

100 Years of Ferroelectricity- A Celebration

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In 1880, the brothers Jacques and Pierre Curie were studying the phenomenon of pyroelectricity. This is the effect whereby crystals which both lack a centre-of-symmetry (i.e. are 'acentric') and possess a unique axis of symmetry exhibit a separation of positive and negative coulombic charge when subjected to a temperature change. They observed something quite unexpected, which was that the mineral α -quartz exhibited a pyroelectric effect. They were well-aware that this should not have been the case because, although α -quartz is acentric, it does not have a unique axis of symmetry. A careful analysis of their experimental conditions showed that that they were subjecting the quartz crystals to a temperature gradient. In doing this, they had subjected the crystals to thermally-induced mechanical stresses and they thus discovered piezoelectricity¹. This ability of acentric crystals to turn mechanical stresses into an electrical signal, and conversely to turn an electrical signal into mechanical strains, received enormous attention and development during World War 1 for use in submarine-detecting sonar equipment. Very large piezoelectric coefficients had been discovered in Rochelle salt (sodium potassium tartrate) and single crystals several centimetres in size were being grown at the time by General Electric (GE)². As has been described by Cady³ and Valasek⁴, J.A. Anderson and W.G. Cady were studying the properties of Rochelle salt for underwater sonar applications around 1918, and had noted anomalous dielectric behaviour. Josef Valasek at the University of Minnesota was studying the piezoelectric and dielectric properties of the GE-made Rochelle salt crystals. He found that between the temperatures of -20 and +20°C, the crystals not only became polar, but the direction of the polar axis could be switched between two opposite states by the application of an electric field of sufficient magnitude and that these states were stable when the field was removed⁵, a characteristic that we now recognize as "ferroelectricity". This work was later reproduced by Kurchatov and co-workers in Leningrad⁶. The effect was initially termed "Seignette electricity", after Elie Seignette who first prepared the compound in La Rochelle in the seventeenth century. Although the concept of "ferroelectricity" was first mooted as a

theoretical possibility by Erwin Schrodinger in 1912⁷, Valasek has indicated that his first awareness of the use of the term as applied to materials that possessed an electrically-switchable spontaneous dielectric polarization was by Hans Mueller (Massachusetts Institute of Technology - MIT) in 1940⁸. At first, the effect was thought to be connected to the presence of polar water molecules and hydrogen bonding. However, as has been reviewed by Kanzig⁹, a major step-forward towards the widespread use of ferroelectric materials came with the independent discovery during the 1940's in the USA, UK, Russia and Japan of anomalous dielectric behaviour and ferroelectricity in the perovskite oxide barium titanate (BaTiO_3). This led eventually to the discovery by H. Jaffe and co workers¹⁰ at the National Bureau of Standards in the USA of exceptional piezoelectric properties in the lead zirconate – lead titanate ($\text{PbZrO}_3\text{-PbTiO}_3$) ceramic solid solution system when the compositions were close to $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$. The Clevite corporation developed a family of piezoelectric ceramics based on this discovery¹¹, which were doped with different elements to confer particular property improvements, such as Fe for stability under high driving fields. (These were given the trademark “PZT”, and while this term is now almost universally applied by the community as a shorthand-term for ferroelectric materials based on the $\text{PbZrO}_3\text{-PbTiO}_3$ solid solution system, it is worth remembering where it came from.)

The switchable spontaneous polarization of ferroelectric materials confers upon them many useful properties with an extraordinarily wide range of applicability, some examples include:

- Piezoelectric coefficients that are very large in relation to non-ferroelectric piezoelectrics, meaning they are widely used in underwater sonar (military and civilian), medical ultrasound equipment, audible sound generators, nano-positioners for optics, magnetic disk memory read heads and ultraprecision equipment such as photolithographic steppers, motors, surface acoustic wave (SAW) and film bulk acoustic resonator (FBAR) devices etc. The global piezoelectric materials market was US\$1.35 billion in 2019, rising to US\$1.84 billion in 2027¹², with the piezoelectric devices market estimated at US\$28.9 billion in 2020, growing to US\$34.7 billion by 2025; at a compound annual growth rate (CAGR) of 3.7%¹³.
- Very high dielectric constants, leading to widespread use in ceramic capacitors. The global ceramic capacitors market is expected to reach a total market size of US\$9.2 billion in 2023, rising from US\$6.1 billion in 2017 at a CAGR of 6.9%¹⁴.
- Very large pyroelectric coefficients, leading to the widespread application of ferroelectric materials to pyroelectric infra-red (PIR) sensors, which are used in intruder sensors, remote light switches, environmental monitors, medical

