating the residue at 700°C. (film 10236D; Table 4). In another series of experiments, it was also obtained together with $Na_4P_2O_7$ by taking the filtrate from an oxalic acid precipitation of lanthanides (from an acid extract of the sinter product), evaporating, and heating the residue at 700°C. (film 10237D).

TABLE 1

Orthorhombic form of Na_3PO_4* and
corresponding cubic lines (Y-Na_3PO_4)

Film 10080C, Rad. Co. K_α

orthorhombic					cubic	
I	d(A)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	$\sin^2\theta_{calc.}$
40	4.335	011	0.04273	0.04311		
50	4.275	101	0.04390	0.04378	111	0.04383
B20	3.690	002	0.05877	0.05844	200	0.05844
30	2.655	020	0.11380	0.11400		
100	2.625	200 112	0.11647	0.11668 0.11611	220	0.11668
20	2.251	121	0.15811	0.15778		
B15	2.229	013	0.16131	0.15999	311	0.16071
10	2.139	202	0.17514	0.17512	222	0.17532
3	1.994	122	0.20154	0.20160		
30	1.853	004	0.23334	0.23376	400	0.23376
W	1.718	031	0.27122	0.27111		
W	1.708	123	0.27456	0.27466		
B5	1.658	114	0.29162	0.29143	420	0.29220
20	1.515	312	0.35006	0.34942	422	0.35064
10	1.426	303	0.39366	0.39401	333	0.39447

* $Na_3PO_4,12H_2O$ was heated at 140°C. for 14 hours, then heated again at 780°C. for another 14 hours.

a = 5.237A.
b = 5.203A.
c = 7.40A.
S.G Pnma (No. 62)

for cubic form a = 7.40A.
(Palazzi, a = 7,413A).

TABLE 2

α-form of Na_3PO_4* (tetragonal)

Film 10154D, Rad. Cu. K_α

Norbert (1966)		Palazzi (1971)		Present work				
I	d(A)	I	d(A)	I	d(A)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
-	-	vvw	7.648	20	7.615	110	0.01025	0.01024
2	6.28	-	-	-	-	-	-	-
-	-	-	-	5	5.753	101	0.01795	0.01785
-	-	-	-	2	4.829	210	0.02548	0.02560
50	4.23	s	4.244	100	4.230	201	0.03321	0.03321
5	3.95	vw	3.955	50	3.930	211	0.03848	0.03833
15	3.81	w	3.825	60	3.817	220	0.04078	0.04096
5	3.41	-	-	15	3.401	310	0.05137	0.05120
-	-	-	-	2	3.264	102	0.05579	0.05604
10	3.12	vvw	3.130	50	3.110	112	0.06143	0.06116
-	-	-	-	2	2.991	320	0.06644	0.06656
10	2.78	-	-	25	2.779	212	0.07690	0.07652
50	2.695	vs	2.705	90	2.694	400	0.08186	0.08192
35	2.62	-	-	2	2.625	-	cubic	form
100	2.547	vs	2.552	100	2.540	330	0.09205	0.09216
15	2.447	vw	2.450	40	2.442	411	0.09963	0.09977
15	2.415	vvw	2.420	40	2.409	312 420	0.10240	0.10240
15	2.274	vvw	2.280	40	2.274	421	0.11487	0.11513
20	2.247	vw	2.257	60	2.249	322	0.11754	0.11748
15	2.236	vvw	2.229	40	2.220	103	0.12036	0.11969
15	2.159	vvw	2.163	50	2.158	500	0.12755	0.12800
10	2.116	vvw	2.122	40	2.115	510 402	0.13284	0.13312 0.13284
-	-	-	-	5	2.076	412	0.13785	0.13796
20	2.056	w	2.063	60	2.055	431 501	0.14063	0.14073
-	-	-	-	5	2.018	511	0.14583	0.14585
-	-	-	-	5	2.000	520	0.14846	0.14848
-	-	-	-	10	1.920	521	0.16108	0.16121
35	1.909	s	1.912	80	1.908	440	0.16333	0.16384
-	-	-	-	10	1.890	313	0.16641	0.16577
5	1.850	-	-	2	1.850	530	0.17362	0.17408
-	-	-	-	2	1.823	502	0.17874	0.17892

TABLE 2 continued

Norbert (1966)		Palazzi (1971)		Present work				
I	d(A.)	I	d(A.)	I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
5	1.799	-	-	20	1.796	600	0.18416	0.18432
-	-	-	-	20	1.728	522	0.19909	0.17892
5	1.72	-	-	20	1.716	611	0.20189	0.20217
5	1.71	-	-	10	1.702	620	0.20505	0.20480
2	1.682	-	-	B20	1.683	540	0.20965	0.20992
-	-	-	-	10	1.663	442	0.21483	0.21476
5	1.657	-	-	20	1.654	621	0.21733	0.21753
2	1.633	-	-	20	1.636	541	0.22203	0.22265
-	-	-	-	10	1.626	204	0.22476	0.22416
-	-	-	-	5	1.606	630	0.23043	0.23040
-	-	-	-	5	1.590	602	0.23504	0.23524
2	1.570	-	-	20	1.575	612	0.23967	0.24036
2	1.550	-	-	-	-	-	-	-
20	1.524	-	-	60	1.526	622	0.25531	0.25572
5	1.506	-	-	-	-	-	-	-
-	-	-	-	20	1.461	443	0.27827	0.27841
10	1.439	-	-	30	1.441	404	0.28632	0.28560
-	-	-	-	5	1.427	414	0.29166	0.29072
-	-	-	-	B5	1.413	730 603	0.29764	0.29636 0.29889
5	1.395	-	-	5	1.392	424	0.30685	0.30608
2	1.349	-	-	B10	1.349	651 800	0.32653	0.32505 0.32768
-	-	-	-	B5	1.336	810	0.33283	0.33280
-	-							
2	1.310	-	-	B10	1.313	633	0.34466	0.34497
-	-			B5	1.285	821	0.36009	0.36089
-	-	-	-	B10	1.278	660	0.36828	0.36864
-	-	-	-	2	1.249	643	0.38095	0.38081
-	-	-	-	5	1.241	831	0.38604	0.38649
-	-	-	-	B10	1.205	840	0.40888	0.40960
-	-	-	-	B5	1.198	900	0.41404	0.41472
-	-	-	-	B5	1.190	910	0.41920	0.41984

TABLE 2 continued

Unit cell dimensions:

Present work	Palazzi and Remy
a = 10.757A.	a = 10.81A.
c = 6.824A.	c = 6.84A.

* $Na_3PO_4,12H_2O$ was dried at 140°C., then heated to 720°C. for 12 hours. Film 10065B showed γ-form together with additional lines. This was heated to 950°C. after 8 months (film 10154D).

TABLE 3

Comparison of β-Na_3PO_4 and
β-Na_3AsO_4 (Palazzi and Remy)

Film 10083C, Rad. Co. K_α

β-Na_3PO_4					β-Na_3AsO_4	
I	d	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d
20	5.78	0.02407	0.02400	020	w	5.986
20	4.42	4095	4050	120	vs	4.568
10	4.33	4261	4236	101	vs	4.371
-	-	-	-	021	s	4.077
20	3.49	6601	6600	200	m	3.528
vvw	3.16	8019	7986	031	-	-
10	3.055	8573	8586	201	-	-
3	2.99	9017	9000	220	mS	3.039
5	2.89	9601	9600	040	mS	2.993
-	-	-	-	131	vvw	2.947
20	2.85	9833	9785	211	vvw	2.894
50	2.78	10346	10344	002	mS	2.782
10	2.65	11405	11586	221	mS	2.666
100	2.62*	11712				
30	2.56	12236	12186	041	vw	2.636
5	2.51	12741	12744	022	vvw	2.524
-	-	-	-	141	vvw	2.467
-	-	-	-	122	vvw	2.376
10	2.35	14552	14586	231	-	-
20	2.179	16934	16944	202	-	-
20	2.137	17594	17544	212	-	-
			17586	051		
-	-	-	-	311	vvw	2.127
15	2.033	19389	19344	222	vw	2.052
10	2.003	19961	19944	042	vw	2.038
5	1.989	20242	20250	330	-	-
10	1.927	21572	21594	142	-	-

TABLE 3 continued

β-Na_3PO_4					β-Na_3AsO_4	
I	d	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d
10	1.885	22549	22594	112	-	-
10	1.870	22896	22836	331	-	-
20	1.810	24454	24450	340	-	-
3	1.685	28219	28200	260	-	-
20	1.584	31939	31944	252	-	-
5	1.571	32469	32436	351	-	-
vw	1.528	34383	34386	431	-	-
10	1.478	36680	36744	402	-	-
10	1.4475	38243	38274	053	-	-
20	1.4235	39519	39474	243	-	-

* Belongs to γ-phase also

Orthorhombic system, space group Pnma (No. 62)

Unit cell dimensions

Present work	Palazzi and Remy
a = 6.963A.	a = 7.05A.
b = 11.547A.	b = 11.97A.
c = 5.562A.	c = 5.57A.

TABLE 4

γ-form of Na_3PO_4 obtained through monazite, Na_2CO_3 sinter reaction (water extraction filtrate was dried at 700°C).

Film 10236D, Rad. Cu. K_α a = 7.39A.

Present work					Palazzi and Remy	
I	d(A)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	I	d(A)
80	4.280	111	0.03243	0.03252	mS	4.280
30	3.700	200	0.04340	0.04336	vw	3.7065
100	2.618	220	0.08671	0.08672	vS	2.6209
10	2.138	222	0.13007	0.13008	vw	2.1399
60	1.851	400	0.17349	0.17344	vw	1.8533
60	1.512	422	0.26012	0.26016	mw	1.5132
10	1.425	333	0.29265	0.29268	w	1.4266
20	1.309	440	0.34674	0.34688	-	-
5	1.251	531	0.37946	0.37940	-	-

Preparation of $Na_4P_2O_7$

$Na_4P_2O_7$ was prepared by heating "Analar" Na_2HPO_4 (dried at 140°C.) for 5 hours at 500°C. (see "Inorganic Syntheses", Vol. III, p. 99). The reaction is:

$$2Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O$$

An X-ray pattern of the product (10091C) agreed with A.S.T.M. Card No. 10-187 ($Na_4P_2O_7$).

Preparation of $Na_2H_2P_2O_7$

$Na_2H_2P_2O_7$ was prepared by heating NaH_2PO_4 at 210°C (Ingerson and Morey, 1943) ($2NaH_2PO_4 \rightarrow Na_2H_2P_2O_7 + H_2O$). $NaH_2PO_4,2H_2O$ was used (Hopkin and Williams Ltd.) instead of the anhydrous salt, but the product (film 10091D) after 12 hours of heating was anhydrous NaH_2PO_4; heating for 5 more hours at 210°C gave a product of which the X-radiogram (10095C) agreed with A.S.T.M. Card 10-192 ($Na_2H_2P_2O_7$).

Preparation and Structure of $NaCaPO_4$

It was suspected from approximate X-ray data given by Bredig (1942) that $Na_3Gd(PO_4)_2$ might have a structure similar to that of β-$NaCaPO_4$; unfortunately, however, Bredig's data were not sufficiently precise for reliable comparison. Attempts were therefore made to prepare β-$NaCaPO_4$ and secure accurate X-ray data. The method given by Frank, Bredig and Frank (1936) and by Frank, Bredig and Kanert (1938) was employed in the preparation. $CaHPO_4$ ("Analar" grade, Hopkin and Williams) and sodium carbonate were dried at 100°C and thoroughly mixed by grinding in the theoretical proportions ($2CaHPO_4 + Na_2CO_3 \rightarrow 2NaCaPO_4 + H_2O + CO_2$). The reaction was carried out at 1150°C. for three hours in a closed alumina crucible to keep the reactants under a moist carbon dioxide atmosphere. The experimental weight loss was 4% higher than theoretical. The

powder pattern of the $NaCaPO_4$ (10165A) showed that it was not isostructural with $Na_3Gd(PO_4)_2$ as prepared in the present work. The $NaCaPO_4$ data did not fit, to an acceptable degree, either the orthorhombic cell of Bredig (1942) or the hexagonal cell of Klement and Dihn (1938, 1940); the data suggest that the true structure may be monoclinic or triclinic. The unindexed data are reproduced in Table 5. Owing to quenching difficulties, some α-$NaCaPO_4$ may have been present, and this possibility must be borne in mind in any use made of the data given.

TABLE 5

X-ray diffraction data of $NaCaPO_4$

Film 10165A, Rad. Cu. K_α

I	d(A.)	I	d(A.)	I	d(A.)
40	5.48	70	2.018	3	1.274
30	4.67	20	1.943	B3	1.260
		70	1.923	B10	1.239
80	3.858	20	1.904	B5	1.211
60	3.813	5	1.819	B5	1.202
5	3.457	15	1.770		
10	3.404	40	1.741		
5	3.188	5	1.709		
25	3.117	25	1.701*		
20	2.881	5	1.673		
5	2.840	10	1.613		
15	2.790*	B10	1.595		
100	2.755	15	1.571		
70	2.707	30	1.555		
90	2.663	15	1.544		
5	2.574	3	1.530		
10	2.426	B10	1.483		
10	2.405*	5	1.439		
30	2.331	20	1.433		
30	2.276	3	1.422		
70	2.204	B15	1.387		
30	2.173	B15	1.353		
30	2.118	B10	1.331		
30	2.0655	B15	1.304		
B10	2.035	5	1.285		

* It may belong to CaO (Card 4.0777)

2.3. Structure of lanthanide oxides; reactions of lanthanide oxides with sodium carbonate.

The individual rare-earth oxides, which are the first step in preparation of the other lanthanide compounds, have now become available at purities of 99 to 99.9% through improvement in the techniques of separating the lanthanide cations. Oxides of the trivalent rare-earth ions exist in three types of structures, designated "A-type" (hexagonal), "B-type" (monoclinic), and "C-type" (cubic). They were first reported by Goldschmidt, then reviewed in detail by many subsequent investigators (see Eyring, 1964). Shafer and Roy (1959) established the reversibility of the transitions between the A-, B- and C-types of structures, and clarified the relationship between structure, ionic size and temperature. Warshaw and Roy (1961) found out that the boundary between A- and B-types is vertical (Fig. 1). Table 6 shows the structures stable for each of the oxides, and their unit-cell parameters. Foex and Traverse (1966), after reviewing all the forms, studied their high-temperature transformations. The hexagonal structures from Sm_2O_3 to Tm_2O_3 were obtained at temperatures over 2000°C.

The tetravalent rare-earth oxides also have cubic structures, but of the fluorite type. Actually the C-type is related to the fluorite structure by a removal of one quarter of the anions, leaving the cations six-coordinate. The production of substitutional solid solutions of C-type sesquioxides with fluorite type oxides is therefore easy, because conversion of the C-structure to the fluorite type, requires only the filling of the otherwise empty anion sites.

In the present work, only the low temperature forms of lanthanide oxides were of interest, since the solid-state reactions described were carried out at moderate temperatures only.

Fig.1.

Temperature stability relationships of rare earth sesquioxide polymorphs (Warshaw and Roy, 1961).

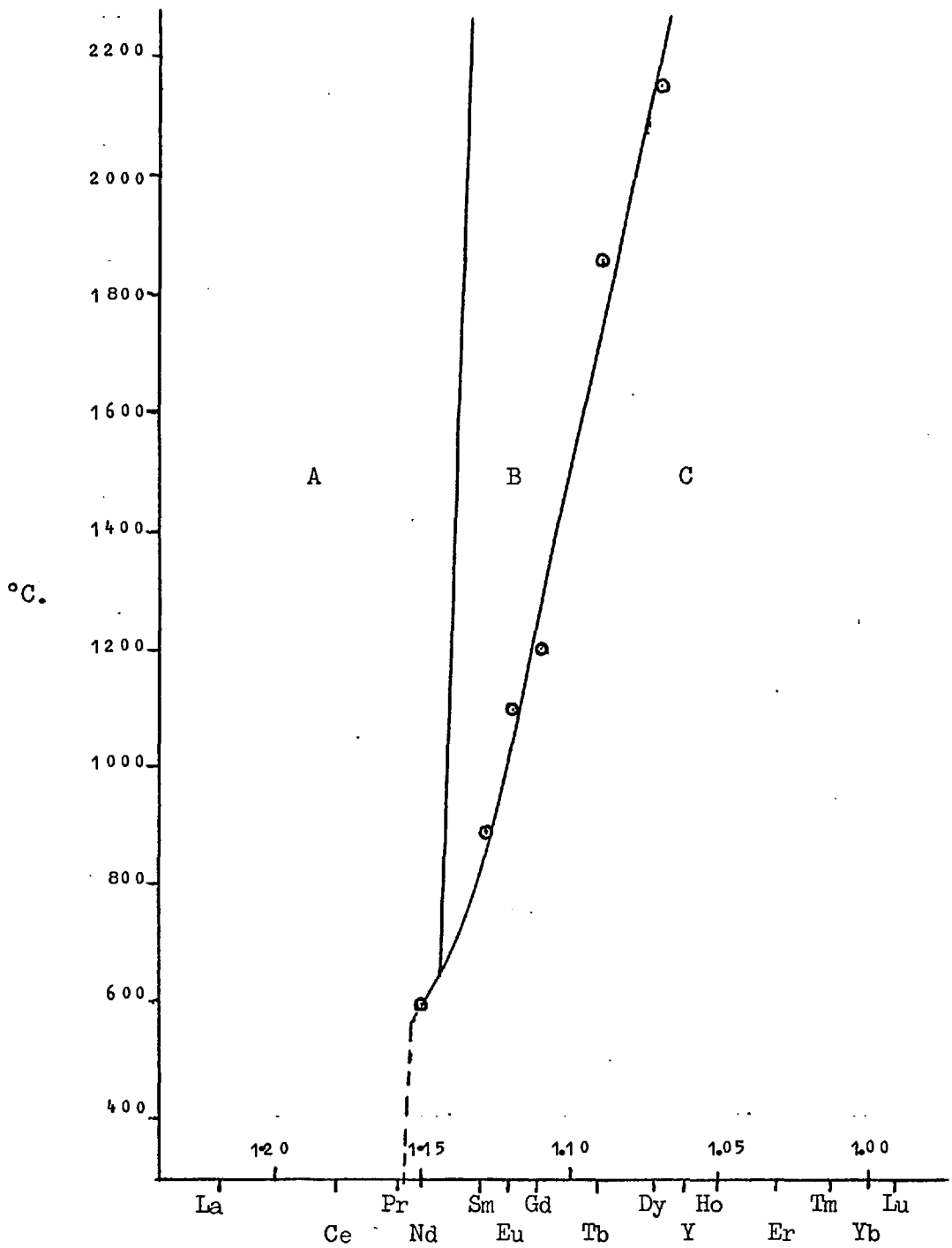


TABLE 6

Cell Constants of Lanthanide Oxides in A.

Oxides	Type A		Type B				Type C
	a	c	a	b	c	β	a
La_2O_3	3.937	6.129					
Pr_2O_3	3.86	6.024					
Nd_2O_3	3.83	5.99	14.35	3.67	8.99	100.34°	11.08
Sm_2O_3	3.86	6.17	14.17	3.63	8.84	99.96°	10.934
Eu_2O_3	3.84	6.14	13.94	3.58	8.67	98.5°	
Gd_2O_3	3.85	6.16	14.06	3.57	8.76	100.10°	10.812
Tb_2O_3	3.83	6.12					10.729
Dy_2O_3	3.82	6.11					10.667
Ho_2O_3	3.80	6.08					10.606
$[Y_2O_3]$	3.81	6.08					10.605
Er_2O_3	3.78	6.05					10.550
Tm_2O_3	3.76	6.02					10.486
Yb_2O_3							10.435
Lu_2O_3							10.118
							10.390
CeO_2							5.411
ThO_2							5.600
$(CeTh)O_2$							5.470

This table refers to the cell constants as given by Eyring (1964) and the A.S.T.M. Card Index. Values for yttrium and thorium oxides are included with the true lanthanide oxides for comparison.

Experimental:

Lanthanide oxides which were used in our investigations were generally from Johnson, Matthey and Co. Ltd., with 99.0% to 99.9% purity range; lanthanum oxide was obtained from Koch-Light Laboratories Ltd. The X-ray diffraction patterns of lanthanum and gadolinium oxides were obtained by using cobalt radiation. The photograph given by gadolinium oxide after heating at 940°C. (10048D) agreed very well with A.S.T.M. Card 12-797 for the cubic structure. In the case of lanthanum oxide heated at 940°C. a photograph (10047C) different from the expected one was at first obtained. The hexagonal lanthanum oxides lines (A.S.T.M. Card 5-602) were present but they were not strong. The additional lines were found to be due to lanthanum hydroxide. It seemed that the oxide absorbed water and was converted into the hydroxide during the 15 hours exposure to X-rays. Water absorption was confirmed by leaving a small sample of lanthanum oxide exposed to the atmosphere and reweighing it. 13.44% of water had been absorbed. The same experiment was repeated with gadolinium oxide, but no detectable absorbtion was observed during 36 hours.

An X-ray powder diffraction photograph of lanthanum oxide (ignited previously at 800°C), was then taken, with the specimen covered by a "Mylar" film (10050C). Only lines of hexagonal lanthanum oxide was observed.

During the later investigation of solid-state reactions it appeared possible that double oxides of lanthanides and sodium might occur among reaction products. $NaGdO_2$ was prepared by Blasse (1964) by heating anhydrous sodium carbonate and gadolinium oxide for 24 hours at 800°C. $NaLnO_2$-type compounds have also been reported by other authors (Hoppe , 1965; Muravyev, Kovba and Spischin, 1960, 1966, 1967) for ytterbium, lutecium, yttrium, samarium, europium,

erbium and thulium. Tests were performed to ascertain if lanthanum forms such a compound, for example by the reaction $Na_2CO_3 + La_2O_3 \rightarrow 2NaLaO_2 + CO_2$. Dried lanthanum oxide was ground together with a 10% excess over the required amount of anhydrous sodium carbonate, and the mixture was heated in a platinum crucible for 16 hours at 700°C, (700°C was chosen because it was the temperature used in later sintering reactions). The observed weight loss was considerably less than the theoretical loss of carbon dioxide (theoretical 41.51%, experimental 3.70%).

The X-ray powder diffraction pattern of the product (Film 10044C) did not show any new phase to be formed. Heating of the initial product was repeated for another 24 hours at 800°C. and for 12 hours at 940°C. The X-ray powder photograph (10047D, 10050A) again indicated that no reaction leading to a crystallised product had taken place. There was no likelihood, therefore, of formation of a sodium lanthanum oxide during sintering reactions with sodium carbonate.

The same attempted sintering reaction was repeated on gadolinium oxide, again with a 10% excess of sodium carbonate for 30 hours at 800°C. After 15 hours the powder was removed from the furnace, weighed, reground and heated again. The loss of weight was still much less than the theoretical amount (theoretical 0.0105 g. experimental 0.0037 g). The X-ray powder photograph (10050D) showed only gadolinium oxide lines. Sodium carbonate lines were very weak. It seems the reaction did not occur at 800°C. as found by Blasse. However, a similar mixture heated at 940°C. for 12 hours lost the theoretical amount of carbon dioxide, and the X-ray pattern (10047A) showed the formation of a new phase; it also had lines of unreacted gadolinium oxide. Blasse reported that $NaGdO_2$ had a tetragonal

structure with lattice parameters of a = 4.66 and c = 10.53 A, but he gave no diffraction data. The patterns obtained fitted these cell constants, but some of the lines remained unindexed. By keeping the same value of c but changing a it proved possible to account for all the lines with a = 14.74 A. The hexagonal indexing of Muravyev, Kovba, and Spischin (1967) with approximate cell parameters of a = 3.37 and c = 16.57 A. for $NaErO_2$, did not fit the data now obtained.

It had been satisfactorily established that "d" spacings belonging to $NaGdO_2$ were not present in any of the X-radiograms obtained in later work. Further attempts to prepare pure $NaGdO_2$ were therefore left for future investigations.

TABLE 7

X-ray Diffraction Data of $NaGdO_2$

(Tetragonal system)

Film 10047 A, Rad. Co. K_α.

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	Remarks	
20	4.42	-	0.04092	-	Gd_2O_3	
100	4.27	311	0.04398	0.04401		$NaGdO_2$
40	4.14	212	0.04663	0.04721	Vaseline	$NaGdO_2$
90	3.126	-	0.08200	-	Gd_2O_3	
vw	2.986	-	0.08982	-	Na_2CO_3	
100	2.795	422	0.10258	0.10244		$NaGdO_2$
30	2.704	-	0.10957	-	Gd_2O_3	
70	2.63	004	0.11575	0.11536		$NaGdO_2$
10	2.55	114	0.12322	0.12272	Gd_2O_3	$NaGdO_2$
w	2.416	-	0.13719	-	-	-
80	2.331	620	0.14737	0.14720		$NaGdO_2$
10	2.307	540	0.15048	0.15088	Gd_2O_3	$NaGdO_2$
5	2.226	602	0.16163	0.16132		$NaGdO_2$
20	2.120	414	0.17814	0.17792	Gd_2O_3	$NaGdO_2$
50	2.047	711 551 640	0.19114 0.19114 0.19114	0.19121 0.19121 0.19136		$NaGdO_2$
50	1.994	613	0.20147	0.20105	NaCl	$NaGdO_2$
40	1.915	-	0.21845	-	Gd_2O_3	
w	1.850	-	0.23408	-	Gd_2O_3	
20	1.814	713 553 820	0.24940 0.24940 0.24940	0.24889 0.24889 0.25024		$NaGdO_2$
50	1.745	624	0.26296	0.26256		$NaGdO_2$
w	1.698	216	0.27792	0.27796	NaCl	$NaGdO_2$
40	1.648	840	0.29480	0.29440		$NaGdO_2$
30	1.628	641	0.30223	0.30161	Gd_2O_3+NaCl	$NaGdO_2$
w	1.592	823 615	0.31594 0.31594	0.31513 0.31641	Gd_2O_3	$NaGdO_2$

TABLE 7 continued

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	Remarks	
5	1.560	734	0.32899	0.32880	Gd_2O_3	$NaGdO_2$
40	1.546	851	0.33491	0.33473		$NaGdO_2$
20	1.537	931	0.33903	0.33841		$NaGdO_2$
		654	0.33903	0.33984		
40	1.480	824	0.36571	0.36560		$NaGdO_2$
w	1.429	606	0.39195	0.39204		$NaGdO_2$
40	1.420	951	0.39792	0.39729		$NaGdO_2$
30	1.395	10.2.2	0.41163	0.41156		$NaGdO_2$
w	1.350	10.0.2	0.43324	0.43289	Gd_2O_3	$NaGdO_2$
		862	0.43324	0.43289		

a = 14.74 A.

c = 10.53 A.

2.4. Preparation and properties (including structures) of lanthanide orthophosphates, $LnPO_4$.

Rare-earth phosphates have been prepared by a number of workers using solution, fusion or hydrothermal methods. $LaPO_4$ was first prepared in 1861 by Hermann by addition of phosphoric acid to a solution of lanthanum sulphate. Other methods using aqueous solutions of lanthanide salts have also been described (Cleve and Höglund, 1872; Frerichs and Smith, 1878; Cleve, 1878, 1885, 1902; Hartley, 1882; Heramhof, 1907; Sarkar, 1926, 1927; Ephraim, 1928, 1929; Hubicki, 1947; Vickery, 1953). The preparation of $CePO_4$ by fusing cerium dioxide with potassium metaphosphate has been carried out by Ouvrard (1888). Radominski´ (1875), Palache, Berman and Frondel (1951) also used fusion methods. The first hydrothermal preparation was reported by Carron, Naeser, Rose and Hildebrand (1958); it required crystallisation from aqueous solutions in a closed system under a pressure of 90 atmospheres, at 300°C. The precipitation method used by most workers was outlined by Buyers and Audrieth (1950) and Buyers, Giesbrecht and Audrieth (1957). The early workers verified the composition of the lanthanide phosphates by chemical analysis for phosphorus and rare-earths. Since no X-ray methods were available at that time, it was possible only to assign formulae depending on chemical analysis, and phase analysis frequently could not be attempted.

The hydrogen-ion displacement method described by Buyers, Giesbrecht and Audrieth (1957) has proved to be the best technique for preparation of pure rare-earth phosphates. The necessary amount of NaH_2PO_4 solution is added to the solution of rare-earth chlorides, after both solutions have been adjusted to pH 4.5. Lanthanide orthophosphates are then precipitated. The reaction is represented by the

following equation:

$$Ln^{3+} + H_2PO_4^- \rightarrow LnPO_4 + 2H^+$$

After precipitation the pH of the solution must be readjusted to 4.5 (to remove the liberated hydrogen-ion) by adding dilute sodium hydroxide solution. The pH of 4.5 is selected by reference to the acid-base titration curves of orthophosphoric acid. It is the first equivalence point in titration of this acid with a strong base. At higher pH values lanthanide hydroxide may also precipitate and upon ignition give oxides or mixed phosphates in the ignited product.

Clearly the reaction described above is very complex in nature. The formation of pure orthophosphates depends on the concentrations, pH and temperature of the solutions. The initial precipitates are gelatinous and they can easily adsorb foreign ions. Limited formation of lanthanide hydrogen phosphates is also probable (Hubicki, 1947); upon ignition these give meta- or pyrophosphates in the product:

$$Ln(H_2PO_4)_3 \rightarrow Ln(PO_3)_3 + 3H_2O;$$

$$2Ln_2(HPO_4)_3 \rightarrow Ln_4(P_2O_7)_3 + 3H_2O.$$

Buyers, Giesbrecht and Audrieth (1957) found that the weight of orthophosphate obtained was slightly higher than the theoretical value, confirming the presence of (probably) metaphosphate and pyrophosphate impurities.

The probability of formation of pyrophosphates is reduced by heating the precipitate and its mother liquor on a water bath for some time (1 hour) after precipitation; this favours hydrolysis of pyrophosphates into orthophosphates, according to the following equation:

$$Ln_4(P_2O_7)_3 + 3H_2O \rightleftarrows 4LnPO_4 + 2H_2PO_4^- + 2H^+$$

If hydrogen-ion is removed by dilute alkali to keep the pH at 4.5 the reverse reaction does not interfere.

A systematic study of these reactions in aqueous solutions has been carried out by Ulyanov, Kazakova and Rumyantseva (1962); Ulyanov and Kazakova (1963); Petushkova and Tananaev (1963); Tananaev and Vasil'eva (1963); Kuznetsov, Vasileva and Tananaev, (1964); Tananaev and Petushkova (1967); Petushkova, Tananaev and Samoilova (1969). Solubility relations and the conductivity and pH of the systems have been studied, and the products obtained have been analysed chemically, thermographically and by X-ray diffraction.

Experimental:

The orthophosphates of the rare-earths were prepared for the present studies by the method of Buyers (1957) outlined above. Chemicals: Rare-earth oxides (99% to 99.9% pure) were in the Ln_2O_3 form except CeO_2 and Tb_4O_7. Other chemicals were of 'AnalaR' grade. Procedure: 1 g. (in some cases 0.1 g. or 0.01 g.) of the lanthanide oxide was dissolved in 10 ml. of 3N hydrochloric acid by gentle heating (CeO_2 required special treatment, see below). 1N sodium hydroxide solution was added slowly with stirring until the pH of the solution reached 4.5 (bromophenol-blue indicator turned green). NaH_2PO_4 solution containing a 50% excess over the theoretical amount was added to the chloride solution with constant stirring. The precipitate and supernatant liquid were kept on the steam bath for 1 hour, and then allowed to stand at room temperature for 12 hours. The liquid was filtered through a No. 40 Whatman filter paper, and the precipitate was washed, first with 2% ammonium chloride solution, then with distilled water. The paper was then carefully burned off and the solid phosphate ignited over a small Bunsen flame, and finally for 1 hour in a muffle at 900°C. All the rare-earth phosphates

(except $PmPO_4$) have been prepared by this same method; YPO_4 was also prepared.

For $CePO_4$ the following modified procedure was used: cerium dioxide was dissolved in concentrated sulphuric acid by boiling with an addition of hydrogen peroxide. Instead of NaH_2PO_4 and sodium hydroxide, orthophosphoric acid and ammonia solutions were used in the precipitation to avoid introduction of sodium ions. Experience showed that another compound, presumably a double sodium lanthanide phosphate, was liable to be precipitated from salt solutions containing sodium salts; it gave a diffraction pattern (10026 B or 10095 D) totally different from that of monazite. This pattern gave an early indication of the occurrence of sodium lanthanide phosphate. With the method mentioned above it proved possible to prepare $CePO_4$ with the expected monazite structure.

The crystal structures of lanthanide phosphates:

The crystal structure of lanthanide phosphates have been investigated by several workers. They have often been found to be isostructural either with xenotime (Vegard, 1927; Strada and Schwendimann, 1934; Hutton, 1957; A.S.T.M. Card No. 11-254) or with monazite (Parrish, 1939; A.S.T.M. Card No. 11-556). Xenotime is the mineral name of yttrium phosphate, YPO_4, crystallized in the zircon structure (tetragonal), which is also isostructural with mineral churchite (Claringbull and Hey, 1953; A.S.T.M. 8-167). The space-group is $I4_1/amd$ and there are four molecules of YPO_4 per unit cell (Swanson, Cook, Gilfrich, Strinchfield, Parks; 1959). Monazite is a mineral consisting of lanthanide and thorium phosphates in solid solution, usually formulated $(Ce,La,Y,Th)PO_4$; it crystallises in the monoclinic system with the space-group $P2_1/N$. There are four molecules of $LnPO_4$ per unit cell (Mooney, 1948). Mooney examined the structures

of $LaPO_4$, $CePO_4$, $PrPO_4$ and $NdPO_4$ by X-ray diffraction and reported that they were dimorphic. The monoclinic form (monazite type), occurs at higher temperatures. The other form, found for the first time by Mooney, (1950) has a hexagonal structure with the space-group $C6_22$. There are three molecules of $LnPO_4$ per unit cell. It has also been reported (Mooney, 1950) that the presence of zeolitic water (0-0.5 molecules) is probably necessary to stabilize this hexagonal structure. Unit-cell constants and density values were given for both structures. Carron, Naeser, Rose and Hildebrand (1958) examined the order of preferential precipitation of adjacent pairs of lanthanide phosphates. The paired phosphates from lanthanum to gadolinium crystallized in the monazite structure, and those from dysprosium to lutetium in the xenotime structure. Carron, Mrose and Murata (1958) correlated crystal structures of rare-earth compounds with the ionic radii of the trivalent lanthanides. The quantitative relationship between the oxygen-central atom distance (A) and the radius of the largest xenotime forming element (B) was given by $A/B \cong 1.86$. This ratio defines the ionic radius limit between the xenotime and monazite structures. In the case of terbium the A/B ratio is $1.75/0.93 = 1.88$ where 1.75 A. = P-O distance and 0.93 A. is the radius (Ahrens, 1952) of the terbium cation. Cell constants for ytterbium and dysprosium orthophosphates were given by Durif (1958) and those for erbium orthophosphate by Swanson, Cook, Isaacs and Evans; 1960.