instrumentation and people sensing^{15,16}. PIR devices are expected to have a market of ca US\$50 million in 2020, reaching US\$68 million by 2025¹⁷, or ca 10% of the total infrared detector market. Any pyroelectric material will also exhibit the electrocaloric effect (ECE). This is a change in temperature engendered by an applied electric field. Some of the earliest measurements were conducted in 1930 by Kobeko and Kurtschatov¹⁸. Thacher measured temperature changes (ΔT) of about 1K at applied fields of up to 30kVcm⁻¹ in PZT-related materials¹⁹ and Shebanov et al²⁰ showed similar values of ΔT in PbSc_{1/2}Ta_{1/2}O₃. Very high electric fields, above the breakdown fields of most bulk materials, are needed to get useful values of ΔT . However, in 2006 Mischenko et al²¹ showed that values of ΔT up to 12K could be obtained in thin films of PbZr_{0.95}Ti_{0.05}O₃ at fields of 480kVcm⁻¹. This has led to a resurgence of interest in the potential applications of the ECE in solid-state refrigeration²²⁻²⁴.

- The switchable spontaneous polarization has led to applications of ferroelectrics in non-volatile memories, or ferroelectric random access memory (FRAM)²⁵ based on thin films of e.g. PZT, SrBi₂Ta₂O₉ (SBT) or, more-recently, HfO₂-based ferroelectric films²⁶. Global markets for FRAM are expected to reach ca US\$340 million by 2025²⁷.
- Ferroelectrics exhibit strong electro-optic (EO) effects, which has led to their widespread use in applications such as photonic switches, EO modulators for fibre-optic communications, laser Q-switches etc. It has been estimated that the global market for LiNbO₃-based modulators will hit US\$36.7 billion by 2026²⁸.
- Barium titanate ceramics can be doped with e.g. Nb or La to make them semiconducting. These materials can show very strong positive temperature coefficients (PTC) of resistance in the region of the Curie temperature T_c ²⁹. These are widely used in self-stabilizing heaters and devices for e.g electric motor protection. The global PTC Thermistors market was valued at US\$285.1 million in 2020 and it is expected to reach US\$343.2 million by the end of 2027, growing at a CAGR of 2.7% during 2021-2027.

The above markets for ferroelectric materials and devices alone are predicted to be worth about US\$80 billion by 2027, with a much greater market-value for the systems using them, indicating that the science and technology of ferroelectric materials has very significant economic importance.

One of the fascinating aspects of ferroelectricity as a phenomenon is that it appears in a very wide range of different material types with diverse physical properties. This greatly increases the potential for applications of ferroelectricity. These include:

- Hydrogen bonded crystals such as Rochelle salt itself (originally used in piezoelectric devices), potassium dihydrogen phosphate, or KDP, (used in electro-optic switches, light modulators and frequency doublers³⁰) and triglycine sulfate, or TGS (used in PIR detectors³¹). Such crystals tend to be water soluble. This simplifies the growth of very large, high quality single crystals, such as the growth of large KDP crystals for EO modulator plates used in ultra-high-power laser systems, but has the disadvantage that the resulting crystals tend to be water sensitive and need careful handling and encapsulation. Recently, crystals of complex molecules such as tetrathiafulvalene (TTF) with halogenated quinones (Q)³² in hydrogen-bonded networks have been shown to exhibit ferroelectric behaviour with significant spontaneous polarizations³³ ($\sim 5 \mu\text{Ccm}^{-2}$) and are exciting considerable interest. Simple organic salts such as diisopropylammonium chloride (DIPAC)³⁴ and diisopropylammonium bromide (DIPAB)³⁵ were found to show excellent ferroelectric properties comparable to those of BaTiO_3 , with high Curie temperatures (440 and 426K) as well as a spontaneous polarization of $23\mu\text{Ccm}^{-2}$, making them competitive with inorganic and polymer ferroelectrics. Besides the above mentioned salts, single component organic crystals with high Curie temperature have also emerged recently, such as *R/S*-3-quinuclidinol and 2-(hydroxymethyl)-2-nitro-1,3-propanediol, with unique homochirality³⁶ and functional properties³⁷. Xiong et al also reported a previously unknown family of all-organic perovskites, including the first metal-free three-dimensional chiral perovskite ferroelectrics³⁸.
- Ferroelectric oxide single crystals such as LiNbO_3 and LiTaO_3 have for many years underpinned a host of applications, such as SAW and bulk acoustic wave (BAW) devices³⁹ (used in e.g. radio frequency or RF filters and sensors), electro-optic photonic devices⁴⁰ and PIR detectors⁴¹. These crystals are (or are close to being) congruently-melting, and are thus relatively simple to grow using the well-known Czochralski method^{42,43}. The discovery by Uchino et al⁴⁴ and others⁴⁵ of very high piezoelectric coupling factors in single crystals of $\text{PbZn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ - PbTiO_3 (PZN-PT) and $\text{PbMg}_{1/2}\text{Nb}_{1/2}\text{O}_3$ - PbTiO_3 (PMN-PT) and more recently in ternary crystals such as $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ - $\text{PbMg}_{1/2}\text{Nb}_{1/2}\text{O}_3$ - PbTiO_3 (PIN-PMN-PT) and $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - BaTiO_3 - $(\text{K}_{1/2}\text{Na}_{1/2})\text{NbO}_3$ (NBT-BT-KNN)⁴⁶ has led to major improvements in non-destructive evaluation (NDE)⁴⁷ and medical ultrasound equipment⁴⁸. These compositions are not congruently melting and so the crystals have to be grown from flux, which has entailed significant development work to obtain acceptable uniformity of composition throughout large crystals⁴⁹.