Schwarz (1963) studied the zircon-type structures and gave the cell parameters of terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium orthophosphates. It has also been reported that terbium orthosphosphate at 1000°C. has the huttonite structure ($ThSiO_4$, Pabst and Hutton, 1951), at 1180°C. both huttonite and

zircon structures, and at 1400°C. the zircon structure alone.

Hexagonal and monoclinic modifications for the orthophosphates of praseodymium, neodymium, samarium, europium and gadolinium were also reported by Henschel (1963). He claimed that even at 1000°C. the hexagonal structure might still be present, but his data for d spacings were not very accurate owing to use of a small camera.

The first single-crystal study on rare-earth phosphates was done by Feigelson (1964), who prepared the necessary crystals by dissolving rare-earth oxides in molten lead pyrophosphate at high temperatures and allowing them to crystallize upon cooling. Previously unreported lattice parameters for samarium, europium and gadolinium orthophosphate were given. Weigel, Scherer and Henschel (1965) also determined the lattice parameters of lanthanide orthophosphates from praseodymium to gadolinium, including promethium, which were prepared by precipitation reactions.

Repko, Orlovskii and Safranov (1971) also gave some cell dimensions for praseodymium and neodymium orthophosphates from single crystal studies.

X-Ray Diffraction Studies:

An investigation of the crystal structures of rare-earth phosphates was considered necessary owing to lack of complete X-ray diffraction data in the literature. Complete diffraction data for the initial phosphates were necessary in any thorough study of their solid-state reactions. Although the cell parameters for the monoclinic structures were quite well established by different workers mentioned in the previous section, a complete list and indexing data were missing in the A.S.T.M. data index and in the literature, except Carron, Naeser, Rose and Hildebrand (1958) who gave a complete list

for the pairs of rare-earth phosphates they examined. An X-ray diffraction data for gadolinium phosphate was given by Bril and Wanmaker (1964, A.S.T.M. Card No. 18-523) but without indexing data.

In the present work pure rare-earth orthophosphates were again prepared. X-ray powder diffraction data were obtained by means of cobalt K_α radiation and a Guinier camera. All the photographs were indexed acceptably on the basis of monoclinic unit-cells having parameters closely comparable with those proposed earlier. These parameters were determined as accurately as possible from the powder data. Special attention was given to gadolinium orthophosphate because it was to be used later in the solid-state reaction studies. It was established subsequently that gadolinium orthophosphate formed in a solid reaction (film 10072 D) gave a powder X-radiogram in close agreement with the standard photograph obtained from the precipitated compound (film 10015 D). A specimen of gadolinium orthophosphate heated at 1150°C. (film 10165 D) showed no change in the X-ray diffraction pattern; the weight loss during heating was 0.88%, which could be attributed to loss of adsorbed water. A specimen extracted by boiling with concentrated hydrochloric acid also showed no change in the d spacings or relative intensities (film 10154 B). Approximately 30% of it, however, was dissolved. Infra-red data for the orthophosphates also agreed with the literature, and showed the presence of discrete PO_4^{3-} groups. The infra-red measurements proved that the orthophosphates prepared did not contain any detectable amount of pyrophosphate impurity.

Results of gravimetric and X-ray diffraction analyses are given in Table 8, together with references.

TABLE 8

Ln in $LnPO_4$	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Theo. weight, g.	1.4357	0.2791	1.4305	1.4219	0.2814	0.0281	1.3917	0.0272	0.2761	0.0275	0.2742	0.0274	0.2720	0.0271	1.6284
Exp. weight, g.	1.2475	0.2732	1.3254	1.2145	0.2689	0.0283	1.3784	0.0247	0.2792	0.0289	0.2810	0.0217	0.2775	0.0277	1.6494
Colour	yellow	green	green	violet	yellow	white	white	white-beige	white	white-pinkish	pink	white	white	white	white
Structure	M	M	M	M	M	M	M	M+X	M+X	X	X	X	X	X	X
Ionic Radius of Ln^{3+} in A.	1.061	1.034	1.013	0.995	0.964	0.950	0.938	0.923	0.908	0.894	0.881	0.869	0.858	0.848	0.90
X-ray Film No.	10037A	10026C	10022A	10015B	10022C	10026D	10015D	10030B	10026A	10030D	10022D	10030A	10022B	10030C	10015C
A.S.T.M. Card No.	4-0635 12-283	4-0632 11-556		4-644	12-430	12-430 18-506	12-427 18-523	12-427 12-428	12-428		9-383	12-429	12-429	12-282	9-377
A.S.T.M. Card No. for $LnPO_4.xH_2O$			20-966			20-1044	21-337	20-1244	20-385 21-316	20-475 20-476	20-391		20-1389	20-654	20-1414

Calculation of Cell Parameters for Lanthanide Orthophosphates:

Satisfactory indexing of powder photographs obtained from monoclinic structures is relatively difficult, and it would not normally be attempted without auxiliary information. The present work, however really represents a refinement of earlier data adequately supported by some single-crystal measurements, allowing much of the indexing to be carried out by analogy. The methods used will be outlined briefly.

It proved possible by initial tests with typical monazite cell parameters and hkl values to index the X-ray powder diffraction data for lanthanide orthophosphates from lanthanum to dysprosium. In the establishment of cell parameters, strong lines with the larger θ values were used.

For the monoclinic system the conventional expression for $\sin^2\theta$ is:

$$\sin^2\theta_{hkl} = Ah^2 + Bk^2 + Cl^2 - Dhl \qquad (1)$$

where $$A = \frac{\lambda^2}{4a^2 \sin^2\beta} \qquad (2)$$

$$B = \frac{\lambda^2}{4b^2} \qquad (3)$$

$$C = \frac{\lambda^2}{4c^2 \sin^2\beta} \qquad (4)$$

and $$D = \frac{\cos\beta . \lambda^2}{2.a.c.\sin^2\beta} \qquad (5)$$

The unit cell has a- and c-axes at an angle β which differs from 90°; the b axis is normal to the ac plane (D'Eye and Wait, 1960). The four "increments", A, B, C and D can be calculated from measured $\sin^2\theta$ values from the photographs, once the hkl values for the lines have been tentatively fixed by comparison with previous data. The four lattice parameters (a, b, c, β) can then be derived as follows:

(i) From (2) and (4) above, $c = a\sqrt{A}/\sqrt{C}$; further, $\cos\beta = \sqrt{1 - \sin^2\beta}$. Substituting for c and $\cos\beta$ in (5), the expression $\sin^2\beta = 1 - D^2/4CA$ results; this can be used to derive β.

(ii) Values of a, b and c are then calculated, by using (2), (3) and (4) above, from A, B and C, respectively; $\sin\beta$ is now known from step (i) above.

Table 9 shows the calculated unit-cell dimensions of the monazite-type lanthanide orthophosphates. Previous literature values are also given for comparison. The ionic radii of the lanthanide cations are plotted against unit-cell dimensions in Fig. 2. The approximately linear plots show the effect of the lanthanide contraction, the ionic radii diminishing with increase of atomic number.

The tetragonal indexing of xenotime structures has been clearly established for erbium orthophosphate by Swanson, Cook, Isaacs and Evans (1960), for yttrium orthophosphate by Swanson, Gilfrich, Cook, Strinchfield and Parks (1959) and for all from terbium to lutetium orthophosphate by Schwarz (1963). The $\sin^2\theta$ values now obtained could, by comparison with the results given in these papers, be tentatively indexed by inspection. The relevant "increments" (only two in this case, in contrast with four in the monoclinic case) were readily derived and the corresponding lattice constants a and c calculated. Results are giving in Table 10. The complete X-ray diffraction data for $LaPO_4$, $GdPO_4$, $HoPO_4$ and $LuPO_4$ are also given in tables 11 and 12.

Recent Published Work:

After completion of the studies on lanthanide orthophosphates described above, a paper appeared by Jaulmes (1972) describing a refinement of the structure of lanthanum orthophosphate. It was by

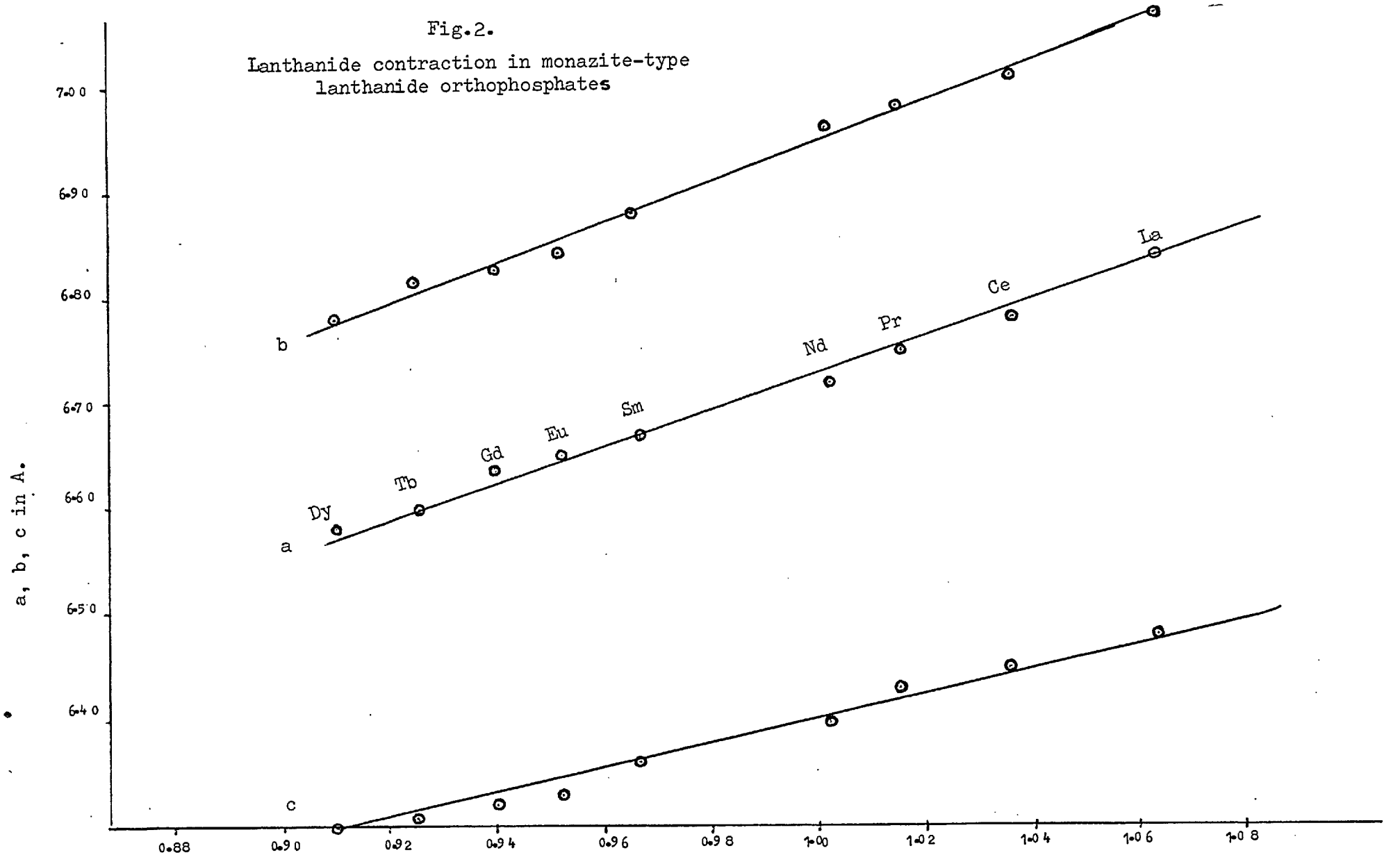
TABLE 9

Unit Cell Dimensions of Monazite-Type Lanthanide Orthophosphates in A.

	Mooney (1948)				Feigelson (1964)				Weigel (1965)				Repko (1971)				Present Work			
	a	b	c	β	a	b	c	β	a	b	c	β	a	b	c	β	a	b	c	β
$LaPO_4$	6.89	7.05	6.48	103°34'													6.85	7.07	6.47	103°38'
$CePO_4$	6.76	7.00	6.44	103°38'													6.78	7.01	6.45	103°50'
$PrPO_4$	6.75	6.94	6.40	103°21'					6.77	6.97	6.42	104°26'	6.74	7.02	6.36	103°24'	6.75	6.98	6.43	103°51'
$NdPO_4$	6.71	6.92	6.36	103°28'					6.73	6.91	6.38	103°48'	6.65	6.92	6.36	103°30'	6.72	6.96	6.40	103°49'
$PmPO_4$									6.72	6.89	6.37	104°17'								
$SmPO_4$					6.66	6.88	6.33	103°21'	6.67	6.86	6.32	104°22'					6.67	6.88	6.36	103°47'
$EuPO_4$					6.63	6.83	6.31	103°05'	6.61	6.81	6.29	103°50'					6.65	6.84	6.33	103°50'
$GdPO_4$					6.60	6.81	6.29	103°28'	6.56	6.74	6.22	104°33'					6.64	6.83	6.32	103°54'
$TbPO_4$																	6.60	6.82	6.31	103°56'
$DyPO_4$																	6.58	6.78	6.30	103°56'

Fig.2.

Lanthanide contraction in monazite-type lanthanide orthophosphates



Ionic Radius in A. (from Templeton and Dauben, 1954).

TABLE 10

Unit Cell Dimensions of Xenotime-Type Lanthanide Phosphates in A.

$LnPO_4$	Carron (1958)		NBS.		Schwarz (1963)		Present Work	
	a	c	a	c	a	c	a	c
$TbPO_4$	6.93	6.078			6.941	6.070	6.935	6.084
$DyPO_4$					6.917	6.053	6.901	6.043
$HoPO_4$					6.891	6.031	6.865	6.009
$ErPO_4$			6.863*	6.007*	6.864	6.007	6.845	6.000
$TmPO_4$	6.831	5.971			6.847	5.994	6.835	5.989
$YbPO_4$					6.824	5.980	6.805	5.971
$LuPO_4$	6.79	5.97			6.798	5.961	6.796	5.960
YPO_4			6.885#	5.982#	6.886	6.021	6.880	6.010

Swanson, Gilfrich, Cook, Strinchfield and Parks (1959)

* Swanson, Cook, Isaacs and Evans (1960)

TABLE 11

$LaPO_4$ (monoclinic) Film 10037A, Rad. Cu. K_α				$GdPO_4$ (monoclinic) Film 10015D, Rad. Cu. K_α				
I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
20	5.220	0.02941	0.02904	$\bar{1}01$	30	5.104	0.03075	0.03078
10	4.855	0.03400	0.03404	110	10	4.696	0.03633	0.03641
25	4.712	0.03608	0.03620	011	50	4.573	0.03831	0.03837
20	4.197	0.04547	0.04524	$\bar{1}11$	70	4.091	0.04787	0.04792
100*	4.130	0.04694	0.04724	101	20	3.982	0.05051	0.05022
10	3.569	0.06290	0.06324	111	10	3.450	0.06732	0.06736
20	3.533	0.06418	0.06400	020	10	3.416	0.06863	0.06856
70	3.326	0.07243	0.07216	200	80	3.224	0.07702	0.07708
-	-	-	-	$\bar{1}02$	10	3.070	0.08499	0.08475
-	-	-	-	002				0.08492
90	3.122	0.08221	0.08204	120	100	3.020	0.08781	0.08783
15	3.012	0.08830	0.08816	210	30	2.910	0.09459	0.09422
w	2.970	0.09103	0.09036	$\bar{2}11$	-	-	-	-
80	2.882	0.09640	0.09684	$\bar{1}12$	100	2.799	0.10226	0.10189
				012				0.10206
20	2.612	0.11740	0.11656	$\bar{2}02$	50	2.550	0.12322	0.12312
			0.11724	102				0.12363
5	2.462	0.13210	0.13296	$\bar{2}12$	B30	2.387	0.14063	0.14026
10	2.449	0.13358	0.13364	112				0.14077
w	2.425	0.13626	0.13616	220	10	2.342	0.14614	0.14564
w	2.350	0.14506	0.14480	022	10	2.282	0.15377	0.15348
			0.14484	$\bar{1}22$				0.15331
-	-	-	-	$\bar{3}01$	5	2.196	0.16608	0.16550
10	2.207	0.16446	0.16420	031	50	2.136	0.17561	0.17549
30	2.153	0.17280	0.17284	$\bar{1}03$	40	2.101	0.18144	0.18118
-	-	-	-	$\bar{3}11$	40	2.093	0.18280	0.18264
30	2.147	0.17377	0.17324	$\bar{1}31$	-	-	-	-
-	-	-	-	221	50	2.070	0.18686	0.18631
-	-	-	-	310	vw	2.047	0.19114	0.19057
-	-	-	-	131	vw	1.977	0.20487	0.20448
B20	1.981	0.20416	0.20496	212	70	1.915	0.21841	0.21802
			0.20516	$\bar{3}12$				0.21717

TABLE 11 continued

$LaPO_4$					$GdPO_4$			
I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
B10	1.955	0.20965	0.20956	301	10	1.890	0.22421	0.22382
Bw	1.911	0.21952	0.21836	$\bar{2}31$	25	1.852	0.23356	0.23313
			0.21956	$\bar{3}21$				0.23406
B20	1.887	0.22495	0.22480	032	60	1.829	0.23931	0.23918
			0.22484	$\bar{1}32$				0.23901
B5	1.882	0.22622	0.22636	320	20	1.818	0.24248	0.24199
			0.22586	311				0.24309
B5	1.809	0.24473	0.24580	023	25	1.753	0.26046	0.25963
B10	1.772	0.25531	0.25446	231				
			0.25600	040				
				222	40	1.726	0.26893	0.26944
B10	1.753	0.26065	0.26096	$\bar{2}32$				
			0.26124	132				
Bw	1.741	0.26449	0.26376	$\bar{3}03$				
			0.26476	$\bar{2}23$	70	1.696	0.27846	0.27839
B5	1.709	0.27437	0.27404	140	B10	1.650	0.29404	0.29351
				041				0.29547
Bw	1.661	0.29035	0.28864	400	5	1.611	0.30866	0.30832
			0.29084	123				0.30806
				$\bar{4}02$	B10	1.591	0.31634	0.31667
				302				0.31582
vBw	1.635	0.29963	0.29956	$\bar{3}31$	-	-	-	-
B5	1.621	0.30504	0.30464	410	5	1.568	0.32592	0.32546
			0.30636	330	5	1.563	0.32796	0.32769
w	1.598	0.31359	0.31316	312	-	-	-	-
				$\bar{1}33$	vw	1.546	0.33536	0.33544
B5	1.581	0.32041	0.32176	204	vw	1.535	0.33990	0.33900
				004				0.33968
B5	1.562	0.32837	0.32816	240	-	-	-	-
-	-	-	-	$\bar{2}41$	vw	1.506	0.35319	0.35311
B5	1.545	0.33536	0.33684	742				
			0.33684	$\bar{4}21$				
B5	1.536	0.33969	0.33920	014	vw	1.497	0.35736	0.35682
			0.33936	$\bar{2}14$				

TABLE 11 continued

$LaPO_4$					$GdPO_4$			
I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
B5	1.474	0.36870	0.36924	$\bar{1}24$	5	1.435	0.38880	0.38863
-	-	-	-	104	B5	1.419	0.39775	0.39783
-	-	-	-	114	Bvw	1.389	0.41533	0.41497
B5	1.379	0.42115	0.41830	340	-	-	-	-

TABLE 12

$HoPO_4$, (tetragonal)					$LuPO_4$, (tetragonal)			
I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
50	4.52	0.03927	0.03914	101	20	4.48	0.03995	0.03984
100	3.435	0.06795	0.06792	200	30	3.41	0.06892	0.06928
15	2.740	0.10686	0.10706	211	15	2.71	0.10913	0.10912
15	2.5565	0.12265	0.12260	112	B30	2.5325	0.12494	0.12472
B15	2.428	0.13593	0.13584	220	10	2.407	0.13834	0.13856
10	2.262	0.15658	0.15656	202	-	-	-	-
25	2.1375	0.17534	0.17498	301	10	2.1165	0.17881	0.17840
25	1.9255	0.21608	0.21642	103	B10	1.9055	0.22055	0.22000
10	1.817	0.24278	0.24290	321	10	1.799	0.24766	0.24768
10	1.759	0.25905	0.25844	312	15	1.7435	0.26357	0.26328
B30	1.7165	0.27176	0.27168	400	B5	1.699	0.27753	0.27712
B5	1.680	0.28396	0.28434	213	B5	1.663	0.28972	0.28928
-	-	-	-	411	5	1.5885	0.31691	0.31696
5	1.536	0.33986	0.33960	420	5	1.521	0.34616	0.34640
B5	1.507	0.35273	0.35226	303	B5	1.494	0.35900	0.35856
-	-	-	-	332	B5	1.4128	0.40143	0.40184
B10	1.380	0.42058	0.42018	323	B5	1.367	0.42825	0.42784

a = 6.865 A.

c = 6.009 A.

a = 6.796 A.

c = 5.960 A.

powder and single-crystal methods. The powder diffraction studies were carried out by Debye-Scherrer (not Guinier) techniques. The d spacings agreed with those recorded in the present work. From single-crystal studies the space-group was found to be $P2_1/a$ and new indices were assigned to the powder lines which did not agree in every case with those derived from the work of Feigelson (1964) or Repko (1971).

Jaulmes's indices were found to fit the $\sin^2\theta$ values now recorded, although the improved resolution secured with the Guinier camera is evident in the recording of some doublets where Jaulmes found only single lines (see Table 13).

Further crystallographic study will be necessary to define the space-group unequivocally.

Infra-red Spectra of Lanthanide Orthophosphates:

The PO_4^{3-} anion has a tetrahedral T_d symmetry in which there are four fundamental vibrational modes. ν_1 and ν_3 correspond to stretchings of the P-O linkages. Antisymmetrical ν_3 occurs as a strong band in the 1080 $cm.^{-1}$ region whereas ν_4 an antisymmetrical deformation band, is in the 500 $cm.^{-1}$ region. The stretching vibration ν_1 is usually found around 970 $cm.^{-1}$ (Griffith and Grayson, 1969, Vol. 6, p. 326). Duval and Lecompte (1947) examined the infra-red spectra of a number of orthophosphates including the lanthanum and cerium compounds, but the first systematic study of monoclinic lanthanide arthophosphates was made by Hezel and Ross (1966). They found five bands in the ν_3 region and four bands in ν_4 region, due to lowering of the T_d symmetry of the phosphorus atom. For gadolinium orthophosphate ν_3 appears at 1105, 1070, 1042, 1028 and 1007 $cm.^{-1}$, ν_1 at 967 $cm.^{-1}$, ν_4 at 629, 583, 575 and 545 $cm.^{-1}$ and ν_2 at 488 $cm.^{-1}$.

TABLE 13

$LaPO_4$ indexing (monoclinic) according to Jaulmes (1972)

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
20	5.22	001	0.02941	0.02936
10	4.855	110	0.03400	0.03400
25	4.712	$\bar{1}11$	0.03608	0.03600
20	4.197	011	0.04547	0.04536
100*	4.13	$\bar{2}01$	0.04694	0.04804
10	3.569	-	0.06290	-
20	3.533	020	0.06418	0.06400
70	3.326	200	0.07243	0.07240
90	3.122	202	0.08221	0.08040
		121		0.08300
vw	2.97	-	-	-
15	3.012	111	0.08830	0.08872
80	2.882	$\bar{1}12$	0.09640	0.09672
20	2.612	002	0.11740	0.11744
5	2.462	012	0.13210	0.13340
10	2.449		0.13358	
w	2.425	220	0.13626	0.13600
w	2.350	$\bar{1}22$	0.14506	0.14472
10	2.207	$\bar{1}31$	0.16446	0.16400
30	2.153	$\bar{2}03$	0.17280	0.17208
30	2.147	$\bar{3}21$	0.17377	0.17328
20	1.993	$\bar{4}12$	0.20171	0.20256
20	1.981		0.20416	
B10	1.955	$\bar{4}01$	0.20965	0.20792
Bw	1.911	221	0.21932	0.22008
B20	1.887	$\bar{4}11$	0.22495	0.22342
5	1.882	-	0.22622	-
B5	1.809	$\bar{3}23$	0.24473	0.24400
B10	1.772	040	0.25531	0.25600
B10	1.753	$\bar{3}32$	0.26065	0.25928

* Vaseline line also.

TABLE 13 continued

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
Bw	1.741	-	-	-
B5	1.709	-	-	-
vBw	1.635	-	-	-
B5	1.621	-	-	-
w	1.598	-	-	-
B5	1.581	-	-	-
B5	1.562	-	-	-
B5	1.545	-	-	-
B5	1.536	-	-	-
B5	1.474	-	-	-
B5	1.379	-	-	-
B5	1.352	-	-	-

$a = 8.300$ A. $b = 7.071$ $c = 6.495$ $\beta = 126°30'$

Data now obtained (Infrared charts 1, 2, 3, 4) for monazite and orthophosphates of cerium, praseodymium, and gadolinium agree very well with these values and show no additional peaks. Petrov et al. (1971) assigned the same bands for gadolinium and praseodymium orthophosphates. Tenisheva, Pavlyukevich and Lazarev (1965) investigated the infrared spectra of monazite- and xenotime-type lanthanide phosphates, and gave some characterisation of the asymmetrization of the PO_4 tetrahedron in the internal field of the crystal. They found that as the radius of Ln^{3+} cation decreases, the intensity of band ν_1 and the distance between the modes of ν_3 vibration both increase. The orthophosphates of the lanthanides with ionic radii less than that of europium (in the present case gadolinium) have spectra similar to that of yttrium orthophosphate. The stretching vibration ν_3 was observed as a strong and broad double band; ν_1 was not present.

During the measurements reported here a comparison was made between yttrium and ytterbium orthophosphate spectra; both compounds have the xenotime structure. Two strong bands were found in the ν_4 region, instead of four in monazite structures, (Infrared charts 16, 17) appearing at 520 and 635 $cm.^{-1}$. Comparison of the infrared spectra of cerium, praseodymium and gadolinium orthophosphates confirmed the reported effect of ionic radius in the intensity of the ν_1 band around 970 $cm.^{-1}$. Non-existence of P-O-P ν_s bands between 800 and 650 $cm.^{-1}$ showed that the orthophosphates as now prepared did not contain any detectable quantity of pyrophosphate.

2.5 Reactions of lanthanide orthophosphates with lanthanide oxides; lanthanide oxide phosphates, $LnPO_4,Ln_2O_3$.

In the course of investigations of the sintering behaviour of lanthanide orthophosphates with sodium carbonate, described later, consideration was given to the formation of compounds of the type $LnPO_4,Ln_2O_3$. Such compounds have been reported in the literature by Russian authors, but not clearly identified. Kuznetsov, Vasil'eva and Tananaev (1964) claimed that lanthanum nitrate reacted with sodium orthophosphate in solution in two stages; first a basic salt of the composition $9LaPO_4,La(OH)_3,28H_2O$ was formed, but this was converted into the normal lanthanum orthophosphate as the sodium orthophosphate concentration was increased. X-ray patterns were reported for the basic phosphate and for the same compound after heating at 400°, 510° and 1200°C. The X-ray photographs were taken with a 57.3-mm. camera and with copper radiation, and the lines were both weak and diffuse. The product obtained by heating at 1200°C. gave a much sharper X-radiogram which resembled that of monoclinic lanthanum orthophosphate. The product obtained at 510°C. was assigned the composition $18LaPO_4,La_2O_3$, which was stated to undergo conversion into lanthanum orthophosphate and lanthanum oxide upon heating; however, most of the strong lines of hexagonal lanthanum oxide were not present in the X-radiogram. An amorphous compound of composition $9GdPO_4,Gd(OH)_3,27H_2O$ was claimed for gadolinium (Kuznetsov, Petushkova and Tananaev, 1964); at 1000°C. this decomposed into $18GdPO_4,Gd_2O_3$, which gave an X-ray photograph similar to that of gadolinium orthophosphate. Compounds of the same type were also reported for cerium (Ul'yanov and Kazakova, 1963) and for ytterbium, samarium and praseodymium (Petushkova, Tananaev and Samoilova, 1969).

Experimental:

Attempts were made to prepare compounds of composition $xLnPO_4.yLn_2O_3$ by solid-state reactions. The starting materials were the reagent-grade oxides and orthophosphates which were prepared in the laboratory by the method already described. After being mixed and crushed well in an agate mortar, appropriately proportioned mixtured were loaded into small platinum crucibles and sintered in a furnace at the temperatures indicated below. After sintering for an adequate period the products were crushed and subjected to X-ray analysis. In some cases samples were resintered after crushing to ensure complete reaction and crystallization.

Table 14 records the results of heating, under a variety of conditions, the orthophosphates of gadolinium, lanthanum and cerium with the corresponding oxides (in the case of cerium, CeO_2). Most of the sintering runs was accompanied by a weight loss of 1-1.5%, ascribed to adsorbed moisture and small quantities of volatilised phosphorus oxides.

Examination of Table 14 showed that compounds of the type $LnPO_4,Ln_2O_3$ were probably formed in these reactions. The intermediate phases obtained were in all cases the same even with differing reaction ratios. Gadolinium and lanthanum intermediates appeared, from their X-radiograms, to be isostructural. Cerium compounds did not react under the conditions used. Careful examination of the X-ray line intensities confirmed that the best molar ratio of reactants was 1:1, and the best reaction temperature was 1150°C. Several crushings between heatings were necessary to obtain the intermediates in good yield. Tables 15, 16 and 17 present X-ray diffraction data for both $GdPO_4,Gd_2O_3$ and $LaPO_4,La_2O_3$; for comparison data are also given for an intermediate obtained later during work on sintering reactions.

TABLE 14

Reactions of Lanthanide Orthosphosphates with lanthanide oxides.

Composition	Temp., duration	Phases Observed*			Film No.
$GdPO_4:Gd_2O_3$	of sintering	$GdPO_4$	Gd_2O_3	$GdPO_4, Gd_2O_3$	
1:1	700°C., 18 hrs.	s	s	None	10106B
1:1	900°C., 18 hrs.	m	m	s	10106C
4:1	900°C., 18 hrs.	s	w	s	10110A
2:1	900°C., 18 hrs.	s	mw	s	10110B
1:2	900°C., 18 hrs.	m	s	s	10111A
1:4	900°C., 18 hrs.	mw	s	s	10111B
1:0.83	950°C., 18 hrs.	m	mw	s	10111C
1:0.69	950°C., 18 hrs.	m	mw	s	10111D
1:1	10106C crushed resintered 960°C. 18 hrs.	w	w	s	10112A
1:0.69	10111D crushed resintered 960°C. 18 hrs.	mw	w	s	10112B
1:1	10112A 1150°C. 18 hrs.	None	vvw	s	10181A
$LaPO_4:La_2O_3$		$LaPO_4$	La_2O_3	$LaPO_4, La_2O_3$	
lg.:lg.	900°C., 18 hrs.	m	m	s	10122A
lg.:lg.	10122A 950°C. 23 hrs.	w	vw	s	10127D
$CePO_4:CeO_2$		$CePO_4$	CeO_2	$CePO_4, CeO_2$	
lg.:lg.	960°C., 18 hrs.	s	s	None	10112C

* s: strong, m: medium, mw: medium-weak,

w: weak, vvw: very very weak.

TABLE 15

X-ray Diffraction data of $GdPO_4$, Gd_2O_3 at 960°C.

Film 10112A, Rad. Co. K_α

a = 11.35 A. b = 7.95 A. c = 8.80 A. (orthorhombic)

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	Remarks		
10	11.61	100	0.00595	0.00620			$GdPO_4$, Gd_2O_3
10	8.84	001	0.01027	0.01029			$GdPO_4$, Gd_2O_3
25	7.95	010	0.01268	0.01270			$GdPO_4$, Gd_2O_3
90	6.49	110	0.01901	0.01890			$GdPO_4$, Gd_2O_3
25	5.745	200	0.02428	0.02480			$GdPO_4$, Gd_2O_3
10	5.425		0.02724				-
5	5.12		0.03053		$GdPO_4$		
5	5.05		0.03151				-
15	4.78	201	0.03511	0.03509			$GdPO_4$, Gd_2O_3
10	4.59		0.03806		$GdPO_4$		
20	4.42	002	0.04105	0.04116		Gd_2O_3	$GdPO_4$, Gd_2O_3
15	4.295		0.04351				-
5	4.115	102	0.04740	0.04736	$GdPO_4$		$GdPO_4$, Gd_2O_3
3	4.005		0.05003		$GdPO_4$		
5	3.97	020	0.05079	0.05080			$GdPO_4$, Gd_2O_3
90	3.86	012	0.05383	0.05386			$GdPO_4$, Gd_2O_3
vw	3.64	112	0.06038	0.06006			$GdPO_4$, Gd_2O_3
5	3.455	121	0.06710	0.06729	$GdPO_4$		$GdPO_4$, Gd_2O_3
5	3.43	310	0.06808	0.06850	$GdPO_4$		$GdPO_4$, Gd_2O_3
5	3.29		0.07405				-
vw	3.25	220	0.07588	0.07560			$GdPO_4$, Gd_2O_3
20	3.225		0.07690		$GdPO_4$		
5	3.16		0.08019				-
30	3.125		0.08200			Gd_2O_3	?
5	3.075		0.08462		$GdPO_4$		
20	3.03		0.08744		$GdPO_4$		
100	2.955	022	0.09208	0.09196			$GdPO_4$, Gd_2O_3
10	2.905		0.09510		$GdPO_4$	Gd_2O_3	
90	2.86	122	0.09807	0.09816			$GdPO_4$, Gd_2O_3
20	2.805		0.10174		$GdPO_4$		
30	2.71	401	0.10910	0.10949		Gd_2O_3	

TABLE 15 continued

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	Remarks		
10	2.67	410	0.11225	0.11190			-
30	2.61	203	0.11754	0.11741			$GdPO_4$,Gd_2O_3
15	2.555	411	0.12265	0.12219	$GdPO_4$	Gd_2O_3	$GdPO_4$,Gd_2O_3
10	2.514		0.12668				-
25	2.467	131	0.13166	0.13079			$GdPO_4$,Gd_2O_3
3	2.394		0.13987		$GdPO_4$		
3	2.387	401	0.14063	0.14036	$GdPO_4$		$GdPO_4$,Gd_2O_3
3	2.363	023	0.14337	0.14341	$GdPO_4$		$GdPO_4$,Gd_2O_3
3	2.342		0.14598		$GdPO_4$		
3	2.309	410	0.15030	0.15000		Gd_2O_3	$GdPO_4$,Gd_2O_3
3	2.292	412	0.15251	0.15306	$GdPO_4$		$GdPO_4$,Gd_2O_3
B3	2.266	032	0.15601	0.15546			$GdPO_4$,Gd_2O_3
B3	2.239	421	0.15980	0.16029	$GdPO_4$		$GdPO_4$,Gd_2O_3
5	2.195		0.16621		$GdPO_4$	Gd_2O_3	?
5	2.188	510	0.16738	0.16770	$GdPO_4$		$GdPO_4$,Gd_2O_3
50	2.175	330	0.16934	0.17010			$GdPO_4$,Gd_2O_3
30	2.148		0.17362		$GdPO_4$		?
50	2.139		0.17514		$GdPO_4$		?
5	2.126	014	0.17727	0.17734		Gd_2O_3	$GdPO_4$,Gd_2O_3
5	2.108	331	0.18028	0.18039	$GdPO_4$		$GdPO_4$,Gd_2O_3
5	2.096		0.18230		$GdPO_4$		
5	2.075		0.18619		$GdPO_4$		
3	2.044	403	0.19183	0.19181	$GdPO_4$		$GdPO_4$,Gd_2O_3
70	2.020	502	0.19631	0.19616			$GdPO_4$,Gd_2O_3
20	1.978	413	0.20470	0.20451		Gd_2O_3	$GdPO_4$,Gd_2O_3
40	1.927	024	0.21572	0.21544			$GdPO_4$,Gd_2O_3
40	1.913	141	0.21896	0.21969		Gd_2O_3	$GdPO_4$,Gd_2O_3
5	1.893	431	0.22367	0.22379	$GdPO_4$		$GdPO_4$,Gd_2O_3
15	1.856	314	0.23264	0.23314	$GdPO_4$	Gd_2O_3	$GdPO_4$,Gd_2O_3
15	1.835	241	0.23801	0.23829	$GdPO_4$		$GdPO_4$,Gd_2O_3
5	1.824		0.24099		$GdPO_4$		
40	1.788	142	0.25076	0.25056			$GdPO_4$,Gd_2O_3
5	1.767	005	0.25668	0.25725			$GdPO_4$,Gd_2O_3

TABLE 15 continued

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	Remarks		
5	1.756	340	0.25989	0.25900	$GdPO_4$	Gd_2O_3	$GdPO_4, Gd_2O_3$
5	1.746	105	0.26296	0.26345			$GdPO_4, Gd_2O_3$
5	1.730		0.26758		$GdPO_4$		
75	1.716	324	0.27184	0.27124			$GdPO_4, Gd_2O_3$
5	1.699	612	0.27729	0.27706	$GdPO_4$		
5	1.685	205	0.28199	0.28207			$GdPO_4, Gd_2O_3$
80	1.665		0.28905			Gd_2O_3	?
25	1.631	143	0.30127	0.30201		Gd_2O_3	
15	1.614	025	0.30765	0.30805	$GdPO_4$		$GdPO_4, Gd_2O_3$
15	1.595	125	0.31472	0.31425	$GdPO_4$	Gd_2O_3	$GdPO_4, Gd_2O_3$
5	1.570		0.32490		$GdPO_4$		
5	1.556		0.33104		$GdPO_4$	Gd_2O_3	
10	1.545		0.33577		$GdPO_4$		
B5	1.531	250	0.34176	0.34230	$GdPO_4$		$GdPO_4, Gd_2O_3$
10	1.512		0.35048		$GdPO_4$		
B3	1.502	720	0.35507	0.35460	$GdPO_4$		$GdPO_4, Gd_2O_3$
B3	1.490		0.36092		$GdPO_4$		
20	1.478	023 044	0.36680	0.36661 0.36784			$GdPO_4, Gd_2O_3$
40	1.4705	006	0.37059	0.37044			$GdPO_4, Gd_2O_3$
B30	1.4275	244	0.39306	0.39264	$GdPO_4$		$GdPO_4, Gd_2O_3$
B10	1.402	216	0.40760	40794			$GdPO_4, Gd_2O_3$
B10	1.393		0.41275		$GdPO_4$		
B30	1.350	316	0.44060	0.43894		Gd_2O_3	$GdPO_4, Gd_2O_3$

TABLE 16

X-ray Diffraction Data of $LaPO_4$, La_2O_3 at 950°C.