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- The fact that ferroelectrics can be polarized by applying an electric field in the poling process means that polycrystalline materials can be given a net spontaneous polarization. Ferroelectric oxide ceramics are much cheaper and easier to make with a very wide range of compositions than oxide single crystals, allowing the physical properties to be “tuned” for particular applications. Ceramics based on BaTiO_3 and $\text{PbZrO}_3\text{-PbTiO}_3$ (PZT) solid solutions (see above), have been the main materials underpinning dielectric, piezoelectric and pyroelectric applications since the 1950’s, although for environmental reasons there has been a growing interest in lead-free ceramic compositions⁵⁰. Various multiaxial molecular ferroelectrics can also be used in polycrystalline form, giving advantages of mechanical flexibility, low processing temperature⁵¹ and simple thin-film fabrication⁵², leading to new opportunities for practical applications⁵³.
- The principle of combining one material with another to form a multi-phase composite to “tune” properties for a particular application, or even to get new properties, has been a principle long applied to materials for structural applications. This principle has also been applied to ferroelectrics, with some of the earliest work being by van den Boomgaard et al^{54,55} who showed that BaTiO_3 -barium ferrite composites made by eutectic melting could show novel magnetoelectric properties. Newnham et al⁵⁶ were the first to apply this principle to the creation of new piezoelectric and pyroelectric materials by making PZT-polymer composites. They described and codified the different “connectivity” patterns defining how the different phases might be structured in 3-dimensions and showed how important connectivity was in determining the properties of the final composite material.
- Thin films of ferroelectrics have been explored for many years for their potential for integrating non-volatile memories onto silicon (FRAM). The first patents were in the late 1950’s^{57,58}, while some of the earliest practical work in the field was on the integration of the Aurivillius-phase⁵⁹ ferroelectric oxide bismuth titanate into the gate of a field effect transistor (FET), reported by Wu and Francombe^{60,61} in the early 1970’s. The field really took-off in the 1980’s, with work on PZT and other Aurivillius oxides such as strontium bismuth tantalate^{25,62}, leading to their ultimate commercialization. More-recently, there has been considerable interest in the discovery of ferroelectric behaviour in thin films of HfO_2 when in solid solution with SiO_2 ⁶³ and ZrO_2 ⁶⁴. The better compatibility of these oxides with silicon integrated circuit (IC) processing promises to lower the technological barriers to the large-scale integration of FRAM onto silicon.

- In 1976, strong piezoelectricity was reported in β -phase polyvinylidene fluoride (PVDF)⁶⁵ after poling. The authors tentatively assigned this to ferroelectricity, although it took some time before this was conclusively proved⁶⁶. Since then, ferroelectricity has also been demonstrated in copolymers of PVDF with trifluoroethylene (TrFE)⁶⁷ and tetrafluoroethylene⁶⁸. There has been extensive application of these materials to piezoelectric^{69,70} and pyroelectric^{71,72} devices. Ferroelectricity has also been observed in the odd-numbered nylons such as nylon-11⁷³. Recently, there has been considerable interest in the potential applications of the ECE in P(VDF-TrFE) copolymers⁷⁴ and terpolymers of P(VDF-TrFE) with chlorofluoroethylene⁷⁵.