Film 10127D Rad. Co. K_α

I	d(A.)	Remarks	I	d(A.)	Remarks	I	d(A.)	Remarks
5	10.92		20	2.945		20	1.785	
5	9.28		20	2.91		10	1.771	
5	8.19		20	2.885		20	1.755	
70	6.81		5	2.795		5	1.740	$LaPO_4$
10	5.847		5	2.70		40	1.721	
5	5.42		5	2.67		40	1.708	
10	5.215	$LaPO_4$	10	2.605	$LaPO_4$	5	1.632	$LaPO_4$
5	4.834	$LaPO_4$	10	2.44		5	1.614	$LaPO_4$
10	4.715	$LaPO_4$	5	2.35		5	1.600	
10	4.435		50	2.265		30	1.527	
10	4.187	$LaPO_4$	15	2.223		10	1.472	$LaPO_4$
50	4.123	Vas.+$LaPO_4$	15	2.214		10	1.457	
70	3.96		5	2.153	$LaPO_4$	5	1.439	
20	3.71	Vas.	5	2.140	$LaPO_4$	30	1.416	
5	3.56	$LaPO_4$	60	2.070		B5	1.352	
5	3.527	$LaPO_4$	5	2.023		B5	1.335	
10	3.39		40	1.981		B5	1.322	
20	3.32	$LaPO_4$	5	1.951	$LaPO_4$	Bw	1.233	
15	3.266		5	1.931		Bw	1.223	
15	3.226		10	1.906	$LaPO_4$			
25	3.115	$LaPO_4$	20	1.884				
100	3.053		10	1.840				
5	3.003	$LaPO_4$	10	1.827				
5	2.973	$LaPO_4$+La_2O_3	10	1.808	$LaPO_4$			
			20	1.794				

TABLE 17

X-ray diffraction data of $GdPO_4$, Gd_2O_3 from $2GdPO_4 + \frac{3}{2}Na_2CO_3$, sintering product (water extraction residue at 950°C.)

Film 10087A, Rad. Co. K_α

I	d(A.)	Remarks			
10	11.52	$GdPO_4$, Gd_2O_3			
20	9.24		$GdPO_4$, Na_3PO_4		
5	8.86	$GdPO_4$, Gd_2O_3			
25	7.93	$GdPO_4$, Gd_2O_3			
100	6.565		$GdPO_4$, Na_3PO_4		
100	6.43	$GdPO_4$, Gd_2O_3			
20	5.765	$GdPO_4$, Gd_2O_3			
10	5.58		$GdPO_4$, Na_3PO_4		
10	5.42	$GdPO_4$, Gd_2O_3			
Bvw	5.03	$GdPO_4$, Gd_2O_3			
10	4.79	$GdPO_4$, Gd_2O_3			
80	4.61		$GdPO_4$, Na_3PO_4		
5	4.41	$GdPO_4$, Gd_2O_3		Gd_2O_3	
5	4.38				
10	4.31	$GdPO_4$, Gd_2O_3			
B40	4.145		$GdPO_4$, Na_3PO_4	Vas.	
10	3.97	$GdPO_4$, Gd_2O_3			
90	3.86	$GdPO_4$, Gd_2O_3	$GdPO_4$, Na_3PO_4		
5	3.735	$GdPO_4$, Gd_2O_3		Vas.	
50	3.49		$GdPO_4$, Na_3PO_4		
20	3.255	$GdPO_4$, Gd_2O_3	$GdPO_4$, Na_3PO_4		
5	3.22				$GdPO_4$
10	3.16		$GdPO_4$, Na_3PO_4		
10	3.12	?		Gd_2O_3	
15	3.035		$GdPO_4$, Na_3PO_4		$GdPO_4$
100	2.945	$GdPO_4$, Gd_2O_3			
5	2.905			Gd_2O_3	$GdPO_4$
80	2.86	$GdPO_4$, Gd_2O_3			
5	2.815				$GdPO_4$
70	2.78		$GdPO_4$, Na_3PO_4		

TABLE 17 continued

I	d(A.)	Remarks			
5	2.705	$GdPO_4, Gd_2O_3$		Gd_2O_3	
80	2.66		$GdPO_4, Na_3PO_4$		
30	2.61	$GdPO_4, Gd_2O_3$			
30	2.462	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$		
5	2.361	$GdPO_4, Gd_2O_3$			$GdPO_4$
20	2.311	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$	Gd_2O_3	
5	2.269	$GdPO_4, Gd_2O_3$			
30	2.234	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$		
5	2.197	?		Gd_2O_3	$GdPO_4$
5	2.187	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$		$GdPO_4$
40	2.171	$GdPO_4, Gd_2O_3$			
20	2.147	?			$GdPO_4$
20	2.135	?			$GdPO_4$
20	2.113	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$		
vw	2.078				$GdPO_4$
10	2.058		$GdPO_4, Na_3PO_4$		
50	2.021	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$		
vw	1.999		$GdPO_4, Na_3PO_4$		
10	1.980	$GdPO_4, Gd_2O_3$		Gd_2O_3	
10	1.961		$GdPO_4, Na_3PO_4$		$GdPO_4$
B40	1.924	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$	Gd_2O_3	$GdPO_4$
5	1.854	$GdPO_4, Gd_2O_3$		Gd_2O_3	$GdPO_4$
5	1.837	$GdPO_4, Gd_2O_3$			$GdPO_4$
B5	1.809				$GdPO_4$
20	1.789	$GdPO_4, Gd_2O_3$			
5	1.766	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$		$GdPO_4$
B10	1.742	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$		$GdPO_4$
60	1.716	$GdPO_4, Gd_2O_3$			
10	1.686	$GdPO_4, Gd_2O_3$			
B60	1.666	?	$GdPO_4, Na_3PO_4$	Gd_2O_3	
B5	1.6325	$GdPO_4, Gd_2O_3$	$GdPO_4, Na_3PO_4$	Gd_2O_3	
10	1.614	$GdPO_4, Gd_2O_3$			$GdPO_4$
10	1.596	$GdPO_4, Gd_2O_3$		Gd_2O_3	$GdPO_4$
10	1.577		$GdPO_4, Na_3PO_4$		
20	1.556		$GdPO_4, Na_3PO_4$		$GdPO_4$

TABLE 17 continued

I	d(A.)	Remarks			
5	1.545				$GdPO_4$
15	1.533	$GdPO_4$,Gd_2O_3	$GdPO_4$,Na_3PO_4		$GdPO_4$
B5	1.5115				$GdPO_4$
5	1.4905				$GdPO_4$
10	1.479	$GdPO_4$,Gd_2O_3			
20	1.470	$GdPO_4$,Gd_2O_3		Gd_2O_3	
B5	1.459		$GdPO_4$,Na_3PO_4		
20	1.4285	$GdPO_4$,Gd_2O_3			$GdPO_4$
5	1.402	$GdPO_4$,Gd_2O_3			$GdPO_4$
5	1.393				$GdPO_4$
5	1.385		$GdPO_4$,Na_3PO_4		$GdPO_4$
30	1.349	$GdPO_4$,Gd_2O_3		Gd_2O_3	

The X-ray pattern attributed to the work of Kuznetsov in A.S.T.M. Card 21-446, and considered to be due to $La_4(P_2O_7)_3, 0.5La_2O_3$ formed at 1000°C., contained a number of lines corresponding with those of $LaPO_4, La_2O_3$. This indicates the need to review Kuznetsov's data, which in any case are hard to reconcile with work on pyrophosphates described later in this Thesis.

The X-ray diffraction data for $GdPO_4, Gd_2O_3$ at 960°C. (Film 10112A) have been indexed in the orthorhombic system with the cell parameters a = 11.35, b = 7.95 and c = 8.80 A. Some lines could not be indexed, and it seems probable that the true symmetry is monoclinic or triclinic. The $GdPO_4, Gd_2O_3$ heated at 1150°C. gave an X-radiogram to which the previous orthorhombic indexing could not be fitted although there was good agreement among strong lines (Table 18).

It is noteworthy that a compound of similar stoichiometry, Gd_3NbO_7 was reported by Garton (1968, see also A.S.T.M. Card 21-336), but the structures were not similar, although a few strong lines in the photographs corresponded.

TABLE 18

X-ray Diffraction data of $GdPO_4$, Gd_2O_3 at 1150°C.
Film 10181A, Rad. Cu. K_α

I	d(A.)	Remarks	I	d(A.)	Remarks
10	10.46		w	2.071	
10	8.84		30	2.016	
5	8.345		w	1.980	
70	6.44		20	1.948	
3	5.906		5	1.926	
5	5.73		10	1.915	Gd_2O_3
			w	1.891	
70	3.84		10	1.857	
40	3.14		10	1.783	
40	3.10	$+Gd_2O_3$	30	1.714	
100	2.94		B5	1.679	
80	2.85		40	1.662	
10	2.816		w	1.471	
5	2.69		w	1.427	
30	2.609		w	1.409	
5	2.459		Bw	1.347	
15	2.167		w	1.282	
B15	2.140				

SECTION 3

PREPARATION AND PROPERTIES OF ALKALI LANTHANIDE PHOSPHATES OBTAINED BY "DRY" REACTIONS AT HIGH TEMPERATURES

3.1. Preparation from lanthanide orthophosphate and sodium carbonate.

The sintering reaction of monazite with sodium carbonate has been known since 1932 (Brunck and Höltje). Solid-state reactions of individual lanthanide phosphates with sodium carbonate, and the intermediate products formed in them, have not been described in the literature. The monazite reactions will be discussed in detail in Section 5; those of individual lanthanide phosphates are considered here.

The reaction between a lanthanide phosphate and sodium carbonate can be represented by the following equation:

$$2LnPO_4 + 3Na_2CO_3 \rightarrow Ln_2O_3 + 2Na_3PO_4 + 3CO_2$$

If the stoichiometric amount of sodium carbonate is used the end product of the reaction is expected to be the lanthanide oxide. Some workers (e.g. Ambrozhii, Luchnikova and Sidorova, 1960) have postulated that compounds of the type Ln_2O_3,CO_2 occur as intermediate products in the decomposition of $Ln_2(CO_3)_3$ and are stable up to 830°C., but there is no support for the formation of such compounds in the reactions studied in this work. The aim in the work now described was to investigate the reaction products when less than the theoretical amount of sodium carbonate is used.

Experimental:

Lanthanum and gadolinium orthophosphates were used in these investigations. They were both prepared in the laboratory by the method already described and their purity was checked by X-ray diffraction as described in Section 2.4. Several mixtures of each phosphate with sodium carbonate, with compositions containing from 17.5% of the theoretical amount of sodium carbonate to a 10% excess

of it were employed. The reactants were weighed and ground together in an agate mortar. The sintering operation was carried out in small platinum crucibles in an electric muffle at 700°C. In a few cases higher temperatures were used to ensure complete reaction. After the sintering operation the crucibles were cooled in a desiccator containing silica gel and weighed. The products were then subjected to X-ray diffraction analysis. The results are summarised below in relation to the initial mixture compositions.

Gadolinium Orthophosphate sintered with 10% excess of Sodium Carbonate:

The reaction proceeded in accordance with the equation given above; the main products were gadolinium oxide and sodium orthophosphate (Film 10037C, Table 19). No unreacted gadolinium phosphate was observed from the X-ray diffraction film. The experimental loss of weight presumed to represent loss of carbon dioxide was in agreement with the calculated value. The product was extracted with cold water, and the insoluble residue was filtered off, dried, and heated to 700°C. again. The X-ray diffraction film showed only gadolinium oxide lines (Film 10041C). The loss of weight on extraction agreed well with the calculated weight of sodium orthophosphate required by the reaction.

Lanthanum Orthophosphate sintered with 10% excess of Sodium Carbonate:

At first a different pattern was observed in the X-ray diffraction film of the product of this reaction (Film 10037D). The difference was found to arise from conversion of lanthanum oxide into the hydroxide by atmospheric moisture during the X-ray exposure. By covering the specimen track with a "Mylar" film the absorption of water was prevented, and the X-radiogram showed the expected products (Table 20). Since a reaction temperature higher than 700°C. was employed, the γ-form of sodium orthophosphate was obtained in this

TABLE 19

Gadolinium Orthophosphate sintered with 10% excess of Sodium Carbonate (700°C.)

Film 10037C, Rad. Co. K_α

I	d(A.)	Remarks
50	4.39	Gd_2O_3 (cubic form)
20	4.235	Na_3PO_4
5	3.94	Na_3PO_4
5	3.81	Na_3PO_4
100	3.11	$Gd_2O_3 + Na_3PO_4$
10	2.98	Na_2CO_3
15	2.88	Gd_2O_3
10	2.78	Na_3PO_4
100	2.69	$Gd_2O_3 + Na_3PO_4$
20	2.60	Na_3PO_4 (γ-form)
40	2.537	$Gd_2O_3 + Na_3PO_4$
10	2.408	$Gd_2O_3 + Na_3PO_4$
5	2.356	Na_2CO_3
40	2.295	Gd_2O_3
10	2.198	Gd_2O_3
40	2.115	Gd_2O_3
10	2.067	Na_3PO_4
30	1.967	Gd_2O_3
100	1.908	$Gd_2O_3 + Na_3PO_4$
20	1.849	$Gd_2O_3 + Na_3PO_4$ (Y-form)
30	1.751	Gd_2O_3
10	1.706	Gd_2O_3
30	1.665	Gd_2O_3
90	1.627	Gd_2O_3
30	1.590	Gd_2O_3
40	1.557	Gd_2O_3
20	1.525	$Gd_2O_3 + Na_3PO_4$
10	1.496	$Gd_2O_3 + Na_3PO_4$ (Y-form)
20	1.468	Gd_2O_3
10	1.441	Gd_2O_3
B10	1.368	$Gd_2O_3 + Na_3PO_4$

TABLE 20

Lanthanum Orthophosphate sintered with 10% excess of Sodium Carbonate (800°C.)

Film 10050B, Rad. Co. K_α

I	d(A.)	Remarks
30	4.285	Na_3PO_4 (γ-form)
70	3.411	La_2O_3 (Hexagonal form)
60	3.071	" " "
100	2.987	" " "
60	2.620	Na_3PO_4 (γ-form)
50	2.283	La_2O_3 (Hexagonal form)
60	1.971	" " "
10	1.852	Na_3PO_4 (γ-form)
60	1.755	La_2O_3 (Hexagonal form)
3	1.706	" " "
30	1.658	" " "
10	1.642	" " "
3	1.535	" " "
3	1.513	Na_3PO_4 (γ-form)
10	1.490	La_2O_3 (Hexagonal form)
3	1.400	Na_3PO_4 (γ-form)

case. Theoretical and observed losses of weight again corresponded (Table 21A). The X-ray pattern (10047B) of the water extraction residue showed only lanthanum hydroxide lines. The loss of weight on extraction, after allowance for excess sodium carbonate, was in satisfactory agreement with the expected weight of sodium phosphate formed.

Sintering of Gadolinium Orthophosphate with 17.5 to 75% of the theoretical amount of Sodium Carbonate:

Mixtures of the reactants in several selected ratios were prepared and sintered at 700°C. In all cases there was a good agreement between experimental losses of weight and calculated values assuming complete expulsion of carbon dioxide from the reacting carbonate. The results of the X-ray diffraction analysis of the products are tabulated in Table 22.

An intermediate product was detected in all experiments employing the smaller proportions of sodium carbonate. As the amount of sodium carbonate employed was increased, the intermediate structure was observed to increase in quantity and the amount of unreacted gadolinium orthophosphate diminished. With 40-50% of the theoretical amount of sodium carbonate, the intermediate predominated, and very little unreacted gadolinium orthophosphate remained. With 75% of the theoretical sodium carbonate, intermediate lines were weaker, but gadolinium oxide and sodium orthophosphate lines became very strong. As before, no intermediate lines were observed when a 10% excess of sodium carbonate was used. Table 23 shows the X-ray diffraction patterns of these products. Use of sodium chloride as an internal standard for film measurements has reduced the recorded intensities of some lines listed in Table 23.

The product obtained by using 50% of the required sodium

$LnPO_4$ + Na_2CO_3 reactions, sintering and water extraction results.

TABLE 21A ($LaPO_4$)

Theoretical Na_2CO_3	50%	10% excess
$LaPO_4$ g.	0.3544	0.3140
Na_2CO_3 g.	0.1205	0.2348
Total	0.4749	0.5488
Loss of weight on sintering g.	0.0503	0.0962
Theoretical loss of weight g.	0.0500	0.0974
Product g.	0.4246	0.4526
Loss of weight on extraction with H_2O g.	0.0640	0.2520*
Theoretical Na_3PO_4 g.	0.1242	0.2201
Combined Na_3PO_4 g.	0.0602	None
X-ray Film No.	10036A	10037D
Remarks	Int. (s) Na_3PO_4 (m) La_2O_3 (vw)	La_2O_3 $La(OH)_3$ Na_3PO_4

TABLE 21B ($LaPO_4$+$GdPO_4$ (1:1))

50%	10% excess
0.1837+0.1837	0.1380+0.1380
0.1203	0.1990
0.4877	0.4750
0.0525	0.0806
0.0499	0.0750
0.4352	0.3944
0.0557	0.2107*
0.1241	0.1864
0.0684	None
10036C	10036D
Int. (s) $GdPO_4$ Gd_2O_3	$La(OH)_3$ (s) La_2O_3 (w) Gd_2O_3 (m) Na_3PO_4 (w)

*Intermediate may be slightly soluble in water or passed through the filter.

TABLE 22

$GdPO_4$ + Na_2CO_3 reactions, sintering and water extraction results at 700°C.

Theoretical Na_2CO_3	17.5%	25%	32.5%	40%	50%	60%	75%	10% excess
$GdPO_4$ g.	0.1801	0.3455	0.1660	0.1597	0.3722	0.1451	0.2716	0.2958
Na_2CO_3 g.	0.0199	0.0545	0.0340	0.0403	0.1173	0.0549	0.1284	0.2051
Total	0.2000	0.4000	0.2000	0.2000	0.4895	0.2000	0.4000	0.5009
Loss of weight on sintering g.	0.0084	0.0246	0.0157	0.0165	0.0514	0.0221	0.0564	0.0833
Theorectical loss of weight g.	0.0083	0.0220	0.0141	0.0167	0.0487	0.0228	0.0533	0.0852
Product g.	0.1916	0.3754	0.1843	0.1835	0.4381	0.1779	0.3436	0.4176
Loss of weight on extraction with H_2O g.	-	-	-	-	0.0513	-	-	0.2070
Theoretical Na_3PO_4 g.	-	-	-	-	0.1210	-	-	0.1923
Combined Na_3PO_4 g.	-	-	-	-	0.0696	-	-	No
Film No.	10053A	10044D	10053B	10053C	10036B	10056A	10044A	10037C
Remarks	$GdPO_4$(s) Int. (s) Gd_2O_3(vw)	$GdPO_4$(s) Int. (s) Gd_2O_3(m)	$GdPO_4$(m) Int. (s) Gd_2O_3(m)	Int.(vs) Na_3PO_4(mw) Gd_2O_3(m) $GdPO_4$(w)	Int.(vs) Na_3PO_4(m) Gd_2O_3 (m) $GdPO_4$(w)	Int. (s) $GdPO_4$(w) Gd_2O_3(s) Na_3PO_4 (m)	Int. (m) $GdPO_4$(w) Na_3PO_4 (s) Gd_2O_3(vs)	Gd_2O_3(s) Na_3PO_4(s)

TABLE 23

$GdPO_4$ + Na_2CO_3 sintering reactions

Rad. Co. K_α

10053A		10051A		10053B		10053C		10051B		10056A		10044A		Film No.
17.5%		25%		32.5%		40%		50%		60%		75%		Na_2CO_3 % theo.
I	d*	I	d	I	d	I	d	I	d	I	d	I	d	Remarks
-	-	-	-	-	-	10	14.68	40	14.70	15	14.83	10	14.89	Int.
-	-	vw	9.45	-	-	-	-	w	9.16	-	-	-	-	Int.
-	-	-	-	vw	7.89	10	7.89	w	7.93	vw	7.91	-	-	Int.
-	-	-	-	-	-	5	7.385	10	7.385	10	7.39	3	7.39	Int.
-	-	-	-	-	-	5	6.940	-	-	3	7.02			Int.
30	6.455	40	6.50	40	6.455	B50	6.455	40	6.50	10	6.52	30	6.56	Int.
vw	5.73	3	5.74	3	5.725	5	5.725	-	-	-	-	5	5.78	Int.
10	5.115	20	5.14	5	5.110	-	-	5	5.14	-	-	5	5.12	$GdPO_4$
-	-	-	-	-	-	vw	4.75	-	-	-	-	-	-	Int.
10	4.71	10	4.705	-	-	-	-	-	-	-	-	-	-	$GdPO_4$
20	4.59	50	4.595	40	4.59	60	4.59	40	4.60	40	4.60	30	4.61	Int. + $GdPO_4$
-	-	-	-	-	-	5	4.404	10	4.42	10	4.42	30	4.44	Gd_2O_3
-	-	-	-	-	-	5	4.28	10	4.29	3	4.28	30	4.30	Na_3PO_4 (γ-form)
80	4.15	100	4.150	80	4.15	80	4.14	B100	4.165	40	4.15	100	4.16	Int. + Vas.
20	4.105	30	4.10	10	4.09	-	-	-	-	-	-	-	-	$GdPO_4$
10	3.995	20	3.995	5	3.99	B3	3.97	-	-	-	-	-	-	$GdPO_4$

*d is given in A.

TABLE 23 continued

17.5%		25%		32.5%		40%		50%		60%		75%		Remarks
I	d	I	d	I	d	I	d	I	d	I	d	I	d	
20	3.845	40	3.855	40	3.845	60	3.84	40	3.85	30	3.85	10	3.85	Int.
40	3.73	40	3.740	40	3.73	40	3.73	40	3.74	15	3.73	70	3.74	Vas.
-	-	-	-	-	-	-	-	10	3.545	3	3.545	-	-	Int.
-	-	10	3.475	B10	3.47	20	3.47	20	3.480	15	3.475	10	3.49	Int.
10	3.45	10	3.455	-	-	-	-	-	-	-	-	-	-	$GdPO_4$
10	3.425	10	3.425	10	3.42	-	-	-	-	-	-	-	-	$GdPO_4$
-	-	-	-	-	-	5	3.335	5	3.330	w	3.330	-	-	Int.
20	3.256	-	-	20	3.256	-	-	-	-	-	-	5	3.28	NaCl + Na_3PO_4
20	3.225	50	3.230	20	3.22	15	3.22	10	3.235	-	-	5	3.23	Int. + $GdPO_4$
-	-	20	3.120	20	3.115	30	3.11	100	3.130	100	3.125	100	3.135	Gd_2O_3 + Na_3PO_4
10	3.07	-	-	5	3.065	-	-	-	-	-	-	-	-	$GdPO_4$
50	3.025	100	3.030	40	3.025	20	3.02	20	3.025	10	3.030	15	3.030	Int. + $GdPO_4$
5	2.99	-	-	w	2.99	vw	2.985	5	3.000	-	-	-	-	$GdPO_4$
30	2.94	80	2.945	50	2.94	100	2.94	70	2.945	40	2.945	20	2.950	Int.
5	2.925	-	-	-	-	-	-	-	-	-	-	-	-	$GdPO_4$
5	2.89	-	-	5	2.895	5	2.90	-	-	-	-	5	2.90	Gd_2O_3 + $GdPO_4$
10	2.852	30	2.850	20	2.852	40	2.85	30	2.850	15	2.855	5	2.86	Int.
100	2.82	-	-	100	2.82	-	-	-	-	-	-	-	-	NaCl
10	2.804	80	2.810	10	2.800	B20	2.795	10	2.810	-	-	-	-	$GdPO_4$

TABLE 23 continued

17.5%		25%		32.5%		40%		50%		60%		75%		Remarks
I	d	I	d	I	d	I	d	I	d	I	d	I	d	
5	2.778	20	2.780	20	2.772	60	2.775	80	2.780	B50	2.780	30	2.79	Int.
vw	2.70	5	2.710	3	2.70	B10	2.700	50	2.710	B40	2.705	80	2.71	Gd_2O_3 + Na_3PO_4
20	2.655	40	2.655	40	2.652	60	2.650	80	2.655	60	2.655	30	2.66	Int.
vw	2.61	3	2.610	7	2.605	10	2.600	5	2.625	3	2.620	40	2.63	$Na_3PO_4(\gamma)$ + Int.
20	2.557	30	2.560	10	2.555	5	2.553	20	2.560	3	2.555	20	2.555	Gd_2O_3 + Na_3PO_4 + $GdPO_4$
-	-	20	2.494	-	-	5	2.513	15	2.492	vw	2.494	10	2.499	Int. + $GdPO_4$
vw	2.458	10	2.462	5	2.457	B10	2.455	10	2.458	15	2.457	5	2.461	Int.
-	-	-	-	-	-	-	-	-	-	-	-	5	2.422	Gd_2O_3
B20	2.391	30	2.392	10	2.391	5	2.391	vw	2.396	-	-	-	-	$GdPO_4$
-	-	3	2.309	10	2.305	10	2.299	10	2.310	B15	2.306	20	2.311	Int. + Gd_2O_3
vw	2.289	5	2.293	vw	2.289	-	-	-	-		-	-	-	$GdPO_4$
5	2.227	20	2.230	10	2.224	15	2.225	15	2.230	10	2.229	10	2.236	Int. + Na_3PO_4
5	2.199	3	2.207	-	-		-	-	-	w	2.205	5	2.209	Gd_2O_3 + $GdPO_4$
-	-	-	-	-	-	vw	2.1810	B5	2.188	3	2.186	5	2.188	Int.
5	2.169	10	2.169	10	2.168	15	2.1665	5	2.174	3	2.170			Int.
30	2.14	30	2.142	35	2.137	40	2.135	15	2.142	10	2.139	5	2.148	Int. + $Na_3PO_4(\gamma)$ + $GdPO_4$
-	-	-	-	-	-	-	-	5	2.123	-	-	20	2.125	Gd_2O_3
10	2.104	30	2.106	10	2.103	10	2.103	10	2.100	10	2.110			Int. + $GdPO_4$
10	2.0955	20	2.098	10	2.0955	3	2.0965	-	-	-	-	-	-	$GdPO_4$
20	2.075	-	-	15	2.074	10	2.072	5	2.081	3	2.076	5	2.076	Na_3PO_4 + $GdPO_4$

TABLE 23 continued

17.5%		25%		32.5%		40%		50%		60%		75%		Remarks
I	d	I	d	I	d	I	d	I	d	I	d	I	d	
-	-	5	2.050		-	5	2.051	-	-	3	2.058	-	-	Int.
5	2.0185	20	2.018	10	2.0165	B30	2.015	10	2.019	3	2.016	10	2.015	Int.
70	1.994	-	-	70	1.994	3	1.993	5	1.999	3	1.998	-	-	NaCl + Int.
-	-	-	-	-	-	3	1.9755	-	-	-	-	-	-	Int.
-	-	-	-	-	-	vw	1.940	10	1.941	10	1.942	-	-	Int.
-	-	-	-	10	1.924	10	1.924	-	-	-	-	-	-	Int. + $GdPO_4$
30	1.914	B50	1.920	40	1.914	50	1.915	40	1.9165	B40	1.915	80	1.916	Int. + Gd_2O_3
10	1.891	10	1.895	5	1.891	3	1.891	-	-	-	-	-	-	$GdPO_4$
20	1.855	20	1.858	10	1.854	5	1.853	5	1.858	w	1.851	20	1.858	Na_3PO_4 + Gd_2O_3 + $GdPO_4$
25	1.833	40	1.836	20	1.832	15	1.832	2	1.834	-	-	5	1.838	Na_3PO_4 + $GdPO_4$
10	1.821	20	1.824	5	1.821	3	1.821	2	1.825	-	-	-	-	$GdPO_4$
vw	1.788	w	1.789	5	1.785	B10	1.786	5	1.794	w	1.786	-	-	Int. + Gd_2O_3
10	1.758	10	1.760	5	1.756	3	1.758	5	1.759	Bw	1.755	10	1.759	Int. + Gd_2O_3 + $GdPO_4$
vw	1.742	-	-	B3	1.741	B10	1.742	5	1.745	Bw	1.739	-	-	Int.
10	1.729	20	1.729	5	1.729	vw	1.728	-	-	-	-	-	-	$GdPO_4$
10	1.713	-	-	20	1.713	B40	1.712	5	1.716	-	-	5	1.713	Int. + Gd_2O_3
20	1.699	30	1.700	10	1.699	3	1.699	5	1.700	vw	1.701	-	-	Gd_2O_3 + $GdPO_4$
-	-	-	-	vw	1.685	3	1.684	-	-	-	-	-	-	Int.
5	1.663	10	1.666	20	1.662	B40	1.662	5	1.667	B10	1.665	10	1.672	Int. + Gd_2O_3 + $GdPO_4$
5	1.655	10	1.657	3	1.654	-	-	5	1.658	-	-	-	-	-

TABLE 23 continued

17.5%		25%		32.5%		40%		50%		60%		75%		Remarks
I	d	I	d	I	d	I	d	I	d	I	d	I	d	
40	1.628	3	1.631	40	1.628	B20	1.628	30	1.632	B20	1.629	50	1.634	Int. + Gd_2O_3
vw	1.613	vw	1.613	vw	1.612	vw	1.610	-	-	-	-	-	-	$GdPO_4$
5	1.595	10	1.598	5	1.595	5	1.595	w	1.596	10	1.595	20	1.598	Gd_2O_3 + $GdPO_4$
B5	1.570	B10	1.571	B3	1.571	B3	1.572	w	1.579	w	1.577	20	1.565	Int. + Gd_2O_3
3	1.551	B5	1.556	5	1.552	B10	1.553	w	1.557	B10	1.559	-	-	Int. + Na_3PO_4
vw	1.535	B5	1.533	5	1.530	B10	1.530	w	1.532	w	1.533	10	1.533	Na_3PO_4 + $GdPO_4$ + Int.
-	-	-	-	vw	1.511	vw	1.511	-	-	-	-	10	1.516	$Na_3PO_4(Y)$ + $GdPO_4$
-	-	Bw	1.502	vw	1.501	vw	1.501	-	-	-	-	5	1.505	Gd_2O_3 + $GdPO_4$
vw	1.468	Bw	1.469	5	1.468	B10	1.468	w	1.473	w	1.471	5	1.474	Int. + Gd_2O_3
-	-	-	-	-	-	5	1.456	w	1.458	w	1.456	-	-	Int.
-	-	Bw	1.423	3	1.425	B5	1.425	-	-	-	-	-	-	Na_3PO_4 + $GdPO_4$
-	-	-	-	3	1.399	3	1.399	-	-	-	-	-	-	Int.
-	-	-	-	3	1.392	3	1.392	-	-	-	-	-	-	Int.
-	-	-	-	-	-	-	-	-	-	-	-	10	1.373	Gd_2O_3
-	-	-	-	-	-	-	-	-	-	-	-	20	1.354	Gd_2O_3

carbonate which had the largest content of the intermediate phase, was extracted with water. There was a small loss in weight after extraction of the product with water, but it was clear that the major part of the sodium phosphate formed in the reaction of sodium carbonate had remained combined in the insoluble intermediate phase. As expected, the X-ray pattern of the water extraction residue after heating at 700°C. (10065C) showed loss of the sodium orthophosphate lines but was otherwise identical with that of the product before extraction with water. Evidently the intermediate phase was not appreciably soluble in water. A more crystalline sample of the intermediate was obtained by heating the water extraction residue at 720°C. overnight (10071D). When this sample was heated to 950°C. (Film 10087A) some low-angle diffraction lines ascribed to the intermediate disappeared; they were still present after heating at 900°C. (Film 10120C, Table 24). No detectable loss of weight occurred in these heating operations at higher temperatures, indicating that the stoichiometry of the intermediate remained unchanged. These intermediate lines for large d-spacings were also obtained in X-radiograms of certain precipitated phosphates (see Section 4.1); they conformed to indexing in the cubic system with a cell constant of 14.547 A., but the responsible phase could not be identified at this stage although it could well be a second crystalline form of the same intermediate.

The water extraction residue was also extracted with dilute hydrochloric acid and the insoluble residue submitted to X-ray diffraction. Only gadolinium orthophosphate lines were observed, showing the solubility of the intermediate phase or phases in dilute hydrochloric acid. (Film 10071A). The appearance of the main intermediate phase at a composition providing only half the sodium carbonate

TABLE 24

The indexing of unidentified intermediate phase in $GdPO_4$ + 50%, Na_2CO_3 treatment (together with identified phase) at 900°C.

Film 10120C Rad. Cu. K_α a = 14.547 A.

I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	Remarks
40	14.63	0.00278	0.00280	100	
20	7.35	1098	1120	200	
B50	6.48	1412	1400	210	$GdPO_4$,Gd_2O_3+$GdPO_4$,Na_3PO_4
50	4.59	2822	2800	310	$GdPO_4$,Na_3PO_4
5	4.40	3063	3080	311	Gd_2O_3
100	4.14	3466	-	-	Vaseline + $GdPO_4$,Na_3PO_4
B20	3.83	4043	-	-	$GdPO_4$,Gd_2O_3+$GdPO_4$,Na_3PO_4
5	3.68	4376	-	-	-
10	3.54	4740	4760	410	
25	3.47	4927	-	-	$GdPO_4$,Na_3PO_4
15	3.33	5359	5320	331	
10	3.24	5637	5600	420	$GdPO_4$,Na_3PO_4
10	3.165	5931	5880	421	$GdPO_4$,Na_3PO_4
70	3.120	6109	-	-	Gd_2O_3 + Na_3PO_4
10	3.028	6478	6440	332	$GdPO_4$,Na_3PO_4
25	2.936	6892	-	-	$GdPO_4$,Gd_2O_3
5	2.840	7363	-	-	$GdPO_4$,Gd_2O_3
70	2.770	7704	-	-	$GdPO_4$,Na_3PO_4
10	2.720	8024	-	-	Na_3PO_4
10	2.700	8143	-	-	Gd_2O_3
50	2.650	8456	8400	520	$GdPO_4$,Na_3PO_4
5	2.570	8982	8960	521	
5	2.547	9158	-	-	Gd_2O_3 + Na_3PO_4
10	2.459	9823	9800	522	
10	2.300	11209	-	-	Gd_2O_3
20	2.255	11681	-	-	$GdPO_4$,Na_3PO_4
w	2.185	12448	-	-	$GdPO_4$,Na_3PO_4
5	2.124	13172	13160	631	$GdPO_4$,Gd_2O_3
20	2.107	13379	-	-	$GdPO_4$,Na_3PO_4

TABLE 24 continued

I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	Remarks
5	2.071	0.13858	-	-	$GdPO_4$
10	2.054	14082	-	-	$GdPO_4$, Na_3PO_4
5	2.014	14645	-	-	$GdPO_4$, Gd_2O_3+$GdPO_4$, Na_3PO_4
10	1.997	14899	14840	720, 641	$GdPO_4$, Na_3PO_4
5	1.958	15494	-	-	$GdPO_4$, Na_3PO_4
2	1.754	19313	-	-	Gd_2O_3
2	1.738	19659	-	-	Gd_2O_3 + $GdPO_4$, Na_3PO_4
2	1.704	20463	-	-	$GdPO_4$, Gd_2O_3+Gd_2O_3
2	1.687	20865			-
B5	1.669	21314	21280	662	Gd_2O_3
B5	1.650	21831	21840	752	$GdPO_4$, Na_3PO_4
40	1.630	22360	22400	840	Gd_2O_3 $GdPO_4$, Na_3PO_4
3	1.597	23305	-	-	Gd_2O_3
B3	1.584	23697	-	-	$GdPO_4$, Na_3PO_4
w	1.562	23345	-	-	Gd_2O_3
10	1.553	24631	24640	664	$GdPO_4$, Na_3PO_4
10	1.529	25402	25380	931	
w	1.471	27472	27470	770	
Bw	1.456	28019	28030	10.0.0	$GdPO_4$, Na_3PO_4
Bw	1.240	38599	-	-	-
Bw	1.209	40665	40660	12.1.0	
Bw	1.177	42851	42900	12.3.0	

required for complete reaction of the lanthanide phosphate indicates that the important intermediate is a double phosphate possessing (at least approximately) the composition $GdPO_4,Na_3PO_4$ (or $Na_3Gd(PO_4)_2$). The stoichiometry of the various reactions described is satisfactorily accounted for on this basis, and later preparations of the double phosphates by solid-state reaction and precipitation confirm the composition suggested.

The additional lines in the powder photograph proved eventually to be those of $GdPO_4,Gd_2O_3$. Table 17 in Section 2.5 lists X-ray diffraction data for this complex mixture of products, and shows that the lines can be satisfactorily assigned.

Sintering of Lanthanum Orthophosphate with 50% of the theoretical amount of Sodium Carbonate:

The X-ray powder diffraction photograph showed the presence of $LaPO_4,Na_3PO_4$ (or $Na_3La(PO_4)_2$) and $LaPO_4,La_2O_3$ as intermediates in the product of sintering at 700°C. (10036A, Table 25). The loss of weight on sintering agreed very well with the calculated value. The loss of weight on extraction with water again showed the retention of much of the sodium phosphate in the form of the insoluble double phosphate intermediate. The X-ray diffraction pattern of the water- extraction residue showed the expected intermediate compounds; very weak lanthanum orthophosphate lines were also present (Films 10065D, 10078C). The unidentified (cubic) phase which was observed in the corresponding gadolinium phosphate reaction was not present in this system.

After heating at 900°C. the sintered product gave $LaPO_4,La_2O_3$ lines which were stronger than those of the 700°C. product (10120A, Table 26). A line of d-spacing 3.23 A. was abnormally strong in this case.

The sintering reactions were also repeated with equimolar

TABLE 25

$LaPO_4$+50% Theoretical Na_2CO_3 at 700°C: Film 10036A.

$CePO_4$+50% Theoretical Na_2CO_3 at 700°C: Film 10127C.

Rad. Co. K_α Rad. Cu. K_α

Film 10036A		Film 10127C		
I	d(A.)	I	d(A.)	Remarks
5	9.48	5	9.24	$LnPO_4$, Na_3PO_4+$LaPO_4$, La_2O_3
20	6.89			$LaPO_4$, La_2O_3
50	6.60	60	6.59	$LnPO_4$, Na_3PO_4
40	4.665	60	4.65	$LnPO_4$, Na_3PO_4
5	4.28			$LnPO_4$, Na_3PO_4
B100	4.15	B70	4.130	$LnPO_4$, Na_3PO_4+Vaseline
B20	3.925	40	3.87	$LnPO_4$, Na_3PO_4+$LaPO_4$, La_2O_3
25	3.52	50	3.507	$LnPO_4$, Na_3PO_4
5	3.305	30	3.29	$LnPO_4$, Na_3PO_4+$CePO_4$
3	3.125	100	3.12	$LnPO_4$, Na_3PO_4+CeO_2
100	3.06	5	3.063	$LnPO_4$, Na_3PO_4+$LaPO_4$, La_2O_3+$CePO_4$
3	2.99	5	2.983	$LnPO_4$, Na_3PO_4+$CePO_4$
25	2.90	20	2.866	$CePO_4$+$LaPO_4$, La_2O_3
100	2.821	90	2.805	$LnPO_4$, Na_3PO_4+Nacl
30	2.695	50	2.70	Na_3PO_4+CeO_2
25	2.675	70	2.670	$LnPO_4$, Na_3PO_4
5	2.630	5	2.60	Na_3PO_4
15	2.486	20	2.474	$LnPO_4$, Na_3PO_4
3	2.329	5B	2.320	$LnPO_4$, Na_3PO_4
10	2.264	25	2.251	$LnPO_4$, Na_3PO_4+$LaPO_4$, La_2O_3
20	2.221			$LaPO_4$, La_2O_3
		B5	2.191	$LnPO_4$, Na_3PO_4
10	2.165	w	2.146	$LnPO_4$, Na_3PO_4
		10	2.131.	$LnPO_4$, Na_3PO_4
3	2.075	10	2.070	$LnPO_4$, Na_3PO_4+$LaPO_4$, La_2O_3
5	2.048	-	-	-
100	1.994			$LnPO_4$, Na_3PO_4+$LaPO_4$, La_2O_3+Nacl
		10	1.983.	$LnPO_4$, Na_3PO_4
		w	1.971	-
10	1.941	30	1.937	$LnPO_4$, Na_3PO_4
20	1.935			$LnPO_4$, Na_3PO_4

TABLE 25 continued

Film 10036A		Film 10127C		Remarks
I	d(A.)	I	d(A.)	
-	-	90	1.909	CeO_2
5	1.792			$LnPO_4$, Na_3PO_4+$LaPO_4$, La_2O_3
5	1.758	Bw	1.757	$LnPO_4$, Na_3PO_4+$LaPO_4$, La_2O_3
25	1.700			$LnPO_4$, Na_3PO_4+$LaPO_4$, La_2O_3
		Bw	1.693	
30	1.628	50	1.628	NaCl+CeO_2

Note: On account of the complexity of the photograph only lower angles are given.

TABLE 26

$LaPO_4$+50% Theoretical Na_2CO_3 at 900°C: Film 10120A.

$CePO_4$+50% Theoretical Na_2CO_3 at 900°C: Film 10106D.

Rad. Cu. K_α Rad. Co. K_α

Film 10120A		Film 10106D		Remarks
I	d(A.)	I	d(A.)	
25	10.91			$LaPO_4, La_2O_3$
15	9.23	vw	9.20	$LnPO_4, Na_3PO_4, LaPO_4, La_2O_3$
10	6.84			$LaPO_4, La_2O_3$
50	6.59	30	6.54	$LnPO_4, Na_3PO_4$
40	4.66	30	4.615	$LnPO_4, Na_3PO_4$
60	4.14	50	4.130	$LnPO_4, Na_3PO_4$+Vaseline
5	3.95	-	-	$LaPO_4, La_2O_3$
15	3.88	25	3.86	$LnPO_4, Na_3PO_4$
50	3.51	30	3.49	$LnPO_4, Na_3PO_4$
5	3.427			$LnPO_4, Na_3PO_4+La_2O_3$
5	3.307	15	3.275	$LnPO_4, Na_3PO_4$
90	3.230	-	-	$LaPO_4, La_2O_3$
		100	3.11	CeO_2
70	3.06	5	3.05	$LnPO_4, Na_3PO_4, LaPO_4, La_2O_3$
15	2.98	5	2.98	$LnPO_4, Na_3PO_4+La_2O_3$
25	2.935			$LaPO_4, La_2O_3$
5	2.890	-	-	$LaPO_4$
60	2.807	60	2.79	$LnPO_4, Na_3PO_4$
25	2.690	50	2.695	$LnPO_4, Na_3PO_4 + CeO_2 + Na_3PO_4$
15	2.67	B20	2.66	$LnPO_4, Na_3PO_4$
5	2.48	5	2.47	$LnPO_4, Na_3PO_4$
10	2.327	5	2.317	$LnPO_4, Na_3PO_4$
15	2.260	20	2.245	$LnPO_4, Na_3PO_4$
5	2.220	-	-	$LnPO_4, Na_3PO_4$
3	2.178	-	-	$LnPO_4, Na_3PO_4$
15	2.137	10	2.123	$LnPO_4, Na_3PO_4$
5	2.076	-	-	$LnPO_4, Na_3PO_4$
5	2.061	-	-	Na_3PO_4
40	2.027	10	2.029	$LnPO_4, Na_3PO_4$
-	-	5	2.002	$LnPO_4, Na_3PO_4$
40	1.992	5	1.976	$LnPO_4, Na_3PO_4$,

Note: On account of the complexity of the photograph only lower angles

mixtures of gadolinium and lanthanum orthophosphates, with 50% of the theoretical sodium carbonate and with a 10% excess of sodium carbonate (Films 10036C, D, Table 21B). Similar results were obtained.

Sintering of Cerous Orthophosphate with 50% of the theoretical amount of Sodium Carbonate:

The sintering operation was carried out at 700°C. for 24 hours. The X-ray diffraction pattern was very simple in comparison with those of the lanthanum and gadolinium products. The intermediate phase $CePO_4,Na_3PO_4$ (or $Na_3Ce(PO_4)_2$) was present but no compound corresponding to the formula $CePO_4,Ce_2O_3$. Instead very strong cerium dioxide lines were observed. Lines of cerous orthophosphate were also present, (Film 10127C, Table 25). The loss of weight on sintering corresponded quite closely with the calculated value, but the loss was to some extent diminished by oxidation of cerium to the tetravalent state. After heating at 900°C. the product showed better crystallisation of the intermediate phase, and cerous phosphate lines no longer appeared (Table 26).

General Conclusion:

The occurrence of double phosphates of the type $LnPO_4,Na_3PO_4$ as intermediate phases has been confirmed in the sintering reactions of all three lanthanide phosphates with sodium carbonate. In the case of cerium the tendency of Ce^{3+} to oxidize into Ce^{4+} favoured the formation of cerium dioxide, so the reaction tended to proceed further to the oxide side. The $LnPO_4,Ln_2O_3$ intermediate did not occur at all in the case of cerium. These individual results are applied later to monazite sintering (Section 5).

3.2. Preparation from lanthanide orthophosphate and sodium orthophosphate.

This investigation was considered necessary to verify the compositions of the intermediate compounds formed during sintering reactions between lanthanide orthophosphates and sodium carbonate. Solid-state reactions of lanthanide orthophosphates with sodium orthophosphate have not been reported in the literature, although such reactions afford an obvious method for synthesis of double phosphates.

Experimental:

The preparations of lanthanide orthophosphates and anhydrous sodium orthophosphate have already been described in Sections 2.2 and 2.4. Appropriate and properly proportioned weighed amounts of these were ground together in an agate mortar, and the mixture reweighed and heated in a small covered platinum crucible at 700°C. for 12 hours. After cooling the crucibles and products were weighed again. The observed weight loss, amounting to 1-3% for different mixtures, was attributed to water absorbed by the sodium salt, and was neglected. Table 27 shows the phases detected by X-ray diffraction from several compositions and heat treatments. The intermediate referred to in this table is the phase of approximate composition $GdPO_4,Na_3PO_4$ found, in the previous part of the work, to be formed in the sintering reaction between gadolinium orthophosphate and sodium carbonate.

Examination of the table proved that the intermediate could be obtained as a single phase product with the reactant composition $GdPO_4+Na_3PO_4$, but at 700°C. the reaction was not complete; the product obtained at 900°C. gave very weak lines of the reactants, but after heating at 1150°C. the product did not give any lines of the component single phosphates. The weight loss in the reaction was negligible.

TABLE 27

Solid-state reactions of gadolinium orthophosphate with sodium orthophosphate

Composition of reactant mixture	Temp.	Time	X-ray Film No.	Remarks*			
				$GdPO_4$	Na_3PO_4	Intermediate	Others
$5GdPO_4, Na_3PO_4$	700°C.	overnight	10055A	s	vw	w	-
$3GdPO_4, Na_3PO_4$	"	"	10054B	s	vw	w	-
$3GdPO_4, 2Na_3PO_4$	"	"	10055B	s	m	m	-
$GdPO_4, Na_3PO_4$	"	"	10054C	s	s	s	-
$2GdPO_4, 3Na_3PO_4$	"	"	10055C	m	s	vs	$GdPO_4, Gd_2O_3$
$GdPO_4, 3Na_3PO_4$	"	"	10054D	m	s	s	
$GdPO_4, 5Na_3PO_4$	"	"	10055D	vvw	vs	m	Gd_2O_3 $GdPO_4, Gd_2O_3$
$GdPO_4, 6Na_3PO_4$	"	"	10056D	vvw	vs	w	Gd_2O_3 $GdPO_4, Gd_2O_3$
$2GdPO_4, Na_3PO_4$	"	"	10060D	s	m	s	-
$GdPO_4, Na_3PO_4$	900°C.	"	10122B	w	vw	vs	-
$GdPO_4, Na_3PO_4$	1150°C.	2 hrs.	10165C	-	-	vs	-
$GdPO_4, Na_3PO_4$	990°C.	3 days	10151A	-	-	vs	-
$2GdPO_4, 3Na_3PO_4$	990°C.	2 days	10151C	-	m	vs	-
$2GdPO_4, 3Na_3PO_4$	990°C.	1 more day	10154C	-	m	vs	-

* vs: very strong s: strong m: medium w: weak vw: very weak vvw: very very weak

An incidental observation of some interest is the appearance of gadolinium oxide and the compound $GdPO_4,Gd_2O_3$ among the reaction products when an excess of sodium orthophosphate is used. This is disclosed, for example, in the compositions $GdPO_4,5Na_3PO_4$ and $GdPO_4,6Na_3PO_4$ in Table 27. This somewhat unexpected result is probably due to the existence of a eutectic between sodium phosphate and $GdPO_4,Gd_2O_3$ which favours formation of the latter compound under certain sets of conditions. As expected, X-radiograms of the water-extraction residues of products obtained at these compositions also showed lines of $GdPO_4,Gd_2O_3$ (Films 10073B, C).

The new (γ-form as described in Section 2.2) form of sodium orthophosphate was observed for the first time in this series of experiments (Film 10056D).

X-ray diffraction analysis was also carried out on the water and acid extraction residues of products from the composition $GdPO_4,Na_3PO_4$ heated at 700°C. The water extraction residue contained gadolinium orthophosphate and the double phosphate intermediate (Film 10071C); the acid extraction residue showed only gadolinium orthophosphate lines, verifying the complete dissolution of the intermediate in dilute hydrochloric acid (Film 10071B). The weights obtained after extracting with water and with acid gave an approximate value for the weight ratio of the combined sodium orthophosphate to the combined gadolinium orthophosphate, which was 0.46. The theoretical value is 0.65, but it is probable that some decomposition of the intermediate compound by water, leading to preferential extraction of sodium phosphate, may be invoked to explain this discrepancy. Some loss of finely-divided material during filtration, increasing the discrepancy, was also considered likely. A compound of composition $3GdPO_4,2Na_3PO_4$ would have a weight ratio of sodium to gadolinium

orthophosphate of 0.43, which would fit the measured value (0.46); however direct synthesis of a single phase of this composition proved impossible (see Table 27 and film 10055B).

X-ray fluorescence analysis of a residue from the evaporated water extraction filtrate, showing the presence of gadolinium, proved the appreciable solubility of the double-phosphate intermediate compound in water. The intermediate was evidently freely soluble in acid solutions, even after heating at 1150°C.

Similar reactions were repeated with lanthanum orthophosphate. The molecular ratio of 1:1 again gave the double phosphate as a single-phase product (see Table 28). The X-ray diffraction study of the lanthanum compound showed it to be isostructural with the analogous gadolinium compound.

The examination of the $\sin^2\theta$ values in the diffraction data from both intermediates (gadolinium and lanthanum compounds) showed that the characteristic ratios of 1:2:3:4:5 ... occur, but with the appearance of a line at the seven fold multiple, which is not allowed for the cubic system. An indexing had been attempted in the body-centered cubic system with a cell constant of approximately 13 A., but some strong lines were left unindexed.

Systematic investigation of the $\sin^2\theta$ values for the gadolinium compound, by the methods described in D'Eye and Wait (1960), has shown that the increments A = 0.00352 and C = 0.00525, for a tetragonal unit-cell, cover all the diffraction lines observed. The tetragonal cell parameters a = 12.974 A. and c = 10.621 A. were calculated from these increments for $Na_3Gd(PO_4)_2$. The establishing of the unit-cell for $Na_3Gd(PO_4)_2$ induced interest in similar compounds of other rare-earth elements. Apart from lanthanum (already included), the cerium, neodymium and yttrium compounds have been prepared under

TABLE 28

Solid-state reactions of lanthanide orthophosphates with sodium orthophosphate

Composition of reactant mixture	Temp.	Time	X-ray Film No.	Remarks			
				$LnPO_4$	Na_3PO_4	Intermediate	Others
$2LaPO_4, Na_3PO_4$	700°C.	overnight	10060A	s	m	vs	-
$LaPO_4, Na_3PO_4$	700°C.	"	10060B	s	s	vs	-
$LaPO_4, 2Na_3PO_4$	700°C.	"	10060C	m	s	vs	-
$LaPO_4, Na_3PO_4$ (700°C.) reheated	1150°C.	"	10170B	-	-	vs	-
$LaPO_4, Na_3PO_4$*	1150°C.	"	10176B	-	-	vs	-
$CePO_4, Na_3PO_4$	1150°C.	"	10170C	-	-	vs	-
$NdPO_4, Na_3PO_4$	1150°C.	"	10170D	-	-	vs	-
YPO_4, Na_3PO_4	1150°C.	"	10170A	-	-	vs	-
YPO_4, Na_3PO_4	1150°C.	more heated	10176A	-	-	vs β-form	-
$GdPO_4, Na_3PO_4$	990°C.	more heated	10151B	-	-	vs β-form	-

* Na_3PO_4 obtained from the dehydration of $Na_3PO_4, 12H_2O$ was employed.

similar conditions (Table 28). Similar structures were obtained for all of them. Tables 29, 30 and 31 show the powder diffraction data and assigned indices for all the compounds obtained.

The absences in the observed indices of the reflections gave the following space-groups for these tetragonal structures: $P\bar{4}2_1c$ (No. 114), $P4_2mc$ (No. 105), $P4_22_12$ (No. 94), $P4_2n$ (No. 86). The lanthanide contraction is noticeable in those structures, as it was with the lanthanide orthophosphates. Table 32 shows the change of cell parameters with respect to ionic radius.

In the case of the yttrium compound (Table 31) there were some weak and diffuse lines in the powder photograph which did not in every case fit the space-group assignment given above, and for which $\sin^2\theta$ did not agree so well with calculated values. This compound requires further examination, preferably by single-crystal techniques.

In the gadolinium and yttrium compounds a second type of structure was found after prolonged heating and rapid cooling (Table 33). This structure may be that of high-temperature forms of $Na_3Gd(PO_4)_2$ and $Na_3Y(PO_4)_2$, obtainable only by quenching from high temperatures. The high-temperature form (provisionally designated the β-form) gives X-ray photographs similar to those of the low-temperature (α) form, but there are slight but distinct differences in lines corresponding with the larger d-spacings. In some tests in which quenching was ineffective, lines of both phases were present in the X-ray pattern. The infra-red spectra of the α- and β-forms (Charts 11, 12, 18) were very similar and showed the presence of orthophosphate anions, as already discussed in Section 2.4. The X-ray data for the β-form could not be indexed.

TABLE 29

X-ray diffraction data of $Na_3La(PO_4)_2$ and $Na_3Ce(PO_4)_2$

Film 10176B Rad. Cu. K_α Film 10170C Rad. Cu. K_α

$Na_3La(PO_4)_2$					$Na_3Ce(PO_4)_2$			
I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc}$
20	9.32	0.00682	0.00682	110	5	9.24	0.00696	0.00690
100	6.61	0.01361	0.01364	200	70	6.56	0.01382	0.01380
10	5.62	0.01877	0.01874	201	5	5.58	0.01907	0.01897
B5	5.41	0.02028	0.02040	002	1	5.35	0.02078	0.02068
10	5.02	0.02361	0.02363	102	-	-	-	-
5	4.84	0.02536	-	-	-	-	-	-
100	4.67	0.02724	0.02722	112	70	4.64	0.02760	0.02758
			0.02728	220				0.02760
w	4.28	0.03251	0.03234	221	-	-	-	-
B100	4.15	0.03447	0.03404	310	70	4.14	0.03472	0.03450
			0.03410	202				0.03450
90	3.89	0.03924	0.03920	311	50	3.87	0.03967	0.03967
100	3.52	0.04786	0.04768	222	70	3.51	0.04824	0.04830
2	3.48	0.04918	0.04931	103	-	-	-	-
10	3.42	0.05089	0.05109	302	-	-	-	-
40	3.31	0.05440	0.05450	312	30	3.28	0.05509	0.05520
			0.05456	400				0.05520
vw	3.14	0.06008	0.05950	401	1	3.14	0.06028	0.06037
40	3.07	0.06301	0.06295	213	20	3.06	0.06365	0.06378
			0.06307	411				0.06382
10	2.995	0.06627	0.06648	331	1	2.98	0.06688	0.06727
100	2.814	0.07505	0.07496	402	100	2.798	0.07586	0.07590
B100	2.69	0.08210	0.08160	004	90	2.675	0.08306	0.08272
			0.08178	332				0.08290
B40	2.484	0.09626	0.09524	204	20	2.470	0.09717	0.09652
15	2.425	0.10107	0.10046	403	-	-	-	-
60	2.332	0.10924	0.10888	224	20	2.324	0.11006	0.11032
			0.10906	512				0.11040
			0.10912	440				0.11040
10	2.266	0.11569	0.11570	314	50	2.250	0.11713	0.11722
			0.11594	530				0.11730

TABLE 29 continued

I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{cal}$
10	2.212	0.12150	0.12104	531	B3	2.201	0.12265	0.12240
10	2.173	0.12581	0.12593	324	-	-	-	-
70	2.142	0.12945	0.12952	442	50	2.130	0.13092	0.13108
w	2.122	0.13240	0.13127	611	5	2.110	0.13314	0.13282
20	2.096	0.13522	0.13456	513	5	2.088	0.13625	0.13623
30	2.085	0.13671	0.13640	620	30	2.073	0.13822	0.13800
20	2.035	0.14353	0.14316	602	10	2.027	0.14460	0.14488
20	2.016	0.14614	0.14579	523	15	2.010	0.14706	0.14658
50	1.992	0.14970	0.14980	424	40	1.979	0.15173	0.15172
B30	1.947	0.15677	0.15680	622	50	1.935	0.15868	0.15868
5	1.876	0.16885	0.16826	603	-	-	-	-
5	1.866	0.17066	0.17050	710 550	5	1.857	0.17230	0.17250
10	1.831	0.17710	0.17732	640	5	1.821	0.17928	0.17940
10	1.790	0.18534	0.18547	415	B5	1.783	0.18798	0.18790
50	1.761	0.19165	0.19095	552 712	B20	1.755	0.19286	0.19318
B10	1.703	0.20484	0.20436	604	B5	1.691	0.20717	0.20692
50	1.676	0.21143	0.21083	226	15	1.670	0.21321	0.21372
5	1.668	0.21357	0.21311	651	-	-	-	-
50	1.649	0.21860	0.21800 0.21824	624 800	20	1.642	0.22040	0.22072 0.22080
50	1.600	0.23209	0.23188	820	20	1.591	0.23448	0.23460
20	1.580	0.23801	0.23864 0.23816	802 406	B20	1.571	0.24099	0.24048 0.2413
20	1.571	0.24080	0.24157	416	-	-	-	-
10	1.559	0.24435	0.24398	733	5	1.550	0.24717	0.24663
-	-	-	-	660	B5	1.543	0.24924	0.2484
10	1.549	0.24754	0.24769	704	-	-	-	-
B10	1.528	0.25436	0.25403	831	B3	1.520	0.25703	0.2568
-	-	-	-	752	B15	1.469	0.27573	0.2759
-	-	-	-	840				0.2760
5	1.454	0.28121	0.28131	901	B5	1.447	0.28376	0.2846
w	1.431	0.29027	0.28961	654	-	-	-	-
-	-	-	-	705	B3	1.4135	0.29823	0.2983

TABLE 29 continued

I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{cal}$
-	-	-	-	833				0.29838
-	-	-	-	921				0.29842
30	1.407	0.30004	0.30002	912	B15	1.401	0.30263	0.30358
w	1.377	0.31330	0.31348	824	-	-	-	-
20	1.348	0.32694	0.32730	932	B10	1.3407	0.33084	0.33118
			0.32712	664				0.33112
			0.32640	008				0.33088
20	1.334	0.33392	0.33394	754	B10	1.328	0.33742	0.33802
5	1.320	0.34073	0.34100	860	-	-	-	-
20	1.246	0.38243	0.38186	952	10	1.240	0.38625	0.38638
10	1.214	0.40331	0.40350	845	B5	1.210	0.40588	0.40525
-	-	-	-	915	B5	1.202	0.41189	0.41215
-	-	-	-	953				0.41223
5	1.196	0.41533	0.41596	104.2	-	-	-	-

TABLE 30

X-ray diffraction data of $Na_3Nd(PO_4)_2$ and α-$Na_3Gd(PO_4)_2$

Film 10170D Rad. Cu. K_α Film 10151A Rad. Cu. K_α

$Na_3Nd(PO_4)_2$					α-$Na_3Gd(PO_4)_2$			
I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
5	9.17	0.00707	0.0698	110	5	9.21	0.00700	0.00704
80	6.54	0.01392	0.01396	200	80	6.56	0.01382	0.01408
2	5.57	0.01913	0.01919	201	5	5.56	0.01919	0.01933
B2	5.30	0.02115	0.02092	002	5	5.35	0.02070	0.02100
80	4.62	0.02788	0.02790	112	70	4.61	0.02796	0.02804
			0.02792	220				0.02816
50	4.13	0.03495	0.03488	202	B50	4.14	0.03470	0.03508
			0.03490	310				0.03520
40	3.85	0.04017	0.04013	311	60	3.84	0.04026	0.04045
70	3.49	0.04890	0.04884	222	70	3.48	0.04908	0.04916
30	3.27	0.05569	0.05582	312	40	3.26	0.05609	0.05620
			0.05584	400				0.05632
3	3.117	0.06111	0.06107	401	-	-	-	-
B15	3.035	0.06450	0.06452	213	30	3.03	0.06469	0.06485
			0.06456	411				0.06509
100	2.784	0.07667	0.07676	402	100	2.775	0.07714	0.07732
100	2.665	0.08366	0.08368	004	100	2.654	0.08436	0.08400
			0.08374	332				0.08418
30	2.465	0.09781	0.09764	204	20	2.457	0.09844	0.09808
30	2.309	0.11143	0.11160	224	20	2.302	0.11213	0.11208
			0.11166	512				0.11252
			0.11168	440				0.11264
40	2.238	0.11852	0.11858	314	40	2.231	0.11934	0.11910
			0.11866	530				0.11968
10	2.188	0.12408	0.12389	531	10	2.181	0.12494	0.12493
40	2.118	0.13239	0.13260	442	40	2.112	0.13325	0.13364
3	2.097	0.13462	0.13436	611	-	-	-	-
3	2.078	0.13761	0.13773	115	-	-	-	-
			0.13781	513	-	-	-	-
30	2.063	0.13957	0.13952	404	30	2.053	0.14094	0.14056
			0.13958	532				0.14074
			0.13960	620				0.14080

TABLE 30 continued

I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc}$
10	2.038	0.14292	0.14301	414	-	-	-	-
-	-	-	-	334	5	2.011	0.14688	0.14736
10	1.999	0.14861	0.14828	523	5	1.997	0.14905	0.14932
30	1.968	0.15330	0.15348	424	20	1.960	0.15469	0.15450
50	1.924	0.16044	0.16052	622	50	1.919	0.16137	0.16180
1	1.848	0.17411	0.17450	710	-	-	-	-
			0.17450	550	-	-	-	-
1	1.838	0.17644	0.17624	701				
B30	1.768	0.19011	0.19008	415	3	1.760	0.19183	0.19109
20	1.745	0.19510	0.19542	552	10	1.738	0.19666	0.19650
B10	1.658	0.21608	0.21620	226	15	1.653	0.21752	0.21716
10	1.633	0.22276	0.22318	316	10	1.628	0.22418	0.22420
10	1.584	0.23689	0.23732	820	15	1.575	0.23950	0.23936
20	1.561	0.24398	0.24428	802	25	1.552	0.24661	0.24628
-	-	-	-	660	20	1.531	0.25341	0.25344
B5	1.461	0.27846	0.27902	516	B10	1.454	0.28121	0.28052
			0.27918	752				0.28148
B2	1.406	0.30043	0.30012	842	-	-	-	-
B2	1.394	0.30564	0.30533	753	-	-	-	-
-	-	-	-	804	vB5	1.387	0.30906	0.30928
B5	1.332	0.33495	0.33496	664	10	1.326	0.33779	0.33744
B5	1.233	0.39050	0.39086	952	5	1.228	0.39366	0.39412

TABLE 31

X-ray diffraction data of α-$Na_3Y(PO_4)_2$

Film 10170A, Rad. Cu. K_α

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
5	9.14	110	0.00711	0.00710
3	6.93	111	0.01238	0.01235
90	6.50	200	0.01407	0.01420
3	5.54	201	0.01937	0.01946
3	5.277	002	0.02134	0.02104
80	4.58	220	0.02831	0.02840
5	4.285	300	0.03235	0.03195
B50	4.123	202	0.03495	0.03524
90	3.826	311	0.04060	0.04076
B40	3.459	222	0.04944	0.04965
5	3.360	302	0.05263	0.05299
10	3.22	400	0.05730	0.05680
3	3.148	410	0.05997	0.06035
40	3.028	213	0.06482	0.06509
1	2.96	322	0.06775	0.06719
B10	2.87	420	0.07198	0.07100
100	2.772	402	0.07737	0.07736
100	2.640	332	0.08524	0.08476
30	2.448	204	0.09911	0.09836
10	2.415	214	0.10186	0.10189
30	2.30	224	0.11225	0.11248
25	2.213	530	0.12136	0.12070
25	2.173	531	0.12581	0.12596
20	2.1255	-	-	-
B20	2.101	610	0.13150	0.13135
		005	0.13150	0.13125
		324	1.13150	0.13031
20	2.070	115	0.13867	0.13860
B20	2.046	620	0.14200	0.14200
10	2.004	334	0.14799	0.14806
20	1.993	215	0.14955	0.14925

TABLE 31 continued

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
5	1.956	424	0.15534	0.15516
10	1.943	-	0.15741	-
70	1.912	622	0.16253	0.16304
B30	1.734	444	0.19770	0.19744
3	1.701	642	0.20540	0.20564
w	1.682	722	0.21000	0.20916
w	1.665	614	0.21446	0.21535
40	1.645	505	0.21950	0.22025
30	1.626	316	0.22457	0.22450
B10	1.566	820	0.24211	0.24140
B30	1.548	802	0.24796	0.24824
B20	1.526	660	0.25512	0.25560
	1.522	704	0.25664	0.25795
3	1.504	750	0.26251	0.26270
B20	1.451	516	0.28219	0.28166
B3	1.430	734	0.29067	0.29006
B10	1.387	555	0.30866	0.30900
5	1.375	407	0.31411	0.31454
B5	1.349	824	0.32653	0.32556
		735		0.33740
B2	1.333	932	0.33433	0.33510
5	1.323	913	0.33907	0.33844
B20	1.318	118	0.34218	0.34310
B3	1.271	844	0.36806	0.36816
B3	1.236	617	0.38860	0.38905
B3	1.227	773	0.39476	0.39490
B3	1.213	934	0.40353	0.40354

TABLE 32

Comparison of cell parameters of
various lanthanide double phosphates

	$Na_3La(PO_4)_2$	$Na_3Ce(PO_4)_2$	$Na_3Nd(PO_4)_2$	$Na_3Gd(PO_4)_2$	$Na_3Y(PO_4)_2$
a(A.)	13.181	13.105	13.030	12.974	12.918
c(A.)	10.779	10.705	10.644	10.623	10.613
r(A.)	1.061	1.034	0.995	0.938	0.900

TABLE 33

β-forms of $Na_3Gd(PO_4)_2$ and $Na_3Y(PO_4)_2$

Rad. Cu. K_α

β-$Na_3Gd(PO_4)_2$ Film 10151B		β-$Na_3Y(PO_4)_2$ Film 10176A	
I	d(A.)	I	d(A.)
5	9.19		
-	-	w	7.66
10	6.99	40	6.955
-	-	20	6.470
50	6.30	100	6.29
vw	5.34	5	5.30
B5	4.96	30	4.94
70	4.60	100	4.587
30	4.186	20	4.285
50	4.133*	B100	4.152*
50	3.839	100	3.82
2	3.493	10	3.48
5	3.382	30	3.37
2	3.338	30	3.32
B2	3.108	B30	3.13
30	2.80	10	2.88
30	2.774	B100	2.77
100	2.654	B100	2.65
		40	2.586
		B10	2.55
3	2.484	10	2.484
10	2.447	30	2.442
		B5	2.415
B5	2.304	B40	2.29
		B5	2.224
B10	2.176	B50	2.173
10	2.131		
-	-	B50	2.118
10	2.087	-	-
-	-	-	-

* Common with vaseline line.