It can be seen from the brief review above that there has been enormous progress over the last 100 years in the science and technology of ferroelectric materials for a huge range of applications since the discovery of the phenomenon by Valasek. This special topic is a collection of papers celebrating the 100th anniversary of that discovery and it is an exciting glimpse into the future of where the field is moving in the future. The papers in this collection are directly related to most of the fields and material-types referred to above.

The understanding the fundamentals of the paraelectric-to-ferroelectric phase transition has been a subject of research for many years. The two main theories are the order-disorder transition in which polar groups in the structure are disordered at high temperature, moving to an ordered state at lower temperature due to cooperative dipole interactions. The other main description is the soft-mode theory first described by Cochran⁷⁶, in which the frequency of a zone-centre phonon mode goes to zero, or “softens”, at the Curie temperature. In both Rochelle salt and KDP the transition order-disorder, driven by the occupancy of the protons in the hydrogen bonds linking the ions. This was first demonstrated by Bacon and Pease⁷⁷ using neutron diffraction. In this collection, we have a new neutron diffraction study by Francher et al⁷⁸ on the field-dependence of the crystallographic structure of KDP as it is cycled around the hysteresis loop. The favoured theory for oxide ferroelectrics is the soft-mode theory, and here we have a perspective by Kamba⁷⁹ discussing the results of broadband dielectric, THz and IR spectroscopic investigations of soft-mode phenomena in H-bonded ferroelectrics, BaTiO₃, relaxors and multiferroics.

While ceramics based on the PZT solid-solution system occupy the bulk of the applications space for piezoelectrics, it has long been recognized that the Curie temperatures of PZT ceramics limits their operational temperature to between 150°C and 290°C. Bell et al⁸⁰ have reviewed how this limits the operational space for piezoelectrics and

have shown how new ceramic compositions based on $\text{BiTiO}_3\text{-PbTiO}_3\text{-K}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ solid solutions can work up to 400°C or even 600°C , while providing useful piezoelectric coefficients to enable diverse novel applications such as applications in sensing deep within operating gas turbine engines or the atomisation of liquid metals.

The need to harvest ambient sources of energy to power micro-devices for the “internet-of-things” (IoT) and flexible / wearable electronics has excited interest in vibrational⁸¹ and flexible piezoelectric energy harvesters⁸². In this issue, Liu et al⁸³ demonstrate how multi-layer stacks of PIN-PMN-PT single crystal wafers can give power outputs which are ca 400x greater than piezoelectric energy harvesters based on conventional PZT ceramic cantilevers. Li et al⁸⁴ give us an interesting perspective on how solution-processed polymeric and composite ferroelectrics based on PVDF exploiting both the piezoelectric and pyroelectric effects can be used to generate useful amounts of energy for flexible electronics. The theme of exploiting PVDF-based materials in energy applications is also addressed by Jiang et al⁸⁵, who address the use of ferroelectric polymer nanocomposites in dielectric energy storage applications, showing that energy storage densities as high as 35.4Jcm^{-3} can be achieved in alternating pure P(VDF-HFP) layers and P(VDF-HFP)/ BaTiO_3 nanocomposite layers. This is more than ten times the level achievable in current commercial polymer dielectric films and offers great potential for new supercapacitors for energy storage.

The ferroelectric / magnetoelectric composite field can reasonably be traced back to the early work on magnetoelectric composites by van den Boomgaard et al^{54,55} referred to above. In this issue, we have an interesting discussion by Yang et al⁸⁶ of the properties of new magnetoelectric composites made using Metglas foils and PZT thick films, with potential applications as magnetic field sensors. Lee et al⁸⁷ review the area of ferroelectric nanocomposites and show that vertically aligned nanocomposites (VANs) offer great potential and new avenues for future research, including new magnetoelectric multiferroics. The intrinsic nanocomposite nature of the Aurivillius oxide systems are proposed to offer some very interesting multiferroic properties, as has already been demonstrated by Keeney et al⁸⁸.