TABLE 33 continued

β-$Na_3Gd(PO_4)_2$ Film 10151B	
I	d(A.)
-	-
-	-
B10	2.018
5	1.977
10	1.930
10	910
-	-
-	-
-	-
5	1.747
5	1.737
5	1.704
5	1.686
5	1.655
5	1.641
10	1.533
5	1.327

β-$Na_3Y(PO_4)_2$ Film 10176A	
I	d(A.)
B50	2.078
B50	2.006
B5	1.970
70	1.924
70	1.906
20	1.888
3	1.872
B1	1.852
B5	1.805
B3	1.784
B30	1.737
B50	1.684
20	1.645
20	1.632
B40	1.555
40	1.529
20	1.521
B5	1.509
B5	1.463
B25	1.433
B20	1.392
B10	1.348
30	1.326
50	1.320
B5	1.281
B3	1.273
B5	1.253
B5	1.238
B1	1.212
B1	1.196

3.3. Preparation from lanthanide oxide, sodium carbonate and $(NH_4)_2HPO_4$.

It proved possible to prepare the double sodium lanthanide orthophosphates by another solid-state reaction, namely:

$$Ln_2O_3 + 3Na_2CO_3 + 4(NH_4)_2HPO_4 \rightarrow 2Na_3Ln(PO_4)_2 + 3CO_2 + 8NH_3 + 6H_2O.$$

This reaction has the marked practical advantages that separate preparation of the lanthanide orthophosphate is avoided, and the somewhat critical process of dehydrating and using a stoichiometric sodium orthophosphate is not required.

The reactants (with gadolinium oxide as the lanthanide source) were ground together after weighing in the proportions determined by the equation, and heated in platinum crucibles. Heating periods were interrupted as appropriate for re-crushing of the reacting solid mixture. As usual, products were examined by X-ray powder diffraction.

At 700°C. the reaction was far from complete after 12 hours with several re-crushing operations during this period. The product was a complex mixture including unreacted gadolinium oxide, gadolinium orthophosphate, and probably sodium orthophosphate and pyrophosphate (Film 10072C). Reheating of the product similarly at 800°C. still did not complete the reaction, and the complex product (Film 10080D) was not investigated in detail. Further reheating at 950°C. caused $Na_3Gd(PO_4)_2$ lines to appear in the X-radiogram (10087C). Finally, heating at 1150°C. gave well-crystallised $Na_3Gd(PO_4)_2$, and the photograph (10234D) showed no detectable lines of other phases. Weight losses throughout these reactions corresponded closely with the equation given earlier.

The method of preparation described here is probably the most straightforward means of obtaining the double orthophosphates. In a

routine preparation the ground and mixed reactants would be heated slowly, with several intermediate re-grinding operations, to a final heating temperature of 1150°C. (High "finishing" temperatures are generally needed in this technique for preparing metal phosphates).

Since this method yielded very well-crystallised products allowing accurate measurement of X-radiograms, data for $Na_3Gd(PO_4)_2$ are appended in Table 34.

TABLE 34

X-ray diffraction data for $Na_3Gd(PO_4)_2$ obtained through $Gd_2O_3+3Na_2CO_3+4(NH_4)_2HPO_4 \rightarrow 2Na_3Gd(PO_4)_2+3CO_2+8NH_3+6H_2O$ solid-state reaction (1150°C.)

Film 10072C, Rad. Cu. K_α

I	d(A.)
50	6.47
60	4.58
B50	4.118
40	3.82
50	3.46
B5	3.24
5	3.02
100	2.77
100	2.64
20	2.448
10	2.299
30	2.223
10	2.174
5	2.123
30	2.108
10	2.071
20	2.050
5	2.008
5	1.995
B5	1.955

I	d(A.)
70	1.914
5	1.743
5	1.734
5	1.681
10	1.650
10	1.627
B5	1.571
50	1.551
30	1.528
20	1.450
vB5	1.387
vB5	1.351
10	1.323
5	1.236
B5	1.225

3.4. Preparation (for comparison) of $NaTh_2(PO_4)_3$

During investigation of the reactions of lanthanide orthophosphates with sodium carbonate at high temperatures, the intermediate double phosphate structures were found to give powder X-radiograms which resembled that for $NaTh_2(PO_4)_3$ (A.S.T.M. Card 16-812; Ranby and Doreen, 1963; Schmid and Mooney, 1964; Matkovic and Sljukic, 1965). The thorium compound was prepared initially by Wallroth (1883). $NaTh_2(PO_4)_3$ was therefore prepared by the solid-state reaction represented by the following equation:

$$6ThO_2 + 8(NH_4)_2HPO_4 + Na_3PO_4 \rightarrow 3NaTh_2(PO_4)_3 + 12H_2O + 16NH_3$$

Reactions of this type had proved useful earlier in the work of the laboratory.

Thorium dioxide was obtained from Thorium Ltd. and $(NH_4)_2HPO_4$ was of AnalaR reagent grade from Hopkin and Williams Ltd. Sodium orthophosphate had been prepared previously in the laboratory. Stoichiometric quantities of the reactants were ground together in an agate mortar, loaded into a platinum crucible, and heated gradually from 100°C. to 700°C. in a muffle furnace; heating was completed with 12 hours at 700°C. The mixture melted during reaction. An X-ray diffraction pattern of the product (Film 10065A) agreed with A.S.T.M. data, but some weak additional lines were present; the use of a Guinier camera probably disclosed these lines not reported by the original workers. The loss of weight corresponded with the equation given above. A better X-ray diffraction pattern (Film 10067A) was obtained after crushing the powder and reheating it at 800°C. The X-ray data are given in Table 35; although they show some resemblance to data for $Na_3Ln(PO_4)_2$ compounds, closer comparison did not allow any isostructural relationship to be identified.

TABLE 35

X-ray diffraction pattern of $NaTh_2(PO_4)_3$

Film 10067A, Rad. Co. K_α

I	d(A.)
40	8.57
100	6.34
B20	5.90
10	5.40
30	5.15
30	4.805
5	4.66
vw	4.44
30	4.37
20	4.27
10	4.19
10	4.095
30	4.005
5	3.925
5	3.585
vvw	3.52
20	3.495
10	3.405
20	3.385
5	3.345
5	3.29
70	3.24
3	3.165
3	3.13
vvw	3.10
50	3.02
20	2.88

I	d(A.)
30	2.85
B10	2.81*
70	2.755
20	2.70
B3	2.665
10	2.62
Bvw	2.56
Bvw	2.523
20	2.439
15	2.397
10	2.348
vw	2.312
20	2.293
B10	2.2515
5	2.2025
5	2.1845
15	2.1645
15	2.152
15	2.1335
15	2.113
5	2.100
B5	2.075
B5	2.051
5	2.032
vw	1.999
B10	1.9825*
5	1.960

I	d(A.)
20	1.9465
15	1.884
5	1.870
B5	1.8535
20	1.825
10	1.7975
10	1.780
vw	1.757
5	1.724
5	1.713
15	1.704*
15	1.697
10	1.689
5	1.6615
5	1.647
10	1.623
Bvw	1.601
Bvw	1.5815
B10	1.556
B10	1.5075
B10	1.470
B5	1.461
B5	1.447
B5	1.435
B5	1.3905

* May belong to ThO_2

SECTION 4

PREPARATION OF ALKALI LANTHANIDE PHOSPHATES AND RELATED COMPOUNDS BY PRECIPITATION METHODS.

4.1. Some pyrophosphates containing lanthanides; $Gd_4(P_2O_7)_3$ and $NaLnP_2O_7$ and their reactions on heating.

There are few publications about the pyrophosphates of the rare-earths. Although their existence has been confirmed by different authors (Cleve, 1878; Rosenheim and Triataphyllides, 1915; Gittelsohn, 1899; Johnsson 1889) little has been reported on their crystal structures. Buyers et al. (Buyers and Audrieth, 1950; Buyers, Giesbrecht and Audrieth, 1957; Giesbrecht and Audrieth, 1958) prepared orthophosphates and pyrophosphates by precipitation reactions from aqueous solutions; they used the hydrogen-ion displacement method. A typical reaction is represented by the following equation:

$$4Ln^{3+} + 3H_2P_2O_7^{2-} \rightarrow Ln_4(P_2O_7)_3 + 6H^+$$

The rare-earth solution was adjusted initially to a pH of 4.6 and after precipitation it was again adjusted to pH 4.6. It has been reported that the precipitation of pyrophosphates is incomplete if stoichiometric quantities are used, especially in the case of yttrium and neodymium. The suggested use of excess pyrophosphate solutions did not lead to precipitation of pure products. The precipitates were gelatinous, and efforts to crystallize them were unsuccessful. The use of high temperatures in the precipitation reactions caused hydrolysis of diphosphates (pyrophosphates) into orthophosphates, as represented by the following equation:

$$Ln_4(P_2O_7)_3 + 3H_2O \rightarrow 4LnPO_4 + 2H_2PO_4^- + 2H^+.$$

Difficulty was experienced in obtaining consistent products even with constant working conditions. X-radiograms of the ignited "orthophosphates" and "diphosphates" were identical, probably because hydrated diphosphates lost phosphoric acid (or phosphorus pentoxide) during ignition:

$$Ln_4(P_2O_7).xH_2O \ldots 4LnPO_4 + 2H_3PO_4$$

Tananaev and Petushkova (1964, 1966) also studied the reaction between gadolinium chloride solutions and pyrophosphate ions. The molar ratios $Na_4P_2O_7$:$GdCl_3$ (denoted by n) used were 0.75 and 1. These correspond, respectively, to the stoichiometric amount of sodium pyrophosphate (to form $Gd_4(P_2O_7)_3$) andexcess of pyrophosphate. The composition of the precipitated solid phase, with both values of n, is given as $Gd_4(P_2O_7)_3,13H_2O$. This compound is reported to be insoluble in water and amorphous to X-rays. It was claimed that the water could be removed altogether at 250°C. Owing to its "zeolitic" nature, the crystal structure remained intact during removal of the water. Powder patterns from samples heated at 700°C. and 900°C. are recorded (Tananaev and Petushkova, 1966). In the present investigation, initial studies did not give results in agreement with the data of Tananaev and Petushkova (1966), although there was not much difference between the methods of preparation. With n = 1 and pH 1 to 2, a crystalline product was obtained. A similar product was also obtained by Giesbrecht and Perrier (1960-1961) in the case of cerium, and this was claimed to be $NaCeP_2O_7,4.5H_2O$.

Preparation of $Gd_4(P_2O_7)_3$:

The necessary amount of gadolinium oxide (Johnson Matthey 99.9% pure) was dissolved in dilute hydrochloric acid. The pH of the solution was adjusted to 4.6 with very dilute sodium hydroxide solution; bromophenol blue (B.D.H, pH 2.8 to 4.6, yellow to blue) was used as indicator. The calculated stoichiometric amount of sodium pyrophosphate solution was added to the gadolinium chloride solution slowly and with constant stirring. Stirring was continued for 6 hours. An amorphous precipitate was formed which was very difficult to filter off; it was allowed to stand overnight prior to

filtration by means of a Whatman No. 40 filter paper. The product was ignited at 900°C. after drying and burning off the paper over a low Bunsen burner flame. The X-ray pattern (10091A) of the product shows a crystalline phase with a cubic unit-cell having a = 8.72 A., in addition to considerable quantities of gadolinium orthophosphate.

In another experiment a 10% excess of the sodium pyrophosphate solution was used and the precipitation was done in the cold to inhibit possible hydrolysis of diphosphates into orthophosphates. The vacuum-dried product was amorphous to X-rays (Film 10093A). Samples heated at 140°, 210°, and 400°C. were also amorphous (Films 10095A, 10093B, 10098D). After heating at 530°C. (Film 10099D) gadolinium orthophosphate lines appear. After heating at 700°C. a new set of lines (as yet unidentified) also appeared, those of gadolinium orthophosphate persisting (Film 10204D). Heating at 900°C. gave finally, a specimen consisting of gadolinium orthophosphate and the cubic phase referred to above (Film 10093C). The weight losses at 210° and 700°C., respectively were 15.63 and 17.72%. The latter figure would correspond to the formula $Gd_4(P_2O_7)_3, 13H_2O$ if the product were pure.

A further attempt was made to prepare gadolinium pyrophosphate from gadolinium chloride and $Na_2H_2P_2O_7$ solutions ($4GdCl_3 + 3Na_2H_2P_2O_7 \rightarrow Gd_4(P_2O_7)_3 + 6NaCl + 6HCl$) by a similar technique. X-ray analysis (Film 10091B) after heating at 900°C. showed a product similar to that obtained earlier, but with more orthophosphate present. There were also some lines which may have arisen from a metaphosphate of gadolinium, such as $Gd(PO_3)_3$. Metaphosphate might result from impurity (such as NaH_2PO_4) in the $Na_2H_2P_2O_7$. The presence of NaH_2PO_4 would lead to the formation of $Gd(H_2PO_4)_3$, which on heating would produce metaphosphate:

$$Gd(H_2PO_4)_3 \rightarrow Gd(PO_3)_3 + 3H_2O$$

(Buyers, Giesbrecht, and Audrieth, 1957).

Clearly the products obtained after heating at 700° and 900°C. do not correspond with those of Tananaev and Petushkova (1966). It therefore appeared necessary to investigate the reactions more carefully. Some experiments have been carried out by reproducing as closely as possible the methods of the earlier workers. Since the pH of the gadolinium chloride solution was not specifically mentioned, tests were performed with two different pH values, namely 3.0 and 4.6. Although the amount of dilute hydrochloric acid used to dissolve gadolinium oxide was kept to a minimum, it was impossible to obtain a solution with a pH as high as 3.0. To avoid the addition appreciable amounts of alkali solution to adjust the pH, the oxide was dissolved in a minimum amount of dilute hydrochloric acid by heating, and the solution was then evaporated to dryness. The residue was dissolved in distilled water containing a drop of dilute hydrochloric acid, and the pH was finally adjusted to 3.0 by adding a drop of diluted ammonia. Another solution was similarly prepared with a pH of 4.6. Four precipitations were done, at the two different pH values, and each at two n values, namely 0.75 and 1. Commercially prepared $Na_4P_2O_7,H_2O$ was used instead of the material prepared in the laboratory. 150 ml. portions of (0.025 x 0.75)M. and 0.025M sodium pyrophosphate solutions were added dropwise to gadolinium chloride solutions (150 ml., 0.025M). Stirring was continued for 12 hours. The white gelatinous precipitates were allowed to stand overnight, and then filtered on a No. 40 Whatman filter paper. The residues were dried for 24 hours in a vacuum desiccator, containing silica gel instead of in air. The filtrates were kept for determination of gadolinium and unreacted phosphate. The X-ray diffraction analysis of the

vacuum-dried products showed amorphous phases (Films 10319A, 10319B, 10319C, 10319D). Samples heated at 130°C. in vacuum for 24 hr. were also amorphous to X-rays (Films 10320A, 10320B, 10320C, 10320D). Dehydration of precipitated products in vacuum was found to be essential to prevent hydrolysis of diphosphates into orthophosphates. Further heat treatments at 680° and 900°C. were also done. Table 36 shows the weight losses at different temperatures for the different products. Satisfactory X-radiograms, showing crystalline material, were obtained from the products heated at 680° and 900°C., but lines due to gadolinium orthophosphate were present in all cases. Evidently the most careful precautions to remove water of hydration at the lowest possible temperature were not effective in preventing hydrolysis of the pyrophosphate. Another set of experiments was performed under exactly similar conditions; except that the drying in vacuum at room temperature was prolonged until the material was constant in weight. This required three days. By this procedure the total loss at 900°C. was reduced from approximately 12% to 10% (Table 36). The X-ray powder patterns of the vacuum-dried products were still amorphous to X-rays (Films 10339A, B, C, D). They were reheated at 130°C. in vacuum till constant in weight, but the products were still amorphous. The samples heated at 680° and 900°C. gave reproducible results closely similar to those obtained previously.

It became abundantly clear during the course of the work just described that lanthanide pyrophosphates could not be studied adequately by attempted use of high-temperature synthetic methods, nor could they be characterised by X-ray powder diffraction alone. It was decided, therefore, to examine the precipitation reactions by full quantitative analysis of the precipitated materials and of the solutions from which they were separated.

TABLE 36

Weight losses at different temperatures for vacuum dried $Gd_4(P_2O_7)_3.xH_2O$.

Set 1

Conditions	n = 0.75 pH = 3.0		n = 0.75 pH = 4.6		n = 1 pH = 4.6		n = 1 pH = 3	
	X-ray No.	% loss	X-ray No.	% loss	X-ray No.	% loss	X-ray No.	% loss
vacuum dried	10319A	-	10319B	-	10319C	-	10319D	-
130°C. (vacuum)	10320A	7.38	10320B	7.02	10320C	7.24	10320D	7.39
680°C.	10328A	12.29	10328B	11.96	10328C	11.47	10328D	12.40
900°C.	10330A	12.68	10330B	12.06	10330C	11.47	10330D	12.48

Set 2

vacuum dried to const. weight	10339A	-	10339B	-	10339C	-	10339D	-
130°C. (vacuum)	10348A	3.99	10348B	3.91	10348C	5.03	10348D	4.09
680°C.	10349A	8.74	10349B	8.66	10349C	10.39	10349D	10.48
900°C.	10350A	9.59	10350B	9.83	10350C	10.57	10350D	10.48

Analysis of Solutions and Products:

The phosphate content of a solution can be determined gravimetrically by precipitation with ammonium molybdate and ammonium nitrate in the presence of nitric acid (Mellor, 1971). The formula of the precipitate is $(NH_4)_3[PMo_{12}O_{40}]$ after drying at 120°-160°C., or $P_2O_5,24MoO_3$ after ignition at 550°C. (Jörgensen, 1936). In practice the composition of the initial molybdophosphate precipitate is uncertain and for high accuracy it is preferable to determine the phosphate by reprecipitation as $MgNH_4PO_4$ after dissolving the molybdophosphate in ammonia solution. The $MgNH_4PO_4$ is preferably ignited to $Mg_2P_2O_7$ at 1000-1100°C. The two principal sources of error are the entrance of molybdenum into the final precipitate and the loss of phosphorus pentoxide at the high temperature of the final ignition. The latter point was verified during the analytical work by taking an X-ray diffraction photograph (10362A) of a "$Mg_2P_2O_7$" precipitate; it contained some $Mg_3(PO_4)_2$ formed by loss of phosphorus pentoxide from $Mg_2P_2O_7$, in spite of careful attention to the need for slow heating of the precipitate.

This gravimetric method, after careful study, was considered to be the best available for determining phosphorus in the presence of rare-earth cations. The detailed procedure outlined by Vogel (1961) was employed.

Lanthanide ions were determined by the standard method of oxalate precipitation in nitric acid solution and ignition of the oxalate precipitate. Where appropriate, sodium content in precipitates were determined by standard flame-photometer techniques after dissolution of the precipitate in dilute hydrochloric acid.

Solutions from gadolinium pyrophosphate precipitations were filtered after keeping because a small precipitate was slowly

deposited. Examination of this precipitate by X-ray diffraction (Film 10373B) after heating at 900°C. showed it to be $Na_3Gd(PO_4)_2$. To the filtrate a few millilitres of concentrated nitric acid were added, and the solution was boiled to hydrolyze any remaining $P_2O_7^{4-}$ ions into PO_4^{3-} ions. The phosphate determination was then completed following the method given by Vogel (1961). The filtrate from the phosphomolybdate precipitation was evaporated to small bulk to expel excess nitric acid, a necessary step because the solution should not contain more than 5% nitric acid in the precipitation of lanthanides with oxalic acid (Schoeller and Powell, 1940). To the cold solution (100 ml.), 100 ml. of saturated oxalic acid solution were added without stirring. After an hour the solution was stirred vigorously and left overnight. After filtering and washing with 2% oxalic acid solution, the residue was ignited to oxide over a Bunsen burner and weighed.

For the analysis of solid products two modifications of the general technique were tested. In the first the pyrophosphate sample was dissolved in dilute nitric acid and gadolinium was precipitated as oxalate. A $MgNH_4PO_4$ precipitation was then carried out by usual methods on the filtrate. It proved necessary to reprecipitate the $MgNH_4PO_4$ before ignition to $Mg_2P_2O_7$; the oxalate in the solution, in the first precipitation, contaminated the precipitate with magnesium oxalate, which was converted into magnesium oxide on ignition.

In the second modification of the general method, the phosphomolybdate precipitation was carried out first. The solid sample was dissolved in dilute nitric acid, and the method used for the solution analysis (see above) was applied. Comparison of the results from the two procedures showed that there was an appreciable phosphorus loss in the phosphomolybdate precipitation when gadolinium was present.

On this account, the first method was employed in the analysis of the precipitated pyrophosphates. Tables 37 and 38 show the gadolinium and phosphorus contents (as percentages of the oxides) for the two sets of gadolinium pyrophosphate preparations; Gd/P ratios (in weight) for the products, and analyses of the residual solutions are also shown.

Although the results are not very reproducible, owing to difficulties in the phosphomolybdate method, they are sufficiently accurate to show that when n = 0.75 the analytical values agree with the theoretical ones for gadolinium pyrophosphate, $Gd_4(P_2O_7)_3$. At n = 1 the gadolinium oxide content decreases and that of phosphorus pentoxide increases, the values moving towards the theoretical values for $NaGdP_2O_7$ and $HGdP_2O_7$. Another important conclusion is that when n = 1 and pH = 4.6 the sodium content of the precipitate is substantially increased.

Determination of Pyrophosphate Content:

A method has been developed to determine the $P_2O_7^{4-}$ content of the precipitated gadolinium pyrophosphate. A weighed amount of vacuum-dried pyrophosphate, prepared under the conditions n = 0.75, and pH = 3.0 (set 1), was treated with a 100 ml. of saturated sodium carbonate solution for 24 hours, with constant stirring. The expected reaction is represented by the equation:

$$Gd_4(P_2O_7)_3 + 6Na_2CO_3 \rightarrow 2Gd_2(CO_3)_3 + 3Na_4P_2O_7$$

The reaction was carried out at room temperature to minimise hydrolysis reactions. After filtration the residue was dried in vacuum desiccator and weighed. It was completely soluble in acids with evolution of carbon dioxide and was amorphous to X-rays (Film 10325A). The filtrate from the carbonate treatment deposited a trace of crystalline product after standing for 2 days. This could not be

TABLE 37A

Analysis of $Gd_4(P_2O_7)_3$. Set 1.

n	0.75	0.75	1.0	1.0
pH	3.0	4.6	4.6	3.0
vacuum dried product g.	1.0830	1.1810	1.4875	0.9960
Mol. H_2O per formula	9.3	8.8	8.3	9.1
Gd_2O_3 %	62.22	61.93	58.81	60.34
P_2O_5 %	40.38	36.75	38.20	39.07
Na_2O %	0.06	0.44	1.88	0.19
Gd/P (in weight)	3.06	3.35	3.06	3.07
Total	102.66	99.12	98.88	99.60

TABLE 37B

Analysis of Solutions. Set 1.

n	0.75	0.75	1.0	1.0
pH	3.0	4.6	4.6	3.0
Initial Gd_2O_3 g.	0.6797	0.6797	0.6797	0.6797
Unprecipitated Gd_2O_3 g.	0.0369	-	-	0.1160
Initial $Na_4P_2O_7,10H_2O$ g.	1.2544	1.2544	1.6725	1.6725
Unprecipitated $Na_4P_2O_7,10H_2O$ g.	0.0554	0.0237	0.0906	0.0832
Gd/P (in weight)	3.35	3.44	2.68	2.21

Theoretical values for $Gd_4(P_2O_7)_3$:

Gd_2O_3: 63.00% P_2O_5: 37.00% Gd/P = 3.34

For $NaGdP_2O_7$:

Gd_2O_3: 51.18% P_2O_5: 40.08% Na_2O: 8.76% Gd/P = 2.53

For $HGdP_2O_7$:

Gd_2O_3: 54.56% P_2O_5: 42.73% H_2O: 2.70% Gd/P = 2.53

TABLE 38A

Analysis of $Gd_4(P_2O_7)_3$. Set 2.

n	0.75	0.75	1.0	1.0
pH	3.0	4.6	4.6	3.0
vacuum dried product g.	1.1393	1.1259	1.2366	1.2391
Mol. H_2O per formula	6.8	6.9	7.5	7.5
Gd_2O_3 %	63.43	64.28	60.79	58.67
P_2O_5 %	37.13	38.48	40.03	41.10
Na_2O %	0.06	0.05	0.44	0.35
Gd/P (in weight)	3.39	3.32	3.02	2.84
Total	100.62	102.81	101.26	100.12

TABLE 38B

Analysis of Solutions. Set 2.

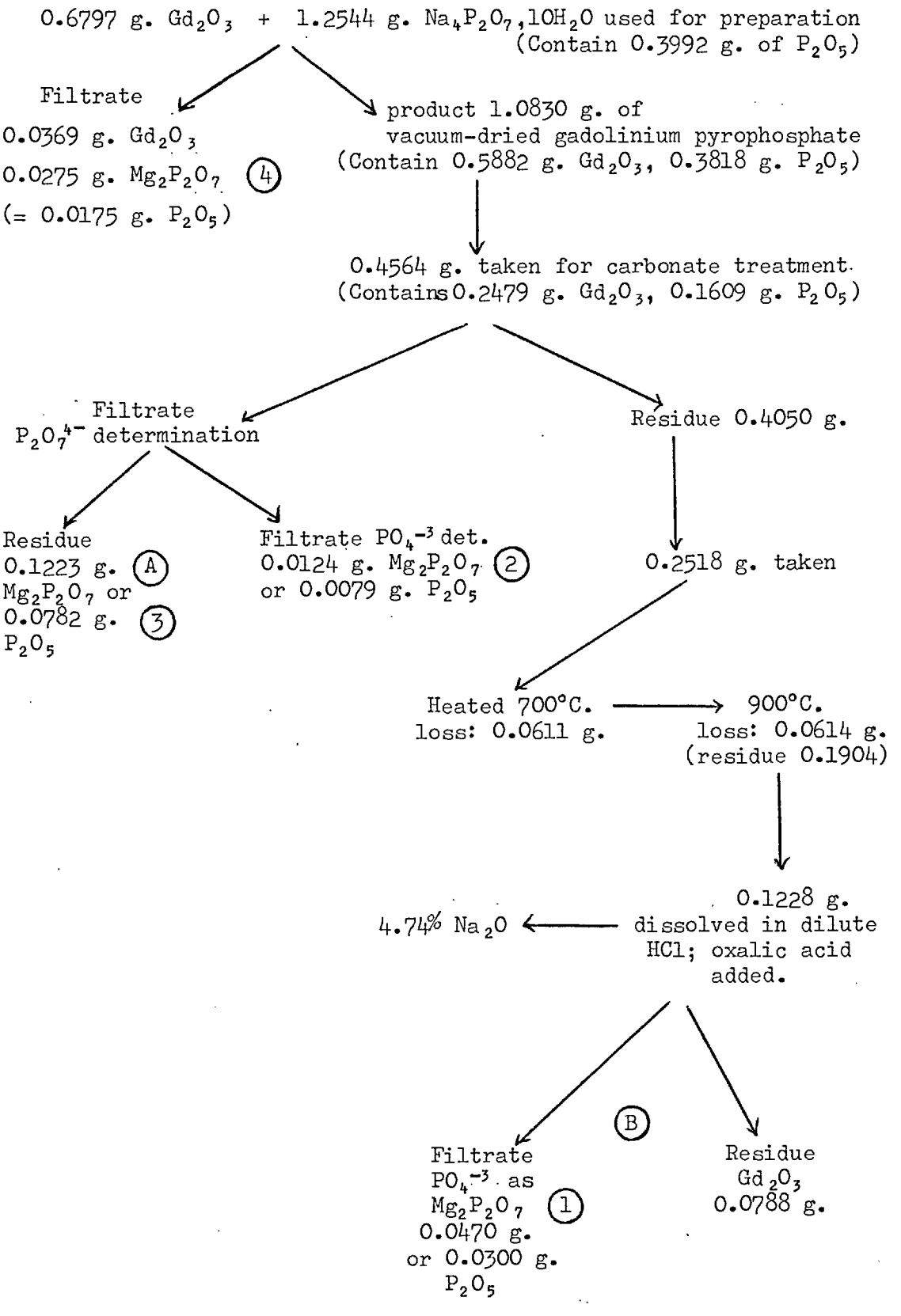
n	0.75	0.75	1.0	1.0
pH	3.0	4.6	4.6	3.0
Initial Gd_2O_3 g.	0.6797	0.6797	0.6797	0.6797
Unprecipitated Gd_2O_3 g.	0.0075	0.0149	0.0131	0.0057
Initial $Na_4P_2O_7,10H_2O$ g.	1.2544	1.2544	1.6725	1.6725
Unprecipitated $Na_4P_2O_7,10H_2O$ g.	0.0193	0.0261	0.3285	0.2119
Gd/P (in weight)	3.63	3.40	3.09	2.88

identified from its rather diffuse X-radiogram (10325B), but it was found to contain 2.32% of sodium, and evolution of carbon dioxide with acid showed it to contain carbonate.

In the sodium-salt filtrate $P_2O_7^{4-}$ was determined by the method given by Erdey (1965). After this $P_2O_7^{4-}$ determination PO_4^{3-} was also determined in the filtrate, in order to establish the degree of hydrolysis. The results of these determinations are recorded at (A) in Table 39. Analysis of the insoluble product of the sodium carbonate treatment, after heating at 900°C., gave 0.0788 g. of gadolinium oxide, 0.0300 g. of phosphorus pentoxide and 0.0058 g. of sodium oxide for 0.1228 g. of the sample. These results, included at (B) in Table 39, indicate the molecular ratios $Gd_2O_3:P_2O_5:Na_2O$ to be 2.17:2.11:0.93 corresponding with the formula $Na_2O,2Gd_2O_3,2P_2O_5$. X-ray diffraction examination of this material after heating at 700°C. (Film 10325C) and 900°C. (10325D) disclosed in both cases, the presence of $Na_3Gd(PO_4)_2$, $GdPO_4$, Gd_2O_3 and $GdPO_4$, with a further unidentified phase which appeared to be cubic (see Section 3.1). Identification of this phase is scarcely feasible from a photograph containing numerous strong lines of other substances, and it must await further study.

Consideration of the weight values shown in Table 39 indicates very satisfactory recoveries of phosphate in the different stages of the separation. The three $Mg_2P_2O_7$ precipitates labelled (1), (2), and (3) represent recovery of 0.1609 g. of phosphorus pentoxide from the sample taken for the carbonate treatment; that sample in fact, is calculated to contain 0.1609 g. of phosphorus pentoxide. Furthermore, the phosphorus pentoxide content of the vacuum-dried gadolinium pyrophosphate plus the small amount recovered in the $Mg_2P_2O_7$ precipitate labelled (4) gives a total of 0.3993 g., closely corresponding

TABLE 39


0.6797 g. Gd_2O_3 + 1.2544 g. $Na_4P_2O_7,10H_2O$ used for preparation
(Contain 0.3992 g. of P_2O_5)
Filtrate
0.0369 g. Gd_2O_3
0.0275 g. $Mg_2P_2O_7$ (4)
(= 0.0175 g. P_2O_5)
product 1.0830 g. of vacuum-dried gadolinium pyrophosphate
(Contain 0.5882 g. Gd_2O_3, 0.3818 g. P_2O_5)
0.4564 g. taken for carbonate treatment.
(Contains 0.2479 g. Gd_2O_3, 0.1609 g. P_2O_5)
Filtrate
$P_2O_7^{4-}$ determination
Residue 0.4050 g.
Residue
0.1223 g. (A)
$Mg_2P_2O_7$ or
0.0782 g. (3)
P_2O_5
Filtrate PO_4^{-3} det.
0.0124 g. $Mg_2P_2O_7$ (2)
or 0.0079 g. P_2O_5
0.2518 g. taken
Heated 700°C.
loss: 0.0611 g.
900°C.
loss: 0.0614 g.
(residue 0.1904)
0.1228 g.
dissolved in dilute HCl; oxalic acid added.
4.74% Na_2O
(B)
Filtrate
PO_4^{-3} as
$Mg_2P_2O_7$ (1)
0.0470 g.
or 0.0300 g.
P_2O_5
Residue
Gd_2O_3
0.0788 g.

with the calculated quantity of 0.3992 g. in the original sodium pyrophosphate. The exact agreement must be regarded as fortuitous, but the correspondence is satisfactory. Such close agreement cannot be established for the gadolinium content of the sample, and the figures given suggest appreciable loss of gadolinium in the sodium carbonate treatment reaction, possibly through formation of a soluble sodium double carbonate.

The proportion of total phosphate separated as pyrophosphate in the separation scheme of Table 39 is 0.0782/0.1609 x 100 = 48.6%. This provides a somewhat insecure basis for claiming that the original compound is a pure pyrophosphate, but evidence abounds for the rapid hydrolysis of pyrophosphates in solution. The correspondence between the actual analytical figures for the gadolinium to phosphorus ratio with the theoretical value, and the successful recovery of a subtantial proportion of the phosphate as pyrophosphate, are together taken to confirm the view that gadolinium pyrophosphate was successfully prepared. Failure to recover the total phosphate content in the pyrophosphate form seems inevitable.

Precipitation of Gadolinium Pyrophosphate from more concentrated Solutions:

The precipitation of gadolinium pyrophosphate was tried again at pH 4.6 and n = 1 but with more concentrated solutions (0.09M). After heating at 700° and 900°C. the product corresponded closely in X-ray behaviour and sodium content (1.17% Na_2O) with the products obtained before (Films 10368B, C).

Discussion of X-ray Diffraction Results:

The interpretation of the powder diffraction photographs from numerous samples prepared in the studies just described has led to the general conclusions below.

1. The complete removal of water of bydration from precipitated gadolinium pyrophosphate is in practice impossible at low temperatures (130°C.), even in vacuum.

2. The presence of water of hydration causes gadolinium pyrophosphate to hydrolyse rapidly to gadolinium orthophosphate on heating. This hydrolysis appears to be well advanced in many samples, the X-radiograms showing strong and well defined lines of gadolinium orthophosphate; in other samples (particularly those prepared in efforts to complete the dehydration at the lowest possible temperatures) the lines are weaker and more diffuse, suggesting incomplete hydrolysis. The extent of hydrolysis cannot be assessed reliably from the photographs, because precipitated gadolinium pyrophosphate never discloses its presence by characteristic diffraction lines.

3. The products obtained on heating the pyrophosphate at the 700°C. contained two phases and gadolinium orthophosphate lines. These were not fully characterised and are referred to provisionally as "Phase 1" and "Phase 2". In different photographs their lines appeared separately (Films 10328C and 10349A, B) or together (e.g. Film 10368B). Phase 1, was successfully indexed in the tetragonal system (a = 12.92, c = 13.56 A. Table 40). Phase 2 corresponded with a decomposition product obtained later by heating $HGdP_2O_7$ at 700°C. or over (see Section 4. p.150)

4. The products of heating the pyrophosphate at 900°C. were consistently similar, and the X-ray photographs of a number of samples were almost identical.

5. Reference was made earlier to a cubic phase in the products of vacuum-dried $Gd_4(P_2O_7)_3$ heated at 900°C. (p. 115). Closer study showed that this structure had many more diffraction lines than those identified later. Microdensitometer traces of several photographs

TABLE 40

$Gd_4(P_2O_7)_3$ heated at 700°C.*

Film 10368B Rad. Fe. K_α

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	Remarks
50	6.54	200	0.02191	0.02240	
60	5.78	210	0.02803	0.02800	
25	4.69	202	0.04261	0.04280	
60	4.58	220	0.04475	0.04480	
B60	4.334	221	0.04993	0.04990	
30	3.92	310	0.05589	0.05600	
5	3.487	312	0.07714	0.07640	
15	3.27	104	0.08769	0.08720	
30	3.147	401	0.09472	0.09470	
5	2.98	331	0.10532	0.10590	$GdPO_4$
20	2.912	402	0.11060	0.11000	
B10	2.884	420	0.11280	0.11200	
5	2.845	412	0.11586	0.11560	
100	2.807	323	0.11908	0.11870	$GdPO_4$
20	2.72	224	0.12683	0.12640	
10	2.669	304	0.13166	0.13200	
vw	2.585	500	0.14033	0.14000	
B5	2.454	215	0.15582	0.15550	
5	2.147	502	0.16060	0.16040	
w	2.289	440	0.17911	0.17920	
3	2.165	325	0.20014	0.20030	
40	2.125	610	0.20770	0.20720	$GdPO_4$
25	2.103	216	0.21196	0.21160	
3	2.047	620	0.22384	0.22400	
60	1.916	107	0.25550	0.25550	$GdPO_4$
20	1.855	632	0.27262	0.27240	$GdPO_4$
40	1.834	416	0.27886	0.27880	$GdPO_4$
20	1.817	336	0.28415	0.28440	$GdPO_4$
50	1.700	730	0.32469	0.32480	$GdPO_4$
20	1.654	723	0.34280	0.34270	$GdPO_4$
B10	1.595	811	0.36820	0.36910	$GdPO_4$
B10	1.567	318	0.38201	0.38240	$GdPO_4$

*Only Phase 1 and gadolinium orthophosphate lines were reported.

a = 12.92 A. c = 13.56 A.

allowed the extra lines to be identified by their maintenance of constant intensity ratio with the stronger lines already assigned. A film obtained with iron radiation (10362C and Table 41) allowed better resolution of the many weaker lines, not readily measured on the earlier photograph (10091A) taken with copper radiation. Evaluation of this film confirmed the cubic symmetry of the structure, but led to a lattice constant (a) of 25.88 A.

The assignment of a cubic cell of such large size requires full confirmation by single-crystal studies before it is unreservedly accepted; such a cell could contain 2000 or more atoms. It is noteworthy that close study of the powder diffraction data allowed indexing on somewhat smaller orthorhombic unit-cells. Nevertheless, Völlenkle, Wittmann and Nowotny (1963) (with other previous workers referred to in their paper) have interpreted the structures of a number of pyrophosphates of quadrivalent metals in terms of similar large cubic cells. It remains to be seen whether the structures of these pyrophosphates can be correlated with that of a gadolinium compound, which must inevitably introduce some new structural feature on account of the higher proportion of cations. It is unfortunate that the stoichiometry of the cubic phase cannot be established from the work now described, because this phase has always appeared in admixture with gadolinium orthophosphate in proportions which cannot be assessed.

Infra-Red Spectra of Lanthanide Pyrophosphates:

The study of infra-red spectra, which include absorption regions due to stretching and bending vibrations of bond systems including phosphorus atoms, provides the most direct method of establishing the presence, in particular compounds, of phosphate ions or groups of particular types. The need to establish clearly

TABLE 41

$Gd_4(P_2O_7)_3$ heated at 900°C.

Film 10362C Rad. Fe. K_α

I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	h'k'0	Remarks	N
20	8.65	0.01252	0.01260	300	100		9
90	6.11	0.02515	0.02520	330	110		18
40	5.20	0.03471	0.03500	430			25
20	5.09	0.03616				$GdPO_4$	
20	4.68	0.04287				$GdPO_4$	
50	4.56	0.04511				$GdPO_4$	
90	4.36	0.04927	0.04900	531			35
vw	4.29	0.05089	0.05040	600	200		36
50	4.09	0.05609	0.05600	620		$GdPO_4$	40
40	3.98	0.05914	0.05880	541		$GdPO_4$	42
60	3.89	0.06195	0.06160	622			44
20	3.85	0.06322	0.06300	630	210		45
80	3.59	0.07264	0.07280	640			52
100	3.53	0.07528	0.07560	633	211		54
vw	3.48	0.07760					
15	3.45	0.07901				$GdPO_4$	
15	3.42	0.08043				$GdPO_4$	
50	3.22	0.09054				$GdPO_4$	
5	3.10	0.09755					
B20	3.06	0.10028	0.10080	660	220	$GdPO_4$	72
90	3.02	0.10306				$GdPO_4$	
3	2.98	0.10532				$GdPO_4$	
3	2.94	0.10842					
40	2.912	0.11060				$GdPO_4$	
3	2.889	0.11238	0.11200	840			80
80	2.80	0.11951			300	$GdPO_4$	
15	2.755	0.12364	0.12320	664			88
15	2.743	0.12466	0.12460	922			89
10	2.724	0.12639	0.12600	930	310		90
50	2.628	0.13581	0.13580	940			97
5	2.614	0.13731	0.13720	941			98
30	2.552	0.14399			311	$GdPO_4$	

TABLE 41 continued

I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	h'k'0	Remarks	N
30	2.53	0.14660	0.14700	10.2.1			105
70	2.417	0.16060	0.16100	953			115
15	2.392	0.16395			320	$GdPO_4$	
15	2.382	0.16543				$GdPO_4$	
10	2.343	0.17083				$GdPO_4$	
10	2.285	0.17961				$GdPO_4$	
20	2.266	0.18263	0.18200	970			130
B20	2.248	0.18568	0.18620	964			133
w	2.220	0.19011	0.19040	10.6.0			136
w	2.202	0.19337				$GdPO_4$	
20	2.173	0.19874	0.19880	965			142
20	2.150	0.20276	0.20300	980	400		145
30	2.137	0.20540				$GdPO_4$	
30	2.116	0.20947	0.21000	10.7.1			150
30	2.104	0.21196	0.21280	10.6.4		$GdPO_4$	152
30	2.094	0.21393	0.21420	966	410	$GdPO_4$	153
30	2.074	0.21805				$GdPO_4$	
50	2.048	0.22367	0.22400	12.4.0			160
5	1.979	0.23950				$GdPO_4$	
w	1.946	0.24774	0.24780	13.2.2			177
20	1.931	0.25151	0.25200	12.6.0	420		180
50	1.916	0.25550				$GdPO_4$	
10	1.892	0.26200	0.26180	13.3.3	421	$GdPO_4$	187
20	1.856	0.27223				$GdPO_4$	
30	1.833	0.27905				$GdPO_4$	
50	1.822	0.28278	0.28280	11.9.0		$GdPO_4$	202
20	1.812	0.28573	0.28560	14.2.2		$GdPO_4$	204
B30	1.779	0.29644	0.29680	14.4.0			212
20	1.767	0.30044	0.29960	14.3.3	422		214
20	1.759	0.30343				$GdPO_4$	
10	1.748	0.30705	0.30660	13.5.5			219
40	1.739	0.31006	0.30940	15.1.0			221
30	1.731	0.31310	0.31360	15.2.0	500	$GdPO_4$	224
10	1.718	0.31775	0.31780	13.7.3	430	$GdPO_4$	227
5	1.713	0.31980				$GdPO_4$	

TABLE 41 continued

I	d(A.)	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	hkl	h'k'0	Remarks	N
30	1.700	0.32449	0.32480	14.6.0	510		232
15	1.691	0.32795				$GdPO_4$	
10	1.681	0.33207	0.33180	15.4.1			237
20	1.654	0.34300				$GdPO_4$	
B10	1.636	0.35027	0.35000	13.9.0			250
5	1.613	0.36050				$GdPO_4$	
5	1.607	0.36302	0.36260	139.3			259
15	1.594	0.36933				$GdPO_4$	
B20	1.564	0.38348				$GdPO_4$	
5	1.544	0.39349				$GdPO_4$	
w	1.535	0.39797				$GdPO_4$	
w	1.529	0.40138	0.40040	14.9.3	440		286
20	1.518	0.40695	0.40600	171.0			290
10	1.504	0.41490	0.41440	16.6.2		$GdPO_4$	296
B5	1.478	0.47933	0.47880	18.3.3			342

a = 25.88 A. a(sub cell) = 8.66 A.

the types of phosphate ions present in lanthanide phosphates or double phosphates rendered necessary a brief study, by infra-red techniques, of compounds occurring in the present investigation.

The usual symbols appropriate to infra-red studies are used in the account below.

Infra-red spectra of pyrophosphates have generally the following stretching modes: ν_{as} (P-O-P) at 1060-850 $cm.^{-1}$ very strong to strong, ν_{s} (P-O-P) at 800-650 $cm.^{-1}$ medium to very weak, ν_{as} (PO_3) at 1170-1030 $cm.^{-1}$ strong to very strong, ν_{s} (PO_3) at 1025-940 $cm.^{-1}$ strong to very strong (Griffith and Grayson, 1969, Vol. 6). The stretching vibration of a M-O-P group in the cubic crystalline pyrophosphates was given by Steger and Leukroth (1960), and Mooney, Toma and Brunvoll (1967) in the 1060-1125 $cm.^{-1}$ region; the deformation mode (δP-O) occurs in the 500-675 $cm.^{-1}$ region. Medium or weak bands between 720 and 680 $cm.^{-1}$ were assigned for most compounds and accepted as the characteristic frequencies for pyrophosphates. (Holmsted and Larsson, 1951).

The infra-red spectra of lanthanide pyrophosphates were first reported by Petrov, Vasil'eva and Pervykh (1966) for lanthanum compounds. Petrov, Tananaev and Pervykh (1967) studied the infra-red spectra of gadolinium ortho- and pyro-phosphates at different temperatures. Data were also reported for samarium, praseodymium, erbium and ytterbium pyrophosphates by Petrov, Kirillov and Petushkova (1970).

In the present work infra-red spectra of gadolinium pyrophosphate samples of the types indicated below were examined.

1. <u>$Gd_4(P_2O_7)_3$ in the vacuum-dried state and heated at 210°C</u>:

The infra-red spectra of two available products were very similar. A very intense and diffuse band was observed between 925 and

1150 $cm.^{-1}$ region. This corresponds to ν_{as} (P-O-P), ν_{as} (PO_3) and ν_s (PO_3) stretching vibrations of the $P_2O_7^{4-}$ anion. The deformation vibrations (δP-O) gave two medium bands at 630 and 550 cm^{-1}. These values agree with those of Petrov, Tananaev and Pervykh (1967), except that a ν_{as} (P-O-P) band at ~ 900 $cm.^{-1}$ was very broad and weak (Charts 5 and 6).

2. $Gd_4(P_2O_7)_3$ heated at 700°C:

The infra-red spectrum of $Gd_4(P_2O_7)_3$ after heating at 700°C. has not been reported in the literature, but the infra-red spectrum of lanthanum pyrophosphate heated previously at 700°C. has been described (Petrov, Vasil'eva and Pervykh, 1966).

The infra-red spectrum of gadolinium pyrophosphate heated at 700°C, was quite different from that of the vacuum-dried product; triplets appeared in the 700-800 $cm.^{-1}$ region. Although the spectrum was very complex on account of the appearance of bands assigned to orthophosphate there was a good agreement with the previous data, which also included bands due to orthophosphate.

3. $Gd_4(P_2O_7)_3$ after partial decomposition by heating at 900°C:

A number of bands were reported by Petrov, Tananaev and Pervykh (1967) for $Gd_4(P_2O_7)_3$ after heating at 1000°C., which agreed with our data. The bands at 460 (δP-O), 495 (δP-O), 505 (δP-O), 685 (δP-O), 760 ν_s (P-O-P), and 800 $cm.^{-1}$ ν_s (P-O-P) given by Petrov et al. were not common with orthophosphates, so they can be regarded as characteristic for the $P_2O_7^{4-}$ anion (Chart 8). Since the observations given above showed without question the presence of the $P_2O_7^{4-}$ anion in the products, the formation and partial hydrolysis of $Gd_4(P_2O_7)_3$ has been confirmed by the infra-red methods.

Some Double Pyrophosphates of Lanthanides

Double pyrophosphates of rare earths have been prepared by several investigators (Giesbrecht and Perrier, 1960-1961; Tananaev and Vasil'eva, 1964; Kuznetsov and Vasil'eva, 1967). It has also been claimed that acid pyrophosphates are formed when acid solutions of rare-earth salts and sodium pyrophosphate solutions are mixed, but this has not been satisfactorily confirmed (Tarayan and Eliazyan, 1958; Petru and Hajek, 1957). Lately Tananaev, Kuznetsov and Vasil'eva (1967) were able to prepare $LaHP_2O_7,3H_2O$ as a very fine crystalline powder. Their criterion of the existence of hydrogen ion in the pyrophosphate was the absence of alkali metals while the $P_2O_4^{4-}/La^{3+}$ ratio remains equal to 1. Tananaev, Kuznetsov and Petushkova (1966) also claimed preparation of some rare-earth alkali double pyrophosphates, and reported some complex X-ray diffraction patterns for $KGdP_2O_7$ and $NaLaP_2O_7$. No investigation has been reported on $HGdP_2O_7$ or $NaGdP_2O_7$; it was decided, therefore, to prepare $NaCeP_2O_7,4.5H_2O$ as outlined by Giesbrecht and Perrier (1960-1961), and then to apply the same method for the preparation of $NaGdP_2O_7$.

Preparation of $NaCeP_2O_7,4.5H_2O$:

Cerous chloride solution was prepared from cerium ammonium nitrate according to the following reaction (Moeller and Brantley, 1950):

$$Ce(NH_4)_2(NO_3)_6 + 4HCl \rightarrow CeCl_3 + 2NH_3 + 6NO_3^- + \tfrac{1}{2}Cl_2 + 6H^+$$

Technical cerium ammonium nitrate allegedly containing 4 mol. of water of crystallisation (Hopkin and Williams Ltd.) was employed. This was ignited first to ceric oxide in a platinum crucible over a Bunsen burner, in order to determine the water content, which was found to be approximately 1.5 mol. The calculated amount of hydrochloric acid was then mixed with a suitable quantity of the cerium ammonium

nitrate, and the solution was evaporated to dryness. The dry residue was dissolved in hydrochloric acid and the solution evaporated again. This procedure was repeated three times, and finally the dry chloride was dissolved in dilute hydrochloric acid; a small insoluble residue was identified as ceric oxide and was allowed for in calculation of the molarity of the cerous chloride solution. To each of two 25 ml. portions of 0.09M cerous chloride solutions, adjusted respectively to pH 2.0 and 4.6, 25 ml. of 0.09M sodium pyrophosphate solutions were added with stirring. Stirring was continued for 4 hours. The gelatinous precipitate was filtered on a No. 40 Whatman filter paper and dried in vacuum. The product was amorphous to X-rays (Film 10099C), but the infra-red spectrum (Chart 10) was in agreement with the one given by Petrov, Vasil'eva and Pervykh (1966) for $NaLaP_2O_7,4H_2O$. When the products were heated to 140°C. they lost approximately 13% of water, but they were still not crystalline (Films 10100C, D). After heating at 500°C. about 4% of more water was lost and the X-ray patterns showed very weak lines of cerous orthophosphate (Films 10102B, C). After heating 700°C. the products gave cerous orthophosphate lines with additional lines which were not immediately identified (Films 10101C, D); further heating at 900°C. resulted in the cerous orthophosphate alone being recorded (Films 10103A, B). Evidently no sodium cerous pyrophosphate had been obtained as a crystalline phase.

A second attempt to prepare hydrated $NaCeP_2O_7$ in crystalline form was successful. The precipitation was carried out very slowly (pH=1-2) and stirring of the precipitate and mother liquor was continued overnight. The solid obtained by filtration and vacuum drying had a very complex X-ray pattern (10103C). A small quantity of product of better crystallinity (Film 10103D) separated when the filtrate was

again allowed to stand overnight. Table 42 shows the d-spacings compared with the values of Giesbrecht and Perrier, 1960, 1961). The two structures correspond very closely except two strong lines (d = 6.29 and 5.755 A.). The appearance of many extra lines is probably due to the use of better camera techniques and cobalt radiation. Slight discrepancies may also arise from the differences in the water content. This was proved in the case of the corresponding gadolinium compound. On the other hand the X-radiogram given for $NaLaP_2O_7,4H_2O$ by Kuznetsov and Vasil'eva (1967) was not in agreement with that of Giesbrecht for $NaCeP_2O_7,4.5H_2O$.

When the precipitated and vacuum-dried sodium cerium pyrophosphate was heated at 200°C. for 5 hours (in air) a weight loss of 15.90% occurred, its characteristic X-ray diffraction pattern was lost, and a few lines appeared evidently associated with a crystalline decomposition product, so far unidentified (Film 10113B). When heating at 200°C. was continued for 48 hours, cerium orthophosphate lines also appeared (Film 10127B). On heating at 400°C. (5 hr.) the weight loss increased to 16.80% and the product became amorphous to X-rays (Film 10104B). After further heating at 570°C. (weight loss 18.10% after 5 hr.) the product gave cerium orthophosphate diffraction lines (Film 10113C), and its infra-red spectrum contained orthophosphate peaks together with additional peaks associated by Corbridge and Lowe (1954) with cyclic metaphosphates. Reheating of the material for five-hour periods at 700°C. and 900°C. brought the weight loss to a constant figure of 19.80%; in both cases the X-radiogram disclosed cerium orthophosphate lines with weak lines of a new phase (Films 10104C and 10105A).

TABLE 42

X-Ray Powder Diffraction Pattern of $NaCeP_2O_7, 4.5H_2O$

Giesbrecht and Perrier (1960-1961) Rad. Cu. K_α (114.6 mm. camera)		Present Work (Film 10103D) Rad. Co. K_α (Guinier camera)	
I	d(A.)	I	d(A.)
100	9.21	100	9.16
-	-	3	7.605
40	6.79	30	6.715
70	6.29	-	-
-	-	90	5.755
50	5.40	40	5.435
60	4.64	40	4.62
90	4.33	B50	4.325
5	4.09	60	4.13*
60	3.79	30	3.775
70	3.40	80	3.40
-	-	10	3.365
80	3.20	80	3.185
-	-	30	3.145
-	-	5	3.10
-	-	5	3.065
-	-	10	3.035
90	2.99	90	2.98
-	-	3	2.92
-	-	3	2.88
-	-	5	2.735
-	-	40	2.71
-	-	15	2.675
30	2.53	10	2.53
-	-	10	2.479
80	2.42	60	2.412
50	2.34	50	2.335
-	-	3	2.304
-	-	3	2.267

* Vaseline line.

TABLE 42 continued

I	d(A.)
50	2.25
-	-
50	2.18
30	2.13
-	-
-	-
-	-
-	-
80	2.03
40	1.943
-	-
-	-
70	1.884
-	-
10	1.813
-	-
-	-
40	1.755
-	-
40	1.711
-	-
40	1.663
30	1.627
40	1.586
40	1.559
20	1.520
-	-
20	1.468
20	1.432
40	1.374
40	1.325

I	d(A.)
30	2.247
10	2.222
30	2.183
20	2.134
10	2.117
15	2.099
2	2.074
2	2.058
B50	2.026
B15	1.958
5	1.919
5	1.908
60	1.871
5	1.836
5	1.815
15	1.797
10	1.773
5	1.752
5	1.738
40	1.699
10	1.672
20	1.656
5	1.629
10	1.579
10	1.557
-	-
B3	1.489
-	-
-	-
-	-
-	-

Preparation of Sodium Gadolinium Pyrophosphate:

The method used successfully, as described above, to prepare a precipitated, hydrated sodium cerium pyrophosphate was also used in an attempt to isolate a corresponding gadolinium compound. Gadolinium chloride solution (0.09M) was prepared by dissolving the oxide in dilute hydrochloric acid, and 0.09M sodium pyrophosphate was used as precipitant. The product had an infra-red spectrum closely similar to that given for $NaLaP_4O_7,4.5H_2O$ (Petrov, Vasil'eva and Pervykh, 1966). The vacuum-dried product gave an X-radiogram (10104D) (Table 43) having a general similarity only with that of the cerium salt; clearly the structures were not identical. In an effort to isolate the anhydrous compound, a number of heat-treatments of the hydrated salt were carried out; these are outlined below.

The vacuum-dried compound, after heating for 5 hours at 700°C., suffered a loss of weight of 15.30%, corresponding with loss of water from $NaGdP_2O_7,4H_2O$ approximately. X-ray pattern (10105C) showed very broad lines. Some lines corresponding with lines of α-$NaLaP_2O_7$ (A.S.T.M. Card No. 21-1131) were present, but agreement was poor otherwise. The specimen was further heated at 700°C. until a total of 28 hours of heating, with a number of interruptions for regrinding of the sample, gave a crystallised product of which the stronger X-ray lines could be indexed in the orthorhombic system (Film 10127A). Some decomposition took place in the later stages of this heating operation. Comparison of the infra-red spectra of the hydrated salt and the heated product (Charts 13, 14) showed splitting of the peak at 500-600 $cm.^{-1}$ into three lines ascribed to orthophosphate formation. There were also additional lines in the 1200-1400 $cm.^{-1}$ region, which could be attributed to acid pyrophosphates or metaphosphates (Corbridge and Lowe, 1954; Serra and Giesbrecht, 1968). Medium or strong

TABLE 43

X-Ray Diffraction Pattern of $NaGdP_2O_7,4.5H_2O$ (approximately)

Film No. 10104D Rad. Co. K_α

I	d(A.)	I	d(A.)	I	d(A.)
B100	9.64	10	2.68	10	1.831
20	6.90	5	2.655	10	1.816
20	6.37	40	2.63	10	1.793
w	6.04	40	2.57	10	1.7805
40	5.755	5	2.483	10	1.750
80	4.955	5	2.461	10	1.741
50	4.79	20	2.410	5	1.7235
50	4.68	5	2.389	5	1.715
50	4.63	15	2.3675	10	1.701
40	4.24	5	2.3475	5	1.684
20	3.785	20	2.250	10	1.651
5	3.68	20	2.204	10	1.613
50	3.56	5	2.188	10	1.591
80	3.455	40	2.1605	5	1.579
60	3.41	5	2.146	5	1.550
w	3.30	B30	2.125	5	1.5325
40	3.185	B10	2.0285	5	1.514
10	3.10	B10	2.0035	5	1.491
B15	3.055	10	1.976	5	1.469
20	3.015	10	1.963	5	1.445
10	2.95	10	1.941	5	1.431
50	2.90	B20	1.914		
30	2.83	10	1.880		
50	2.74	10	1.866		
10	2.70	10	1.859		

absorptions at 1400-1200 $cm.^{-1}$ occur in acid salts and can be attributed to P-OH linkage (Corbridge, 1956). A fresh comparison showed that the product of heating the hydrated sodium cerium pyrophosphate (see p. 137) at 200°C. had an X-radiogram closely corresponding with that of the new orthorhombic phase obtained at a much higher temperature (700°C.). When this product, heated previously at 700°C. was heated at 760°C. overnight, it decomposed completely into gadolinium orthophosphate and another unidentified compound (Film 10113A). Infra-red spectra (Chart 9) of this final decomposition product showed a very strong absorption band in the 1205-1315 $cm.^{-1}$ region, a strong absorption near 1000 $cm.^{-1}$, and three bands at 700-800 $cm.^{-1}$ which are characteristic of the cyclic metaphosphates (Corbridge and Lowe, 1954). The X-radiogram was unchanged (Film 10105B) by reheating the sample at 900°C. after which the loss of weight was 19.54%. Further study showed that the final decomposition product admixed with gadolinium orthophosphate, resembled those of some metaphosphates but no close fit could be found.

Analysis of the initial sodium gadolinium pyrophosphate hydrate after correction for loss of water at 700°C. shows the product at that temperature to contain 57.63% of Gd_2O_3, 40.42% of P_2O_5 and only 0.11% of Na_2O, which added to the total of 98.16%. The Gd/P (by weight) was 2.46. The theoretical percentage of Na_2O in $NaGdP_2O_7$ should be 8.71%. It was therefore abundantly clear that the product initially obtained was not $NaGdP_2O_7$ or a hydrate of this compound. The orthorhombic X-ray pattern might belong to a solid solution of $HGdP_2O_7$ with $NaGdP_2O_7$; $HGdP_2O_7$, if its existence is confirmed, could be isostructural with the sodium compound. $HGdP_2O_7$ would contain Gd_2O_3 54.56% and P_2O_5 42.73%. This analysis cast doubt upon the sodium content assumed by Giesbrecht (1960-1961) in

his cerium compound, since he calculated the Na_2O content by difference and did not determine sodium by analysis.

The work described up to this point indicates that compounds previously believed (by other workers as well as ourselves) to be alkaline lanthanide pyrophosphates are in fact hydrogen lanthanide pyrophosphates retaining some alkali metal, presumably replacing hydrogen by solid solutions. Further studies on thermal decomposition of the initial precipitated product was therefore undertaken to characterise the supposed $HGdP_2O_7$ as clearly as possible by X-ray diffraction, and to elucidate its mode of decomposition at high temperatures. The precipitated product heated at 130°C. in vacuum for 4 hours showed a weight loss of 13.55%; the product gave X-radiogram (10213A) different from that of the original material (10104D). Infra-red examination (Chart 19) confirmed the presence of hydroxyl, and the characteristic diphosphate absorption bands were present. Further 3% weight loss occurred at 650°C. The X-ray patterns (10213B, 10224D) of samples heated for 2 and 8 hours at 650°C. were identical and different from that of the 130°C. product. Infra-red absorption characteristics (Charts 22 and 26)were also the same. Samples heated for 2 and 8 hours at 700°C. lost approximately 1% more water; the X-ray films (10213C and 10225D) were again identical but different from those obtained earlier, and it proved possible to index them in the orthorhombic system (Table 44). The infra-red data charts (21 and 27 respectively) showed more band splitting in comparison with the 650°C.products; the longer heating period (Chart 27) gave much stronger and sharper peaks. These were in agreement with diphosphate lines especially as found in acid diphosphates, which have a characteristic strong band at 1300 $cm.^{-1}$.

At 750°C. the product decomposed after heating for 2 hours

TABLE 44

$HGdP_2O_7$ heated at 700°C. (indexed in orthorhombic system)

Film 10213C Rad. Cu. K_α

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
B100	6.63	011	0.01351	0.01300
20	6.22	110	0.01533	0.01530
30	5.43	020	0.02016	0.02000
80	4.64	021	0.02760	0.02800
w	4.28	002	0.03243	0.03200
80	3.48	201	0.04899	0.04920
B20	3.382	022	0.05195	0.05200
10	3.31	211	0.05420	0.05420
30	3.08	122	0.06259	0.06230
vBw	3.027	310	0.06482	0.06500
50	2.92	221	0.06974	0.06920
60	2.842	202	0.07359	0.07320
w	2.53	300	0.09284	0.09270
		222		0.09320
		122		0.10230
vB20	2.395	311	0.10359	0.10570
Bw	2.223	321	0.12025	0.12070
30	2.174	050	0.12566	0.12500
Bw	2.132	241	0.13077	0.13120
B10	2.078	330	0.13761	0.13770
B5	2.036	151	0.14322	0.14330
B10	2.007	024	0.14753	0.14800
B5	1.973	043 242	0.15267	0.15200 0.15320
B10	1.922	-	0.16092	-
20	1.882	152	0.16771	0.16730
B10	1.861	340	0.17151	0.17270
B5	1.784	061 032	0.18670	0.18800 0.18470
B5	1.757	243	0.19251	0.19320

TABLE 44 continued

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$
10	1.739	402	0.19648	0.19680
B5	1.682	105	0.21000	0.21030
B5	1.656	422	0.21663	0.21680
B5	1.630	162	0.22367	0.22230
B5	1.504	154	0.26257	0.26330
B5	1.425	016	0.29242	0.29300

Note: The following lines were obtained in another film

5	10.92	010		
5	4.42	120		
w	3.98	012		

a = 7.59 A.

b = 10.90 A.

c = 8.62 A.

without any detectable further loss of water (Film 10213D). Infra-red spectra of it (Chart 20) were exactly the same as obtained before from the product heated at 760°C. (see p. 142).

Table 45 shows the comparison of X-ray data from products at different temperatures.

Another sample of the precipitated compound was prepared by using $Na_4P_2O_7,10H_2O$ from Hopkin and Williams Ltd. instead of the material prepared in our laboratory to check the reproducibility of the results now reported. The precipitation was prepared at pH 1-2, and the residue was dried in vacuum for 3 days, by which time constant weight had been reached. The X-ray pattern (10351A Table 46) identical with that of the earlier product vacuum-dried at 130°C. (10213A). This indicates that a considerable amount of water can be removed from the hydrate at room temperature in vacuum.

Further heat treatments were then carried out, normally for 5-hr. periods. In vacuum at 130°C., the weight loss was only 1.63%; the X-radiogram (10351B) was closely similar to that given by the same initial product dried in vacuum at room temperature (10351A), but with a slight general decrease in d-spacings. This behaviour indicates removal of zeolitic water. After heating at 680°C. (weight loss 4.46%) a different X-radiogram was obtained (10351C), which corresponded with those recorded earlier for similarly treated material (10213B, 10224D). After heating at 900°C. the X-radiogram showed the decomposition product obtained previously at 750°C. (Film 10213D Table 45) and gadolinium orthophosphate lines (10366A); the aggregate weight loss was then 6.02%. As a final test the residue was heated at 900°C. for 2½ days; loss of phosphorus pentoxide then increased the weight loss to 8.00%, and the residue gave the gadolinium orthophosphate X-ray diffraction lines alone

TABLE 45

X-Ray Diffraction Patterns of $HGdP_2O_7$ heated at different temperatures

Rad. Cu. K_α

Film: 10213A 130°C.vacuum dried		10213B 650°C.2 hr.		10224D 650°C.8 hr.		10213C 700°C.2 hr.		10225D 700°C.8 hr.		10213D 750°C.2 hr.	
I	d(A.)	I	d(A.)	I	d(A.)	I	d(A.)	I	d(A.)	I	d(A.)
-	-	-	-	-	-	-	-	vw	10.65	-	-
100	6.62	100	6.56	B100	6.54	B100	6.63	100	6.63	10	6.62
20	6.08	25	6.12	B20	6.10	20	6.22	10	6.19	-	-
-	-	-	-	-	-	-	-	-	-	40	5.60
30	5.57	30	5.47	30	5.44	30	5.43	30	5.39	-	-
-	-	-	-	-	-	-	-	-	-	40	5.02
w	4.82	-	-	-	-	-	-	-	-	-	-
80	4.59	80	4.59	70	4.59	80	4.64	70	4.63	10	4.56
-	-	-	-	-	-	-	-	-	-	100	4.12*
-	-	-	-	-	-	-	-	-	-	10	3.84
-	-	-	-	-	-	-	-	-	-	20	3.68
80	3.51	80	3.47	90	3.47	80	3.48	90	3.47	15	3.54
20	3.457	-	-	-	-	-	-	-	-	9	3.45
-	-	-	-	-	-	-	-	-	-	5	3.41
w	3.376	60	3.395	B40	3.382	B20	3.382	B10	3.376	-	-
50	3.30	50	3.27	B40	3.28	10	3.31	B10	3.31	3	3.29
-	-	-	-	-	-	-	-	-	-	B20	3.21
60	3.103	50	3.07	40	3.06	30	3.08	B10	3.07	-	-
10	3.03	w	3.02	-	-	Bw	3.03	Bvw	3.02	80	3.01
60	2.92	60	2.91	50	2.91	50	2.92	25	2.91	-	-
-	-	-	-	-	-	-	-	-	-	40	2.89
-	-	-	-	10	2.82	60	2.842	35	2.84	70	2.80
70	2.78	60	2.79	20	2.79	-	-	-	-	-	-
15	2.583	B20	2.54	10	2.54	w	2.53	Bw	2.52	vB10	2.596
-	-	-	-	-	-	-	-	-	-	vB10	2.542
10	2.46	10	2.43	10	2.42	B20	2.40	B10	2.39	B10	2.39
w	2.35	vB10	2.32	vB10	2.32	Bw	2.32	Bw	2.32	-	-
B10	2.30	-	-	-	-	-	-	-	-	3	2.28
5	2.19	w	2.19	-	-	-	-	-	-	5	2.19

* Vaseline line also.

TABLE 45 continued

I	d(A.)	I	d(A.)	I	d(A.)	I	d(A.)	I	d(A.)	I	d(A.)
20	2.178	-	-	15	2.16	30	2.17	20	2.17	5	2.16
w	2.156	B5	2.132	Bw	2.127	Bw	2.132	Bw	2.134	10	2.136
B10	2.085	-	-	-	-	B10	2.078	15	2.074	20	2.096
5	2.064	B10	2.065	5	2.063	-	-	-	-	10	2.067
-	-	B5	2.037	-	-	B5	2.036	-	-	-	-
B5	2.020	-	-	-	-	B10	2.010	-	-	-	-
10	1.995	B10	1.986	vB5	1.980	B5	1.973	Bvw	1.999	-	-
vB5	1.951	-	-	-	-	-	-	-	-	vB5	1.955
-	-	B10	1.925	vB5	1.924	B10	1.922	vBw	1.918	vB10	1.914
-	-	30	1.880	20	1.875	20	1.882	10	1.875	-	-
30	1.851	B20	1.847	B10	1.844	10	1.861	10	1.858	5	1.854
-	-	-	-	-	-	-	-	-	-	vBw	1.828
-	-	B5	1.802	-	-	-	-	-	-	-	-
B30	1.788	-	-	-	-	-	-	-	-	-	-
B40	1.751	B10	1.762	B10	1.759	B5	1.757	-	-	-	-
-	-	-	-	B10	1.732	10	1.739	B10	1.737	B10	1.739
B10	1.719	w	1.718	-	-	-	-	-	-	B10	1.725
B10	1.693	-	-	-	-	-	-	-	-	B10	1.695
-	-	10	1.676	5	1.675	B5	1.682	-	-		
-	-	-	-	-	-	B5	1.856	-	-	B5	1.649
-	-	-	-	-	-	B5	1.630	-	-		
-	-	w	1.613	-	-	-	-	-	-	B5	1.614
-	-	-	-	-	-	-	-	-	-	B3	1.564
-	-	-	-	-	-	B5	1.504	-	-	vBw	1.500
B10	1.458	w	1.454	-	-	-	-	-	-	-	-
	-		-	-	-	B5	1.425	-	-	-	-
-	-	w	1.388	-	-	-	-	-	-		
-	-	-	-	-	-	-	-	-	-	Bw	1.337
-	-	-	-	-	-	-	-	-	-	Bw	1.301
B10	1.272	-	-	-	-	-	-	-	-		

TABLE 46

X-Ray Diffraction Patterns of $HGdP_2O_7$ (prepared with more concentrated solutions) at different temperatures•

Rad. Cu. K_α

Room temp. (vacuum) 10351A		130°C. 10351B		680° 10351C		900° 10366A*	
I	d(A.)	I	d(A.)	I	d(A.)	I	d(A.)
B100	6.607	100	6.58	100	6.50	10	6.16
15	6.066	20	6.025	20	6.067	10	5.83
25	5.539	30	5.539	40	5.42	50	5.64
10	4.738	w	4.76	-	-	10	5.13
90	4.575	100	4.563	90	4.575	40	5.07
100	3.506	100	3.49	100	3.46	15	4.72 #
w	3.45	25	3.44	70	3.382	30	4.593#
40	3.284	50	3.287	60	3.27	15	4.007#
40	3.086	50	3.089	60	3.063	10	3.951
w	3.025	10	3.02	-	-	30	3.869
50	2.917	50	2.914	70	2.905	30	3.706
70	2.775	70	2.771	60	2.788	30	3.563
Bvw	2.581	B10	2.568	5	2.533	20	3.461#
vw	2.48	vw	2.481	-	-	20	3.440#
vw	2.452	Bw	2.452	5	2.423	10	3.39

• Only lower angle region was given for comparison.

* Rad. Fe. K_α

\# $GdPO_4$ lines.

(Film 10373D). It is worthy of note that the 900°C. decomposition product appeared to correspond with "Phase 2" referred to in connection with gadolinium pyrophosphate (p. 127).

Analytical data related to the initial precipitated double pyrophosphate are tabulated below.

	Gd/P ratio by weight	$\%Gd_2O_3$	$\%P_2O_5$	$\%Na_2O$	$\%H_2O$
Mother liquor	2.61				
Vacuum-dried product	2.66	55.05	41.09	0.02	3.84*
Product after heating at 130°C.	2.66	55.96	41.77	0.02	2.25*
Product after heating at 700°C.	2.66	57.61	43.00	0.02	NIL
Theoretical for $HGdP_2O_7$	2.53	54.56	42.73		2.70
" " $Gd_2O_3,2P_2O_5$	2.53	56.08	43.92		

* By difference.

These results confirmed the identity of the matieral dried at 130°C. as $HGdP_2O_7$. The loss of water at 700°C. may be attributed to the reaction:

$$2HGdP_2O_7 \rightarrow Gd_2O_3,2P_2O_5 \text{ (or } Gd_2P_4O_{13}) + H_2O.$$

The formula $Gd_2P_4O_{13}$ fits the general formula for condensed chain phosphates, $M^{I}_{n+2}P_nO_{3n+1}$ (Van Wazer, 1958), 6 M^{I} cations being replaced by two gadolinium cations. The experimental loss of weight of the 130°C. product at 680°C. was 4.46-1.63 = 2.83%, in a good agreement with the theoretical loss of 2.70% for the reaction given above.

According to Wells (1962) anhydrous salts of the type $M_3HP_2O_7$ ought not to exist, because stable frameworks of P_2O_7 groups linked by hydrogen bonds are not possible for the H/O ratios involved in these compounds However the existence of anhydrous $Na_3HP_2O_7$ and $(NH_4)_3HP_2O_7$ has been confirmed by Hubbard (1949), Partington (1928) and Frazer, Smith and Lehr (1965). Furthermore Tananaev, Kuznetsov and Vasil'eva (1967), and Petrov, Vasil'eva and Pervykh (1966) also claimed that they

obtained $HLaP_2O_7$, which was reported to be stable at 1000°C. The gadolinium compound clearly decomposed at 750°C. The 900°C. product X-ray analysis showed gadolinium orthophosphate and a decomposition product obtained before and probably a metaphosphate, found perhaps by a reaction such as $Gd_2O_3, 2P_2O_5 \rightarrow GdPO_4 + Gd(PO_3)_3$. Prolonged heat treatment would tend to cause loss of phosphorus pentoxide, for example by the reaction $Gd(PO_3)_3 \rightarrow GdPO_4 + P_2O_5$. The presence of the orthophosphate alone in the product of prolonged heating at 900°C. (Film 10373D) confirms this type of reaction. It was therefore established that it was impossible to introduce sodium in a double pyrophosphate precipitated at about pH 1-2. As it had been shown earlier that the amount of sodium introduced was the highest at pH = 4.6, and n = 1. The precipitation was carried out under the same conditions, but with reactants having four times the concentration used previously. Only 1.17% Na_2O could be introduced into the product, in comparison with the previous result of 1.88% Na_2O. It was impossible to work at a pH higher than 4.6, because precipitation of gadolinium hydroxide would then interfere.

A number of decomposition tests were carried out on the product of this last precipitation but their results do not differ substantially from those already reported, and repetition of the details is considered unnecessary in this Thesis.

Attempted Preparation of Sodium Gadolinium Pyrophosphates by "Dry" Reactions:

On account of the failure to prepare sodium gadolinium pyrophosphates by precipitation routes, some thought was given to the use of possible "dry" reactions to prepare anhydrous double salts. In particular, the successful use of sintering reactions to prepare sodium lanthanide orthophosphates suggested the feasibility of

reactions such as the following:

$Gd_2O_3 + 4(NH_4)_2HPO_4 + Na_2CO_3 \rightarrow 2NaGdP_2O_7 + CO_2 + 6H_2O + 8NH_3$.

This will be seen to be a modification of a reaction investigated earlier (see p. 107).

A number of attempts to carry out this reaction under various conditions failed completely; the products always proved to be known gadolinium phosphates (usually the orthophosphate) with mixtures of phosphates incorporating the alkali reactants.

Direct interaction of gadolinium pyrophosphate with anhydrous sodium pyrophosphate:

$$Gd_4(P_2O_7)_3 + Na_4P_2O_7 \rightarrow 4NaGdP_2O_7$$

(in fact, the most obvious simple method of synthesis) gave complex mixtures of products in which gadolinium usually appeared as its simple orthophosphate.

Clearly, double sodium lanthanide pyrophosphates of the anticipated composition have so far eluded successful synthesis.

4.2. Sodium lanthanide orthophosphates, $Na_3Ln(PO_4)_2$.

Double orthophosphates of the type $Na_3Ln(PO_4)_2$ were prepared by solid-state reactions and established crystallographically in Section 3.2. $Na_3Ce(PO_4)_2$ (Film 10026B) was prepared accidentally by a solution reaction, as described in Section 2.4, and it appeared worthwhile, if possible, to prepare $Na_3Gd(PO_4)_2$ by means of solution reactions, and compare the product with the corresponding cerium compound, and the compounds obtained by solid-state reactions.

In an attempted preparation of cerous orthophosphate a precipitate produced by a considerable excess of Na_2HPO_4 was obtained, the weight of which was considerably greater than the expected weight of cerous orthophosphate. The conditions of formation at once suggested that a sodium double salt had been obtained; its X-radiogram (10026B) showed excellent correspondence with one for $Na_3Ce(PO_4)_2$ prepared by solid-state reaction (10170C), although a few extra lines were present indicating the presence of some impurities.

The only sodium lanthanide orthophosphates reported in the literature are $4GdPO_4,Na_3PO_4,12H_2O$, $4GdPO_4,Na_3PO_4$, $Na_3Pr_2(PO_4)_3,7H_2O$ and $Na_3Pr_4(PO_4)_5,12H_2O$, obtained by Petushkova and Tananaev (1963), Kuznetsov, Petushkova and Tananaev (1964), Petushkova, Tananaev and Samoilova(1969) when a high ratio of PO_4^{3-} to Ln^{3+} was employed in precipitation reactions. Their X-ray data for $4GdPO_4,Na_3PO_4$ (Kuznetsov, Petushkova and Tananaev, 1964), show gadolinium orthophosphate lines plus those of some other compound, and they do not fit the data now obtained very well although there are some common lines.

Experimental:

To 50 ml. of 0.025M cerous chloride solution (prepared as described in Section 4.1), 50 ml. of 0.05M sodium orthophosphate

solution were added with continuous stirring. The initial pH of the cerous chloride solution was 1.5. A very gelatinous precipitate began to form at pH 2. The final pH was 10. The precipitate was filtered off, washed, dried, and ignited at 700°C. for 3 hours. The same experiment was repeated with gadolinium chloride solution. The weights of the two residues were both considerably less than values calculated by assuming double phosphates to be formed. The X-ray powder photographs of the products (10101A, 10101B) showed only cerous orthophosphate lines in the one case, and gadolinium orthophosphate lines and very weak lines of the double compound in the other.

In a second set of experiments a very substantial excess of sodium orthophosphate was used ($PO_4^{3-}/Ln^{3+} = 10$), and stirring after precipitation was continued overnight. The precipitates were filtered off, washed, and dried in vacuum. Both lost about 20% by weight of water during ignition at 700°C. The weights obtained were higher than the theoretical weights of single orthophosphates, showing the formation of double orthophosphates. Films 10107A (cerium) and 10107D (gadolinium) confirm the formation of double orthophosphates, but their lines are not very strong.

In a further series of tests, the lanthanide chloride solution was added to the phosphate solution, instead of the reverse; X-radiograms of the products (10107B, 10107C) contained appreciably stronger lines of the double orthophosphates. This results is not unexpected, because under the conditions used precipitation begins in the presence of a large excess of phosphate. The double phosphate lines, in the case of cerium, are much weaker than those of the corresponding gadolinium compound, showing that the tendency of gadolinium to form double orthophosphate is higher than that of cerium.

The effect of heating at 900°C. was tried on both products of cerium and gadolinium, (Film 10109A, B, C, D). Again the cerium double salt gave very weak lines, but the gadolinium double phosphate lines were quite strong; lines of the single orthophosphates were present in each case. Both X-radiograms had double phosphate lines in agreement with those of the compounds described in Section 3.2. Table 47 shows recorded double phosphate lines for the precipitated products.

It was concluded that the preparation of the double orthophosphates is possible through solution reactions, but they were always formed together with the lanthanide single orthophosphates. The use of an excess of sodium orthophosphate is essential.

Use of NaH_2PO_4 instead of Na_3PO_4, in still greater excess ($PO_4^{3-}/Ln^{3+} = 16$), did not improve the situation (Films 10111A, B). The gadolinium salt was again formed to a greater extent than the cerium compound.

The problem was left for future investigation, since the experiments had proved the identity of the products obtained from solution and from solid-state reactions.

TABLE 47

Structures of $Na_3Ln(PO_4)_2$ Type obtained by Precipitation

Rad. Co. K_α

$Na_3Ce(PO_4)_2$ Film 10107B		$Na_3Gd(PO_4)_2$ Film 10107C	
I	d(A.)	I	d(A.)
10	6.59	B20	6.52
-	-	B15	6.01
30	4.69*	60	4.575
-	-	30	4.30 ?
-	-	20	3.84
20	3.51*	10	3.47
5	3.07	w	3.07*
5	2.805	vB100	2.80*
w	2.68	30	2.655
20	2.13*	60	2.103*
20	1.900*	40	1.918*
5	1.757	20	1.757*
5	1.592	-	-
5	1.553	-	-
10	1.533	20	1.536*

* Common with $LnPO_4$ lines.

SECTION 5

REACTIONS OF MONAZITE WITH SODIUM CARBONATE

5.1. Sintering reactions of monazite with sodium carbonate and their promotion by fluoride.

Monazite is essentially an orthophosphate of the rare-earth elements and thorium. It usually contains 3-10% of thorium oxide and about 60% of rare-earth oxides (Eyring, 1964). Throughout these studies, Australian monazite was employed, the composition of which was given by Kraitzer (1964, Table 48).

TABLE 48

Constituent	Analysis %
ThO_2	7.3
Ce_2O_3	27.5
U_3O_8	0.34
Eu_2O_3	0.014
Rare-earth oxides	57.7
P_2O_5	28.9
Insoluble in H_2SO_4	2.5

A spectrographic analysis of the rare-earth oxides was also given by the same author (Kraitzer, 1964).

TABLE 49

Constituent	Analysis %
Y_2O_3	2.5
Pr_6O_{11}	3.5
Nd_2O_3	11.8
La_2O_3	15.6
Sm_2O_3	2.7
Gd_2O_3	1.6
Tb_4O_7	0.28
Dy_2O_3	0.3
Ho_2O_3	0.05
Er_2O_3	0.03
Yb_2O_3	0.03

An X-ray diffraction photograph of this sample of monazite (Table 50) agreed well with the A.S.T.M. data (Card 4-0612). Strong zircon lines also appeared in the photograph, together with some weak unidentified lines.

TABLE 50

X-Ray Diffraction photograph of monazite (82 hr. at 700°C.)

Film: 10136A Rad. Cu. K_α

I	d(A.)	Remarks	I	d(A.)	Remarks
Bw	6.66	?	10	1.867	M
Bw	6.26	?	B10	1.799	M
50	5.22	M	10	1.767	M
20	4.82	M	B10	1.742	M
50	4.69	M	40	1.716	$ZrSiO_4$
50	4.20	M	10	1.694	M
20	3.547	M	w	1.654	M
20	3.510	M	w	1.631	M
60	3.310	M,$ZrSiO_4$	B3	1.573	?
5	3.148	?	B5	1.535	M
80	3.105	M	w	1.434	?
10	2.996	M	w	1.414	?
100	2.875	M	3	1.381	$ZrSiO_4$
20	2.606	M	B5	1.343	?
20	2.524	$ZrSiO_4$	B3	1.330	?
B10	2.338	M	w	1.306	?
40	2.191	M	w	1.281	?
60	2.151	M	w	1.234	?
20	2.129	M	5	1.169	?
5	2.070	$ZrSiO_4$			
B30	1.969	M			
B10	1.900	M			
30	1.877	?			

M = Monazite structure.

Monazite Sodium Carbonate reactions with fluoride promotes:

There are many solution methods in the literature for the breakdown of monazite; some of these are commercially applied. Those mainly used are direct treatment with sulphuric acid or caustic soda solution. Fusing of monazite with sodium carbonate has been tried by Brunck and Höltje (1932). Kaplan and Uspenskaya (1958) worked on the sintering of monazite with sodium carbonate and lime, and proved the positive effect of added fluoride on the reactivity of the monazite. Kurup and Moosath (1957, 1958) claimed that the optimum amount of sodium carbonate to obtain lanthanide and thorium oxides was more than three times the theoretical requirement. 95% of the phosphate content could be removed as soluble phosphate by their method. They did not refer to the mechanism of the reaction. The solid-solid reactions between individual rare-earth phosphates and sodium carbonate at 700°C. have already been studied in Section 3.1. It was found that a new compound with a tetragonal structure ($Na_3Ln(PO_4)_2$) was formed when less than the theoretical amount of sodium carbonate (approximately 50% of the theoretical requirement was used. This could be explained by the following equation:

$$2LnPO_4 + \tfrac{3}{2}Na_2CO_3 \rightarrow \tfrac{3}{2}CO_2 + \tfrac{1}{2}Ln_2O_3 + LnPO_4, Na_3PO_4 .$$

This new double phosphate phase was found to be soluble in dilute hydrochloric acid.

In the light of these experiments with individual rare-earth phosphates, the same sintering method was applied to Australian monazite.

Examination of some preliminary X-ray diffraction films of monazite sintered with sodium carbonate, obtained by Welch (1966) using 5:0.66, 5:1.50 and 5:3.00 ratios of monazite to a 20:1 mixture of sodium carbonate and sodium fluoride showed the presence of

monazite lines in the first case, with the stronger line at intensity 40. In the second case the intensity was reduced to 10, and in the pattern of product from the 5:3.00 mixture no monazite lines occurred. Sodium orthophosphate lines were very strong. The remaining lines were found to be due to intermediate double phosphate described earlier.

From the known composition of the monazite the amount of sodium carbonate just sufficient to convert thorium and cerium phosphates into oxides, but leave the other rare-earths in the double phosphate phase was calculated. It was considered likely, in any case, that the existence of the stable tetravalent state for cerium and thorium would cause these two elements to remain preferentially in the oxide phase. By dissolving the product in concentrated hydrochloric acid, after sintering, the trivalent rare-earths could be extracted in the filtrate, and leaving ceric oxide and thorium oxide in the residue. Then the rare-earths in the filtrate were precipitated by oxalic acid (Schoeller and Powell, 1940), and the oxalate ignited to oxides. Several mixture proportions have been tried, close to the calculated proportion of sodium carbonate, in the sintering reactions. The acid extraction residues and oxides were analysed by X-ray diffraction and X-ray fluorescence methods to establish the distribution of rare earths and thorium in the products. Optimum conditions for practical use were established according to the composition of the two fractions.

Experimental:

Materials used:

1) Monazite: Finely crushed monazite (mesh -120), as received from Australian source.

2) Sodium carbonate: Anhydrous, "AnalaR" reagent (Hopkin and

Williams Ltd.)

3) Sodium fluoride: B.D.H., normal reagent grade.

4) Sodium fluorosilicate: B.D.H., normal reagent grade.

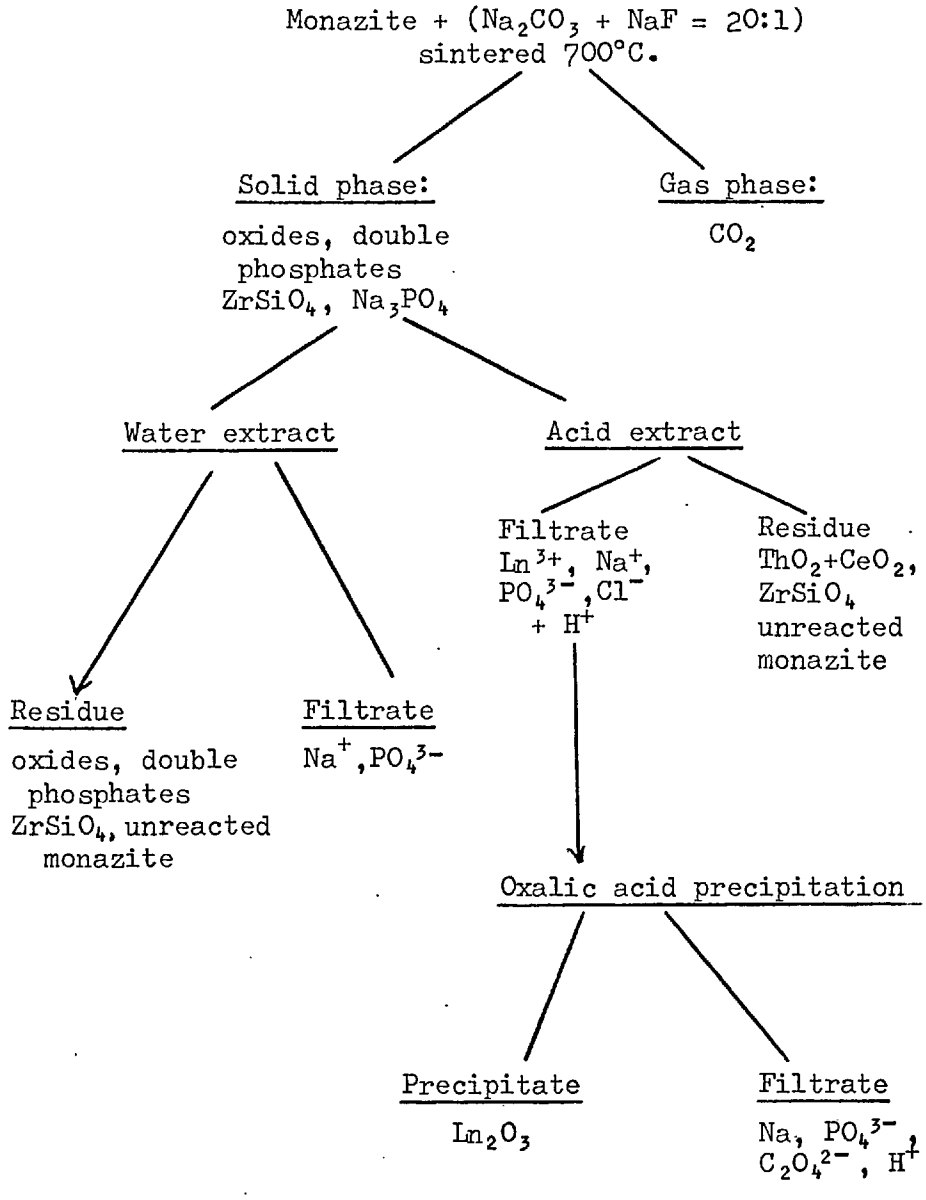
5) Hydrochloric acid: d = 1.18, "AnalaR" (Hopkin and Williams Ltd.)

6) Oxalic acid: "AnalaR" (B.D.H.)

5 g. of monazite was mixed with the calculated amount of a previously prepared mixture of sodium carbonate and sodium fluoride in the weight ratio 20:1. The mixture was transferred to a platinum crucible and heated at 700°C. for 16 hours, in an electric muffle furnace; the crucible and products were then cooled and weighed. The product was crushed thoroughly in an agate mortar, heated for a further period of 72 hours, cooled, and weighed again. To 1 g. of the sintered product, 10 ml. of concentrated hydrochloric acid were added with stirring. After 15 minutes the mixture was diluted with 50 ml. of water and filtered. The residue was washed on the filter with distilled water, and the paper burned off over a small Bunsen flame in a platinum crucible. The crucible was transferred to a muffle furnace at 700°C., left for 2 hours, cooled and weighed, giving the weight of ignited insoluble oxides. The filtrate was diluted to 200 ml., and 200 ml. of 4% oxalic acid solution were added without stirring. After an hour the liquid was stirred vigorously and left overnight. The precipitate was filtered on a No. 40 Whatman filter paper, washed with 2% oxalic acid solution and ignited over a Bunsen burner. The ignition was begun slowly, then finished with about five minutes over the full flame. The oxides of lanthanides (possibly with thorium) were then cooled and weighed. The procedure followed is outlined in Table 51.

TABLE 51

Procedure for the treatment of monazite.



Results and Discussion:

Table 52 shows the results obtained from fourteen monazite: Na_2CO_3 + NaF (20:1) compositions tested. Experimental weight losses due to carbon dioxide evolution were less than the theoretical amount, because of the inevitable uptake of oxygen to give the higher oxidation states of cerium and thorium. X-ray diffraction studies were carried out on the sintered products, water and acid-extraction residues, and oxides in the acid-extraction filtrates. The numbers of the X-ray powder photographs and X-ray fluorescence charts are tabulated in Table 53. The sintered products were shown from the X-radiograms to contain a solid solution of ceric and thorium oxide, with trace amounts of other lanthanide oxides, the intermediate double phosphate, sodium orthophosphate (only in the case of high sodium carbonate proportions, Table 54) and zircon, $ZrSiO_4$. No lines of unreacted sodium carbonate were ever detected. The strongest line of monazite (d = 2.87 A.) was very weak up to mixture No. 11. After that, in mixtures 12-14, the amount of sodium carbonate was not enough to break down the monazite structure completely, so the intensity of this line increased. The intensities of lines of the intermediate double phosphate increased as the amount of sodium carbonate decreases (Table 55). A decrease was also noted in the amount of sodium orthophosphate as the proportion of sodium carbonate falls. In passing from mixture 1 to mixture 14, the diffraction lines which belong to ceric oxide and thorium oxide solid solution shift to higher diffraction angles, corresponding to smaller cell constants. This observation proved that the cerium and thorium oxide solid solution retains less of the other lanthanides as the series is passed through. Although in subsequent samples this effect cannot easily been seen due to small differences, the comparison

TABLE 52

Monazite: Na_2CO_3 + NaF sintering reactions.

No.	Mon: Na_2CO_3 + NaF	Wt.* after sintering	Exp. wt. loss	Theo. wt. loss	Acid residue	Oxides	Recovery Total	Water ext. residue	Soluble Na_3PO_4	Theo. Na_3PO_4	Combined Na_3PO_4
1	5:2.5846	6.6162	0.9684	1.0190	1.3563	2.2879	3.6442	4.4692	2.1470	2.6969	0.4499
2	5:2.3805	6.4904	0.8901	0.9385	1.7823	1.9010	3.6833	4.8269	1.6635	2.4840	0.8205
3	5:2.3100	6.4455	0.8645	0.9107	2.6555	1.0487	3.7042	4.8419	1.6036	2.4105	0.8069
4	5:2.2500	6.4164	0.8336	0.8871	2.5762	1.0703	3.6465	4.9342	1.4822	2.3478	0.8656
5	5:2.1763	6.3635	0.8128	0.8580	2.4843	1.1753	3.6596	5.1200	1.2435	2.2709	1.0274
6	5:2.1100	6.3320	0.7780	0.8319	2.4638	1.1689	3.6327	5.1789	1.1531	2.2017	1.0486
7	5:2.0400	6.2879	0.7521	0.8043	2.4108	1.2148	3.6256	5.3133	0.9746	2.1287	1.1541
8	5:1.9200	6.2055	0.7145	0.7570	2.2805	1.3696	3.6501	5.4987	0.7068	2.0035	1.2967
9	5:1.8000	6.1246	0.6754	0.7097	2.2042	1.4442	3.6484	5.6922	0.4324	1.8783	1.4459
10	5:1.6800	6.0560	0.6240	0.6623	2.1596	1.5176	3.6772	5.8132	0.2428	1.7531	1.5103
11	5:1.6200	6.0234	0.5966	0.6387	2.2268	1.4872	3.7140	5.8023	0.2211	1.6905	1.4694
12	5:1.5600	5.9806	0.5794	0.6150	2.2666	1.4671	3.7337	5.8257	0.1549	1.6279	1.4730
13	5:1.4400	5.9060	0.5340	0.5877	2.3157	1.4605	3.7762	5.8582	0.0478	1.5026	1.4548
14	5:1.3200	5.8296	0.4904	0.5204	2.5545	1.3349	3.8894	5.7870	0.0426	1.3774	1.3348

* in g.

TABLE 53

X-Ray Diffraction Film and Fluorescence Chart Numbers of Sintered Products, Water Extraction Residues and Oxides.

Specimen No.	Sintered product	Water ext. residue	Acid ext. Residue		Oxides	
			X.R.D	X.R.F	X.R.D	X.R.F
1	10136B	10140C	10147B	6	10147D	3
2	10136C	10140B	10147A	5	10147C	2
3	10246A	10247C	10246D	29	10247B	31
4	10224A	10227A	10225A	7	10226A	10
5	10136D	10140A	10140D	4,15	10151D*	1,14
6	10224B	10227B	10225B	8	10226B	11
7	10224C	10227C	10225C	9	10226C	12
8	10234C	10235C	10237C	22	10236C	19
9	10234B	10235B	10237B	21	10236B	18
10	10234A	10235A	10237A	20	10236A	17
11	10246B	10249A	10246C	23	10247A	27
12	10242C	10247D	10244C	30	10245C	32
13	10242B	10249C	10244B	25	10245B	28
14	10242A	10249B	10244A	24	10245A	26

* No: 5 Oxalic acid oxides: X-ray diff. studies repeated. The numbers were 10154A, 10226D.

TABLE 54

X-Ray Diffraction Photograph of 5:2.58 Monazite:Na_2CO_3 sintered combination (10136D) and water extraction residue (10140C)

Film 10136D		Film 10140C			
I	d(A.)	I	d(A.)	hkl	Remarks
15	6.60	20	6.62		Int.
10	4.62	10	4.63		Int.
15	4.40	-	-		$ZrSiO_4$+Na_3PO_4
20	4.29	-	-		Na_3PO_4
15	3.88	5	3.87		Int.
10	3.505	15	3.52		Int.
5	3.294	10	3.30		$ZrSiO_4$
B100	3.153	100	3.167	111	Oxides
5	2.86	10	2.873		Monazite
10	2.809	15	2.812		Int.
B40	2.734	B70	2.742	200	Oxides
10	2.670	B10	2.686		Int.
30	2.629	-	-		Na_3PO_4
5	2.524	5	2.52		$ZrSiO_4$
vw	2.250	10	2.219		Int.
5	2.134	5	2.138		Int.
3	1.985	-	-		Int.
B80	1.931	B70	1.937	220	Oxides
10	1.709	-	-		$ZrSiO_4$
B60	1.649	B50	1.652	311	Oxides
vBw	1.574	B5	1.578	222	Oxides
5	1.379	vB3	1.367	400	Oxides+$ZrSiO_4$
-	-	vB3	1.257	331	Oxides
-	-	vB3	1.225	420	Oxides.

TABLE 55

X-Ray Diffraction Photograph of Product from Sintering of Mixture No. 10: Double Phosphate Lines Indexed.

Film 10234A Rad. Cu. K_α ("Int." = $Na_3Ln(PO_4)_2$)

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	Remarks
5	9.28	110	0.00690	0.00690	Int.
60	6.59	200	0.01367	0.01380	Int.
50	4.646	220,112	0.02753	0.02760	Int.
10	4.439	-	-	-	$ZrSiO_4$
25	3.878	311	0.03950	0.03967	Int.
50	3.506	222	0.04833	0.04828	Int.
10	3.29	312	0.05479	0.05518	Int.+$ZrSiO_4$
B100	3.142				Oxides
5	3.058	411,213	0.06354	0.06382	Int.
5	2.862	-	-	-	Monazite
60	2.802	402	0.07568	0.07588	Int.
50	2.722	-	-	-	Oxides
60	2.676	004,332	0.08293	0.08272	Int.
vw	2.522				$ZrSiO_4$
5	2.322	512	0.11019	0.11038	Int.+$ZrSiO_4$
15	2.252	314,520	0.11713	0.11722	Int.
15	2.132	442	0.13077	0.13108	Int.
15	2.071	620	0.13852	0.13800	Int.
B5	1.983	424	0.15110	0.15172	Int.
B80	1.927	-	-	-	Oxides
B5	1.754	552,712	0.19303	0.19318	Int.
5	1.712				$ZrSiO_4$
w	1.668	226	0.21339	0.21372	Int.
B50	1.642	-	-	-	Oxides
w	1.591	820	0.23467	0.23460	Int.
B20	1.570	-	-	-	Oxides

TABLE 55 continued

I	d(A.)	hkl	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	Remarks
B5	1.468	840	0.27573	0.27600	Int.
Bw	1.400	912	0.30303	0.30358	Int.
5	1.379	-	-	-	$ZrSiO_4$
B5	1.345	852	0.32858	0.32773	Int.
B10	1.247	-	-	-	Oxides
B10	1.216	-	-	-	Oxides

Cell constant of the oxides (cubic)
a = 5.450 A.

Cell constants of the intermediate, $Na_3Ln(PO_4)_3$ which was indexed in the tetragonal system.
a = 13.105 A.
c = 10.705 A.

Results are in between the cell constants of lanthanum and neodymium double orthophosphates.

between the cell constants of samples from mixtures 1, 7 and 10 showed an appreciable change in "a" (Table 56).

TABLE 56

Mixture	1 (5:2.58)	7 (5:2.04)	10 (5:1.68)
Sintered product oxide a in A.	5.471	5.468	5.450

The reported cell parameters are listed in Table 57.

TABLE 57

Oxide	a in A.
CeO_2	5.441
$CeO_2 + ThO_2$ (75% CeO_2 + 25% ThO_2)	5.470
ThO_2	5.600

Water extraction results:

The weight of water extraction residues increased as the amount of sodium carbonate decreased which corresponds with the decrease in quantity of sodium orthophosphate (Fig. 3). But the combined sodium orthophosphate figure, obtained by subtracting soluble sodium orthophosphate from the theoretical weight was found to increase up to mixture 10, and then to decrease again (Fig. 4). This mixture gave the maximum proportion of double phosphate. The weight of combined sodium orthophosphate was 1.5103 g. at this composition, which corresponds to 3.68 g. of $Na_3Ln(PO_4)_2$, if the average molecular weight of the double phosphate is taken to be 400. 3.68 g. of $Na_3Ln(PO_4)_2$ is calculated to give 1.51 g. of oxides when it is dissolved and the oxalates are precipitated. The experimental value was 1.5176 g.

Fig. 3.

Monazite (5 g.) + Na_2CO_3 + NaF (20:1)
sintering reactions, water extraction results

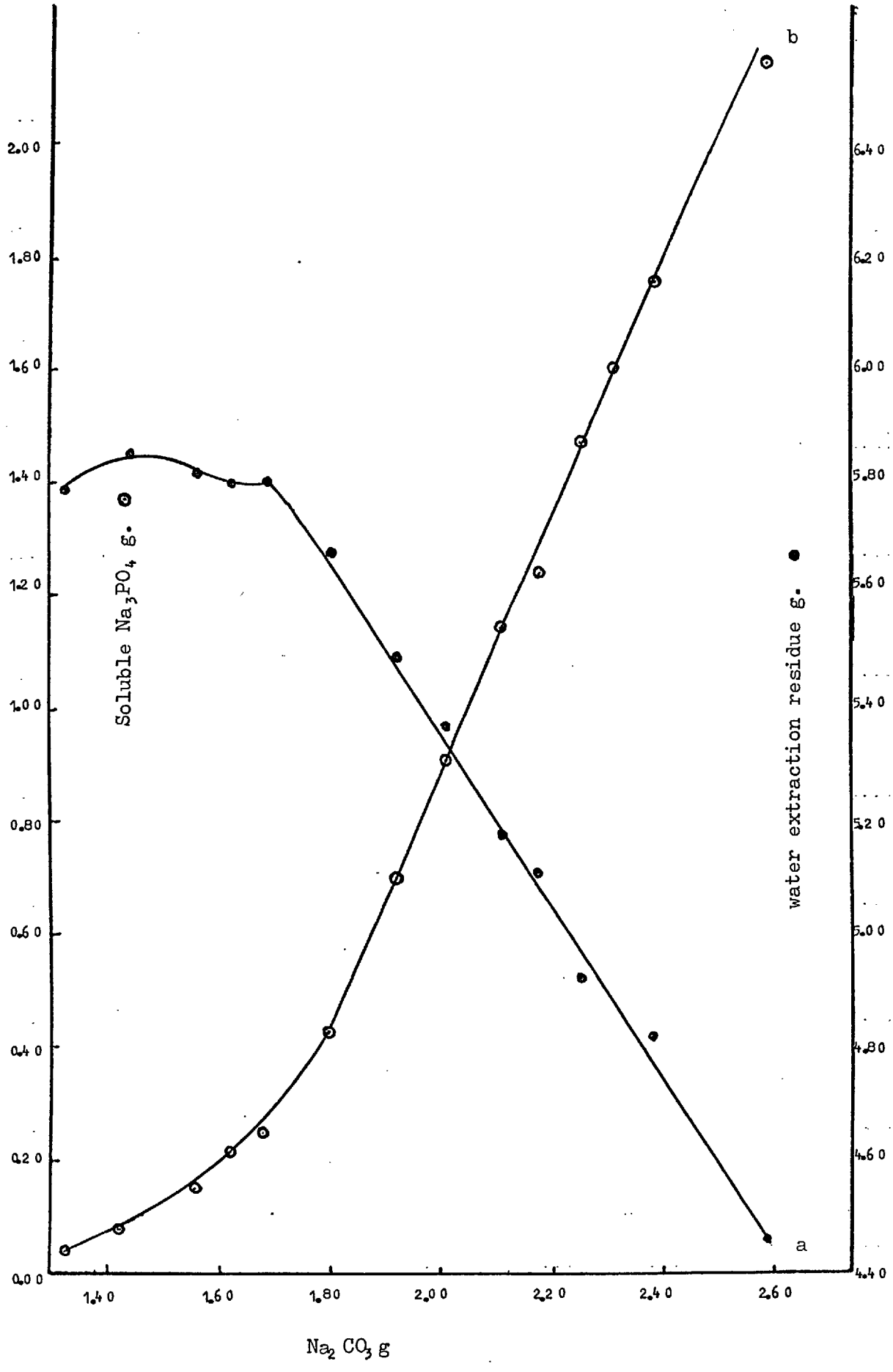
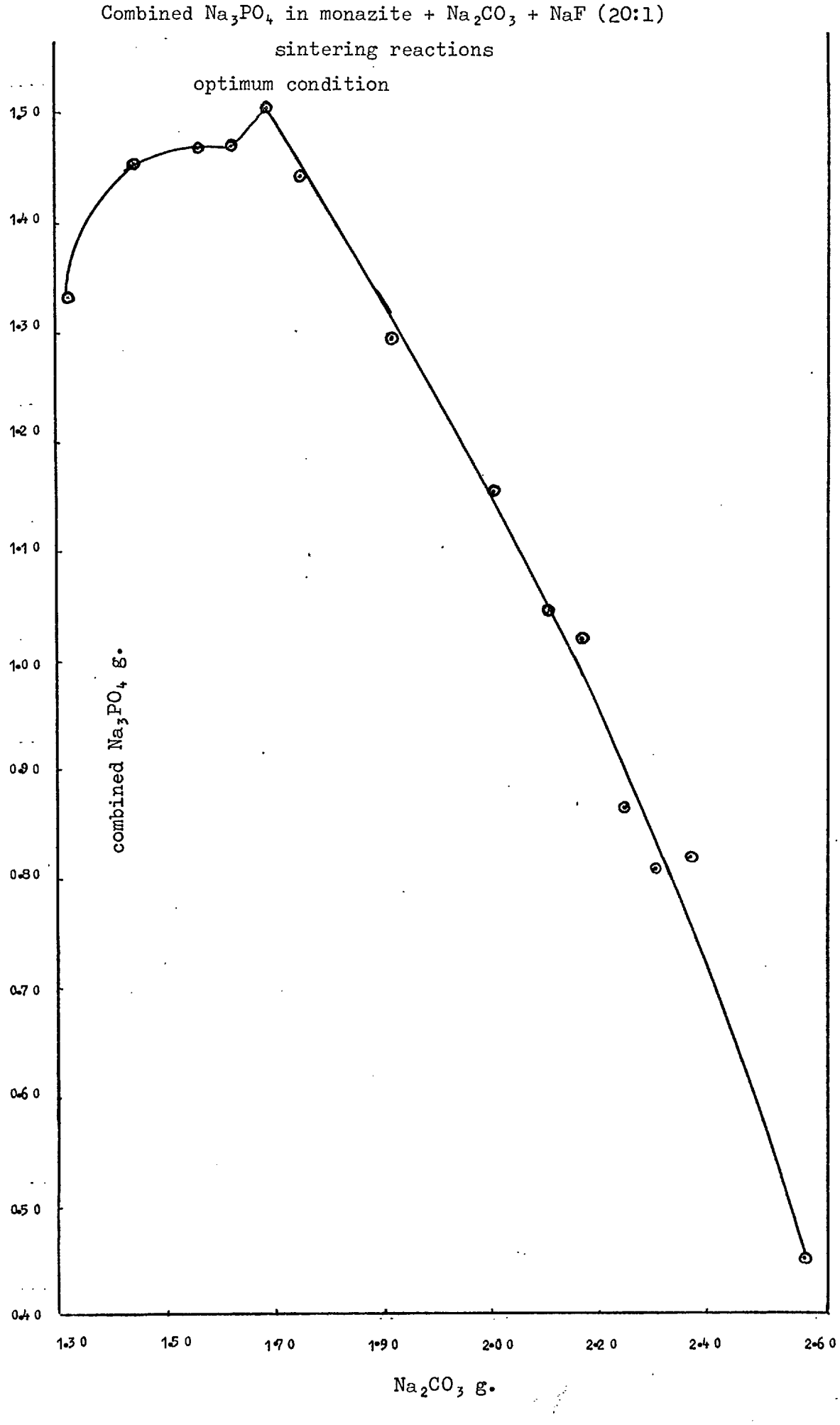


Fig. 4.


Combined Na_3PO_4 in monazite + Na_2CO_3 + NaF (20:1)
sintering reactions
optimum condition
combined Na_3PO_4 g.
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
1.30
1.50
1.70
1.90
2.00
2.20
2.40
2.60
Na_2CO_3 g.

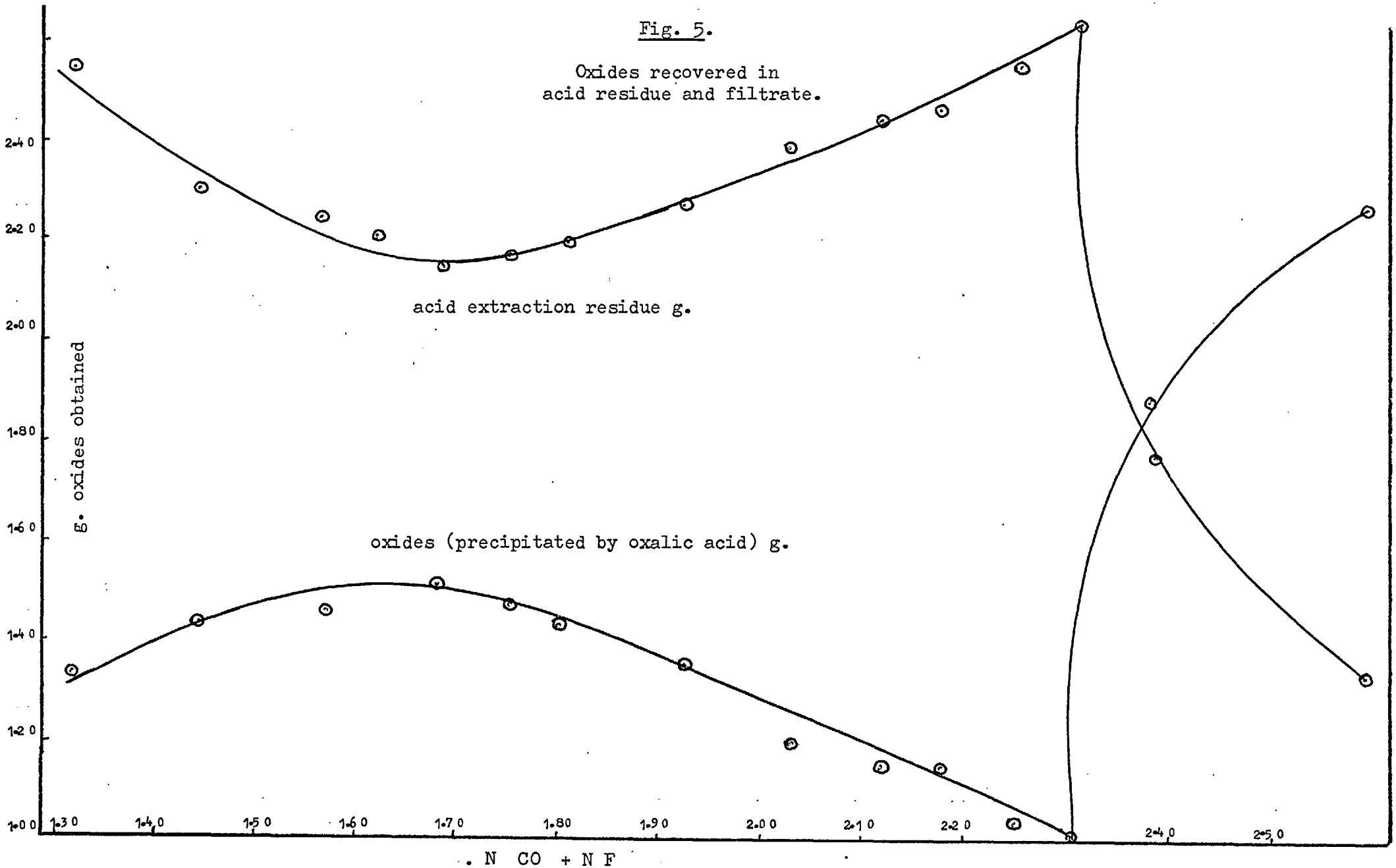
The water extraction filtrate was evaporated to dryness and the residue ignited at 700°C. The X-ray diffraction photograph showed the γ-form of sodium orthophosphate identified earlier (Section 2.2, Film 10236D).

Acid extraction residues and oxides:

As seen from Table 52 the amount of acid extraction residue increased up to mixture No: 3, then decreased up to No: 10. The increase after this composition corresponded to unreacted monazite. For the oxides precipitated and filtered off the reverse was, of course, true. The values are plotted in Fig. 5. The total recovery of oxides, which is the sum of the two oxide fractions, is approximately constant up to No: 10. The observed increase after this value is due to retention of unreacted monazite. An X-ray powder diffraction photograph (10147B) of the product from mixture 1, acid extraction residue, showed lines of the ceria-thoria solid solution (A.S.T.M. 2-1303), weak zircon lines, and lanthanide sesquioxide (Ln_2O_3) lines. In the No. 14 acid extraction residue (Film 10244A) some weak lines appeared resembling those of ThP_2O_7. It was noticed that the cubic sesquioxide (rare-earth oxides other than ceric oxide) did not always enter a solid solution with thoria and ceria.

From No. 1 to No. 3 sesquioxide formation declined, the sesquioxide-forming lanthanides becoming progressively incorporated into the solid solution of ceria and thoria and becoming acid-insoluble. Because of the similarities of both structures, the addition of the tri-positive lanthanide oxide favoured a continuous change from the fluorite structure of ceria to the C-form of tri-positive lanthanide oxides (Topp, 1965). After No. 3, the amount of sodium carbonate was insufficient to turn all the phosphates into oxides. There was therefore a gradual increase in the formation of double-phosphate inter-

Fig. 5.


Oxides recovered in
acid residue and filtrate.
acid extraction residue g.
g. oxides obtained
oxides (precipitated by oxalic acid) g.
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
1.30
1.40
1.50
1.60
1.70
1.80
1.90
2.00
2.10
2.20
2.40
2.50
. N CO + N F

mediate, which was soluble in acid. The decrease in the acid residue is explained by this sequence of changes. Table 58 shows data for the acid extraction residues from mixtures 1 and 10 and the Miller indices of the oxide lines. Powder photographs of the oxides precipitated by oxalic acid in the filtrate showed the solid solution of the remaining rare-earth oxides, mainly in the cubic form. Although lanthanum oxide has been claimed to be very unstable in the cubic form, a solid solution of it with smaller rare-earth ions gives a stable cubic form (Shafer and Roy, 1959). When the specimen was heated to higher temperatures, the oxides were partly converted into the hexagonal form, but the cubic form was also present. The intensities of the cubic lines were weak in the No. 10 case and the a value corresponded also to thorium oxide (Table 59). This could be due to thorium impurity passing over to the sesquioxide side by forming a double phosphate, since X-ray fluorescence analysis disclosed some thorium present.

The cell constant a was 5.545A. for No. 1 mixture for the cubic form. It increased to 5.593A. for mixture No. 10. Table 60 shows the cell parameters for cubic (thoria, ceria and sesquioxides) and hexagonal (sesquioxides) forms.

X-Ray Fluorescence Analysis:

X-ray fluorescence analysis was carried out with tungsten radiation and a quartz analyzing crystal. The spectra of the monazite, acid extraction residues of the sintered products, and oxides have all been recorded. The instrumental conditions were 40 kV., 18 mA., time constant 16, scale factor 4 x 0.8, scanning speed $\frac{1}{4}^{\circ}$ of 2θ per minute, chart speed 400 mm/hr. The filtrate after an oxalic acid precipitation was evaporated and its X-ray scan was also recorded; the spectrum disclosed the presence of thorium,

TABLE 58

X-Ray Diffraction Photographs of the Acid

Extraction Residue of Products for Mixtures Nos. 1 and 10

Rad. Cu. K_α Rad. Cu. K_α

No. 1 Film 10147B		No. 10 Film 10237A				
I	d(A.)	I	d(A.)	hkl(1)	hkl(2)	Remarks
25	4.44	3	4.48	211		Oxides, $ZrSiO_4$
40	3.31	10	3.31	-	-	Oxides(Hex), $ZrSiO_4$
B100	3.16	vB100	3.15	222	111	Oxides
B50	2.73	vB60	2.73	400	200	Oxides
w	2.59	-	-	411		
20	2.52	5	2.529	-	-	$ZrSiO_4$
10	2.33	-	-	332	-	
5	2.22	-	-	422	-	
5	2.188	-	-	500	-	
2	2.143	-	-	510	-	
10	2.064	5	2.072	-	-	$ZrSiO_4$
B70	1.931	vB80	1.926	440	220	Oxides
20	1.710	3	1.718	-	-	$ZrSiO_4$
B60	1.645	vB80	1.643	622	311	
B5	1.574	10	1.573	440	222	
5	1.475					$ZrSiO_4$
5	1.378					$ZrSiO_4$
B10	1.363	vB15	1.363	800	400	Oxides
5	1.288			660		Oxides
B10	1.251	vB30	1.250	662	331	Oxides
B5	1.218	vB20	1.218	840	420	Oxides

(1) Belongs to sesquioxides (cubic system)

(2) Belongs to ceria and thoria (cubic system)

TABLE 59

Change of the d-spacings of oxides (ceria and thoria + sesquioxides) in 3 different monazite:Na_2CO_3+NaF mixtures.

Rad. Cu. K_α

Film 10147D Film 10226C Film 10236A

No. 1		No. 7		No. 10		Cubic		Hex.	Remarks
I	d(A.)	I	d(A.)	I	d(A.)	hkl		hkl	
2	6.41	vw	6.43	-	-		111		Oxides
-	-	B5	4.54	-	-		211		"
-	-	60	3.36	50	3.357			100	"
B100	3.20	B100	3.22	B10	3.22	111	222		"
-	-	40	3.03	50	3.03			002	"
		100	2.935	100	2.935			101	"
B40	2.775	B20	2.795	vw	2.777	200	400		"
		Bvw	2.64				411		"
		vw	2.38				332		"
		40	2.25	30	2.247			102	"
		3	2.19	vw	2.194		510		"
B60	1.962	B40	1.973			220	440		"
		50	1.940	50	1.935			110	"
		Bvw	1.812				611		"
		50	1.732	40	1.730			103	"
B50	1.672	B40	1.683	vB10	1.677	311	622	200	"
		30	1.635	40	1.631			112	"
		25	1.618	30	1.615			201	"
B5	1.601					222			"
		vw	1.518	w	1.514		633	004	"
		10	1.468	10	1.461			202	"
B5	1.386	vw	1.397			400	800		"
		B10	1.292	B20	1.290			203	"
B5	1.272	vw	1.282			331			"
B5	1.239	vB15	1.244	B20	1.238	420		211	"
		B10	1.195	B10	1.192			114	"

TABLE 60

Change of cell parameters* of oxides with 3 different monazite:Na_2CO_3+NaF mixtures.

Rad. Cu. K_α

Film 10147D No. 1		Film 10226C No. 7	Film 10236A No. 10
Cubic form (ceria and thoria)			
a	5.545 A.	5.585 A.	5.593 A.
Cubic form (sesquioxides)			
a	11.001 A.	11.162 A.	11.200 A.
Hexagonal form (sesquioxides)			
a		3.880 A°	3.870 A°
c		7.006 A°	= 6.997

* For comparison see Table 6 p. 31.

lead, uranium, iron and trace amounts of rare-earths.

To estimate the relative concentrations of the individual rare-earths in acid extraction residue and oxide fractions, some of the peaks which corresponded to lanthanum, cerium, thorium, samarium and neodymium were measured. Since some of the main peaks overlapped others, weaker peaks which correspond without overlap to a single element were chosen. The only single cerium peak was interfered with by the tungsten $L\beta_1$ line ($n = 2$) at $2\theta = 45.10°$. This caused some errors when the cerium concentration was very low. At the beginning of the series the results were reasonably good. Since standards having appropriate known compositions were not available, the exact concentrations were not calculated; instead, peak-height ratios of the main elements in both fractions were found. The measurement of Sm/Ce or Nd/Ce ratios from the corresponding charts showed that mixture 10 (ratio 5:1.68) gave optimum separation of thorium and cerium from the other lanthanides though there were slight differences between mixtures 9, 10 and 11 in the case of Sm/Ce ratios in the rare-earth oxides (Table 61). When the lanthanum and cerium concentrations were being compared, counting methods were applied; the fixed-time technique was employed with a 1-minute counting time. In the acid residues the results obtained were very good; the highest Ce/La ratio occurred in mixture 10. In the oxides the same mixture was found to be optimum, but there were irregularities in the figures (Table 62). The separation factor in the optimum condition was approximately 100 times that in the No. 1 case.

Effect of acid concentration:

Table 63 shows the effect of acid concentration on product. No. 10, which was found to represent the optimum conditions for the pure products, and the highest yield. From XRF measurements it was

TABLE 61

Nd/Ce and Sm/Ce Peak Height Ratios in Oxalic Acid Oxides (from XRF Charts).

Mixture No.	Nd/Ce	Sm/Ce
1	0.267	0.187
2	0.398	0.215
3	1.701	0.914
4	1.593	1.083
5	1.667	1.022
6	2.375	1.273
7	2.489	1.722
8	2.843	1.595
9	2.971	1.768
(10)	3.033	2.020
11	2.570	2.010
12	2.423	1.990
13	2.168	1.630
14	1.906	1.700

Note: Individual values have no absolute significance.

TABLE 62

Ce/La and La/Ce in Acid Extraction Residue and Oxalic Acid Oxides by Counting Methods (background correction applied).

No.	Separation factor (1)	Ce/La in acid residue	La/Ce in oxide	La/Th (2) in oxide
1	5.28	15.03	0.351	
2	9.75	16.89	0.577	
3	66.17	19.92	3.322	
4	95.54	29.28	3.263	
5	120.53	35.14	3.435	
6	148.83	35.95	4.142	
7	173.34	38.14	4.545	
8	193.22	44.46	4.346	1.37
9	398.40	107.97	3.690	1.84
10	596.92	111.18	5.369	2.63
11	431.77	96.81	4.460	1.47
12	279.14	71.03	3.931	
13	287.67	77.54	3.715	
14	120.99	42.32	2.859	

(1) Separation factors were calculated as given by Weaver(1954). The following formula was used:

$$S.F = \frac{La/Ce \text{ in oxide}}{La/Ce \text{ in acid residue}}$$

(2) There were some irregularities in the couting of Th due to the use of a Geiger Muller counter, which is limited at low concentrations of heavier elements.

TABLE 63

Acid Extraction Results of Mixture 10 Products with different Acid Concentrations, and comparison of X-ray fluorescence measurements.

Acid:H_2O in ml.	Acid residue *	Oxide precipitated	Th/La	Ce/La	La/Th	La/Ce
			Acid residue		Oxides	
2:8	0.3501	0.2555	42.29	24.75	1.783	3.882
4:6	0.3432	0.2604	58.66	33.46	1.000	3.337
6:4	0.3396	0.2619	66.83	35.42	0.957	3.008
8:2	0.3408	0.2607	69.00	35.69	0.908	2.740

* 1 g. sintered product was taken for extraction.

found that ceria and thoria dissolved as the acid concentration increased. On the other hand, dilution of the hydrochloric acid did not diminish the extraction of $Na_3Ln(PO_4)_2$, since there was little difference between the weights of the oxides recovered at different acid concentrations.

Effect of fluoride ion on sintering:

To show the effect of sodium fluoride, four other sintering experiments were done with monazite and sodium carbonate alone, Na_2CO_3:NaF in 50:1 ratio, Na_2CO_3:NaF in 100:1 ratio, Na_2CO_3+Na_2SiF_6 containing the same amount of fluorine as 20:1 Na_2CO_3+NaF mixture, Na_2CO_3+CaF_2 likewise containing the same amount of fluorine as the 20:1 Na_2CO_3+NaF mixture. Samples were sintered at 700°C. and weighed every 2 hours (Table 64). The reason for not reaching the theoretical loss was the absorption of oxygen to convert cerium into its higher oxidation state.

Figure 6 shows the positive effect of fluoride on the loss of carbon dioxide. The carbon dioxide evolution reaction was complete after about 6 hours in the case of Na_2CO_3+NaF (20:1) or with CaF_2 and Na_2SiF_6 mixtures. But in the X-ray powder diffraction pattern monazite was still present when carbon dioxide evolution was complete. The intensity of the strongest line was 10 but intermediate was also very strong (Film 10267C). Prolonged heating probably would induce sodium phosphate to combine with the remaining monazite to form the acid-soluble intermediate.

TABLE 64

Loss of CO_2 in g. when Sintering Monazite with Mixtures of Fluoride with Sodium Carbonate

Na_2CO_3		Na_2CO_3+NaF 100:1		Na_2CO_3+NaF 50:1		Na_2CO_3:NaF 20:1		Na_2CO_3:Na_2SiF_6 1.6203:0.0597		Na_2CO_3+CaF_2 1.6057:0.0743	
Hours	loss in g.	Hours	loss in g.	Hours	loss in g.	Hours	loss in g.	Hours	loss in g.	Hours	loss in g.
2	0.1794	2	0.3188	2	0.3217	2	0.5799	2	0.5484	2	0.6043
4	0.2320	4	0.4062	4	0.4025	4_{10}	0.6017	4	0.6078	4_5	0.6130
6	0.2599	6	0.4597	6	0.4997	6_{10}	0.6060	6	0.6155	6	0.6144
9_{10}	0.3488	9_{15}	0.5406	9_{15}	0.5613	10_{10}	0.6067	9_{15}	0.6189	10	0.6148
12_{10}	0.4064	12_{15}	0.5748	12_{15}	0.5905	11	0.6107	12_{15}	0.6189	19	0.6148
17_{25}	0.5031	17_{25}	0.6126	17_{25}	0.6219	16_{30}	0.6095	17_{25}	0.6189	29	0.6148
Theo. loss g.	0.6973		0.6903		0.6835		0.6623		0.6723		0.6665

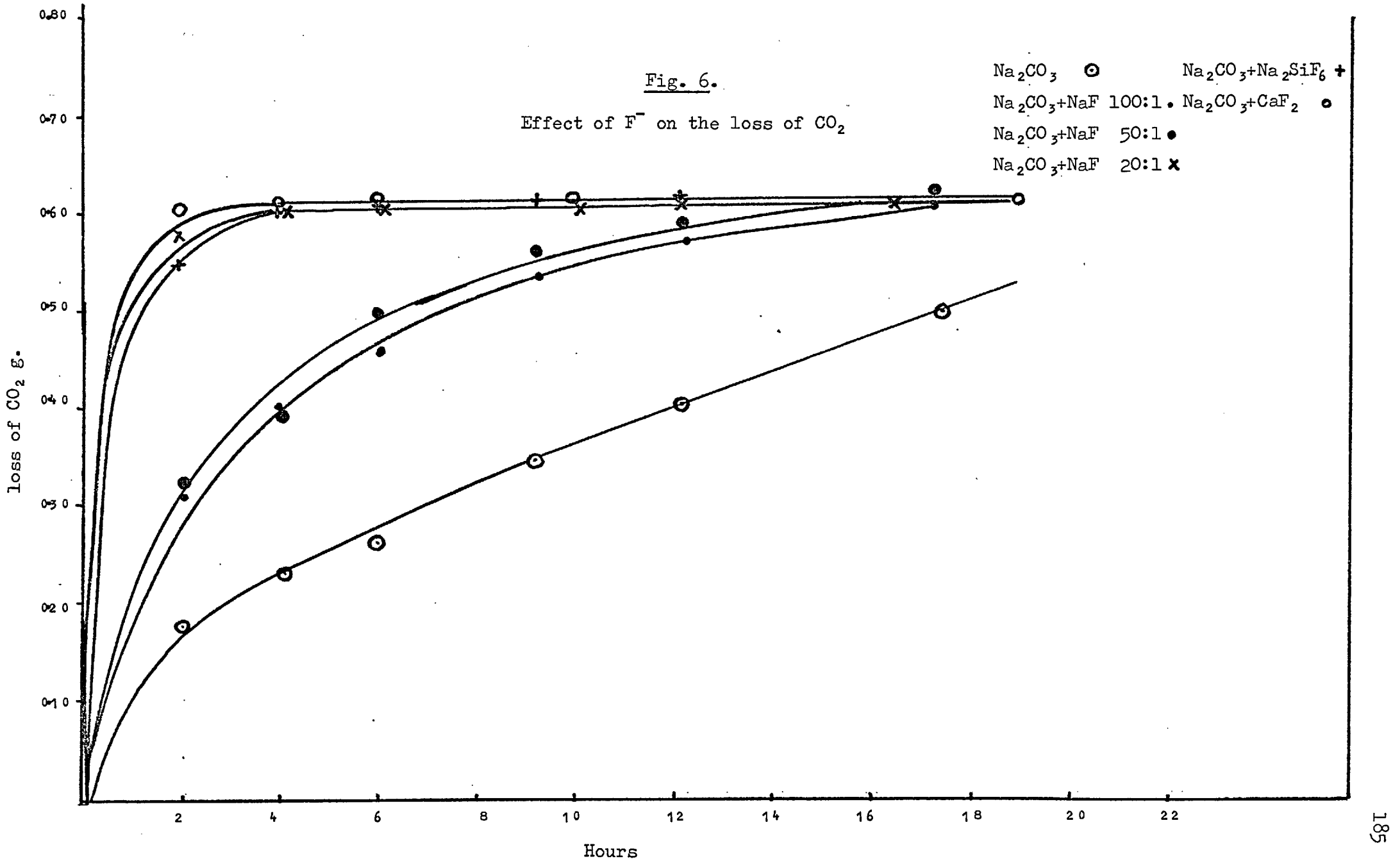


Fig. 6.
Effect of F⁻ on the loss of CO2
Na2CO3
Na2CO3+NaF 100:1
Na2CO3+NaF 50:1
Na2CO3+NaF 20:1
Na2CO3+Na2SiF6
Na2CO3+CaF2
loss of CO2 g.
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
2
4
6
8
10
12
14
16
18
20
22
Hours

5.2. Possible process route for utilization of monazite:

According to the chemical analysis of monazite the percentages of oxides were as follows:

CeO_2	28.8
ThO_2	7.3
Insoluble in acid	2.5
	38.6%
Other rare earth oxides	30.2%

Theoretically from 5 g. of monazite we should obtain 38.6 x $^5/_{100}$ = 1.930 g. of acid residue and 30.2 x $^5/_{100}$ = 1.510 g. of oxides in the acid extraction filtrate. This gives a total of 3.440 g. of oxides. For the optimum sintering condition (mixture No. 10, 5:1.68 ratio) 2.1596 g. of acid residue, and 1.5176 g. of oxides were recovered in the experiments described. The acid residue was found to be slightly larger than the theoretical quantity, probably on account of unreacted monazite. The sum of the acid extraction residue and the oxides was 3.6772 g., again somewhat in excess of theoretical. The difference corresponded to about 4.5% of unreacted monazite. It might also be due to higher oxidation states of praseodymium and terbium, which form non-stoichiometric oxides with the approximate compositions Pr_6O_{11} and Tb_4O_7. The oxalate method is very reliable for light rare earths and yttrium, but the formation of non-stoichiometric oxides of the heavier rare earths is a disadvantage. Increase in the sodium carbonate did not decrease the amount of acid residue, and the total recovery was about the same for all the cases up to No. 12, increasing afterwards on account of more unchanged monazite. The No. 10 case showed a good separation of the two fractions, proved by X-ray methods.

So by using the optimum amount of Na_2CO_3+NaF mixture (20:1),

sintering at 700°C. for 6 hr., and extracting the product with dilute hydrochloric acid, it should be possible to decompose monazite and extract nearly 95% of the oxides in the form of two separate fractions. Initial semi-quantitative results showed that the ceria-thoria solid solution did contain minor amounts of other rare-earth oxides; likewise the rare-earth oxides other than cerium contained minor amounts of ceria. The separation of thoria was not as complete as that of ceria, showing the tendency of thorium to form a double-phosphate intermediate. But from the point of initial separation the results are very good.

SECTION 6

GENERAL REVIEW AND DISCUSSION

6. General review and discussion.

The ultimate object of this work was a thorough investigation of the solid-state reactions of lanthanide orthophosphates with sodium carbonate. Lanthanide orthophosphates from lanthanum to lutetium (except promethium) were prepared in the laboratory and their identity was confirmed by X-ray diffraction analysis, and by infra-red absorption methods.

The sintering reactions of gadolinium and lanthanum orthophosphates with sodium carbonate gave the expected products (sodium orthophosphate and lanthanide oxides) with the stoichiometric amounts of sodium carbonate. When less than the theoretical amount of sodium carbonate (e.g., approximately 50% of the theoretical) was used, an intermediate product, eventually characterised as $LnPO_4, Na_3PO_4$ and $LnPO_4, Ln_2O_3$ was detected.

The following investigations were found to be necessary to clarify the reaction products and the general mechanism of the reaction:

1. Determination of hitherto unrecorded X-ray data for sodium orthophosphate.
2. Characterisation of double oxides of lanthanides and sodium, $NaLnO_2$.
3. Characterisation of lanthanide oxide phosphates, $LnPO_4, Ln_2O_3$.
4. Characterisation of sodium lanthanide orthophosphates, $LnPO_4, Na_3PO_4$ ($Na_3Ln(PO_4)_2$).
5. Study of gadolinium pyrophosphate, $Gd_4(P_2O_7)_3$, and sodium gadolinium pyrophosphate, $NaGdP_2O_7$.

The results of these investigations are reviewed below.

1. Investigation of both dehydrated $Na_3PO_4, 12H_2O$ and the orthophosphate prepared in the present work for the first time showed that

sodium orthophosphate had crystal modifications additional to those already reported. An orthorhombic form of sodium orthophosphate obtained at temperatures over 700°C. was established; its X-ray d-spacings agree with those of the alleged cubic form of sodium orthophosphate reported by Palazzi and Remy (1971), and referred to as the "high temperature γ-form". A β-form of sodium orthophosphate which was not reported by Palazzi and Remy, was also established.

2. Sodium gadolinium oxide ($NaGdO_2$) was prepared by the method described by Blasse (1964); but at 940°C. instead of 800° C., its X-ray diffraction data which were not reported by him, have been listed. The compound is tetragonal with the cell parameters a = 14.74 and c = 10.53 A.; this value of c agrees with that of Blasse, but not a. Only by changing a, it was possible to account for all the lines. The reactions did not give any crystallised product in the case of attempted sodium lanthanum oxide preparations.

The d-spacings of sodium gadolinium oxide were not present in the products of gadolinium orthophosphate and sodium carbonate sintering reactions.

3. Lanthanide oxide phosphates, $LnPO_4$, Ln_2O_3, for gadolinium and lanthanum, were prepared through solid-state reactions. The d-spacings corresponding to these compounds were found among the reaction products of some lanthanide orthophosphate and sodium carbonate sintering reactions.

4. Sodium lanthanide orthophosphates were prepared successfully through solid-state reactions for the first time. They were obtained as single-phase products at 1150°C. with the reactant composition $LnPO_4$+Na_3PO_4. The X-ray diffraction data for sodium lanthanide (lanthanum, cerium, neodymium, gadolinium and yttrium) orthophosphates were indexed in the tetragonal system. The infra-red data confirmed

the presence of orthophosphate ions.

5. "Gadolinium pyrophosphate" was prepared by the methods described by Buyers, Giesbrecht and Audrieth (1950, 1957, 1958) and Tananaev and Petushkova (1964, 1966). The X-ray diffraction data of products dried or heated under a variety of conditions were closely examined, and conditions of formation of the anhydrous pyrophosphate were defined. The products heated at 700°C. and 900°C. were crystalline and different from each other. The X-ray diffraction data given for "$Gd_4(P_2O_7)_3$" by Buyers and Audrieth (1950) were identical with those of the orthophosphate, owing to complete hydrolysis into orthophosphate during preparation. The very complex data of Tananaev and Petushkova (1966) for "gadolinium pyrophosphate" heated at 700° and 1000°C. also disclosed gadolinium orthophosphate lines.

The formation of hydrogen gadolinium pyrophosphate was also reported for the first time in the present work; its X-ray diffraction data after heating at a number of temperatures are given. Sodium lanthanide pyrophosphates could not be prepared by precipitation and need further investigation. Lanthanide pyrophosphates or double pyrophosphates were not found among the products of sintering reactions of lanthanide orthophosphate and sodium carbonate.

The application of the sintering method to the naturally occurring phosphates, particularly the mineral monazite, has been worked out and was proved to be very successful. By using the optimum amount of sodium carbonate (containing 1:20 of sodium fluoride) and dissolving the product by dilute hydrochloric acid it was possible to break down monazite and to separate its basic oxide content into ceria plus thoria and sesquioxides.

SECTION 7

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