The pyroelectric and electrocaloric effects continue to excite interest. In this issue Neumann et al⁸⁹ have taken some of the PIN-PMN-PT single crystal materials originally developed for piezoelectric applications and explored their use in practical PIR detectors. They show that it is possible to obtain performance figures-of-merit that are 5x greater than those of comparable devices based on LiTaO_3 , one of the normally-preferred materials for use in this application. This is a remarkable performance increase, although it also comes at significantly-increased device fabrication costs. Velarde et al⁹⁰ review the present and future

status of ferroelectric thin films for use in a range of pyroelectric applications, including the recovery of electrical energy from waste heat sources – something that offers considerable promise. Berenov et al⁹¹ present a detailed study of the pyroelectric properties of sputtered Nb-doped PZT thin films and show that photonic stimulation of the films with visible light can considerably increase the magnitudes of the measured pyroelectric coefficients, an effect that remains unexplained. Crossley et al⁹² present a very detailed practical study of the thermodynamics of the ECE in PST ceramics under adiabatic and isothermal conditions, something that could be of real importance in potential future applications of this material. Barman et al⁹³ present measurements of a remarkably high ECE ΔT of 13.5K at a field of $1,000\text{kVcm}^{-1}$ in a $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ thin film heterostructure.

Since the work^{60,61} in the early-1970's incorporating bismuth titanate ferroelectric thin films into the gate of an FET to make the first FeFET, the possible use of ferroelectric thin films as active components in semiconductor devices have continue to excite great interest, especially as our understanding of the materials we can use and the technologies for their fabrication improve. Kim et al⁹⁴ review the current status of FeFET technology, discussing the use of a wide range of potential ferroelectrics into the gate, ranging from PZT, through $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) and PVDF to the ferroelectric semiconductor In_2Se_3 and exploring their potential for use in novel devices, including artificial synapses to mimic the operation of brain cells. The phase structure of HfO_2 -based ferroelectric films has been of considerable interest since ferroelectricity was first discovered in them^{63,64}. Here, Onaya et al⁹⁵ provide a detailed study of the phase structure of $\text{Hf}_{0.43}\text{Zr}_{0.57}\text{O}_2$ films using synchrotron-radiation based XRD, particularly evaluating the effects of the post-metallization annealing (PMA) temperature on the formation of the orthorhombic phase present in the films and how this correlates with “wake-up” effects and remanent polarization in the films. Spreitzer et al⁹⁶ provide a research update on the growth of ferroelectric oxide thin films on silicon, with a particular view towards their applications in piezoelectric micro electromechanical systems (MEMS), electro-optic devices for communications applications and catalysis and a consideration of the complexities of the silicon-ferroelectric interface. It is clear from this review that PZT thin films are still very interesting for a range of applications and Do et al⁹⁷ provide a detailed structural study of the mechanisms behind the switching fatigue effects that occur in PZT thin films on Pt electrodes, showing that there is a large increase in coercive field, caused by the formation of a non-ferroelectric layer of binary oxides and diffused Pt at the Pt/PZT interface. Hanrahan et al⁹⁸ provide a report on the growth of antiferroelectric PbHfO_3 films from 20 to 200nm thick by atomic layer deposition (ALD). The films possess high energy storage densities (16Jcm^{-3} @ 2MVm^{-1}) and excellent (221% @ 50MVm^{-1}) tunability of the dielectric constant. Das et al⁹⁹ and Tian et al¹⁰⁰ provide

evaluations of new future direction for ferroelectric thin films in the form of superlattice structures of $\text{PbTiO}_3/\text{SrTiO}_3$ which can form new topological structures such as skyrmion and vortex features offering new potential functionalities for information storage, multiferroicity and optoelectronics. The pyroelectric properties of doped HfO_2 ferroelectric thin films have been exciting interest recently for their potential applications in PIR sensing and energy recovery applications^{101,102}. In this collection, Mart et al¹⁰³ present measurements of pyroelectric coefficients of up to $-142\mu\text{Cm}^{-2}\text{K}^{-1}$ at the morphotropic transition from the ferroelectric orthorhombic to the centrosymmetric phase in films doped with 4.8 at % Si, when a bias field of ca 1MVcm^{-1} is applied. This is significantly higher than the pyroelectric coefficients measured previously in doped HfO_2 thin films, which are typically around $-80\mu\text{Cm}^{-2}\text{K}^{-1}$ (in e.g. a film doped with 8.9 at % La¹⁰⁴).

The regions with different polar directions in a ferroelectric (domains) and the walls at their interfaces have long been of great interest for the effects they have on the physical properties of the materials. This ranges from the earliest work by Matthias and von Hippel¹⁰⁵ on the effects of domains on the dielectric properties of BaTiO_3 , by Kittel¹⁰⁶ on domain wall energies, by Mitsui and Furuichi¹⁰⁷ on domain wall velocities in Rochelle salt and KDP to that of Arlt¹⁰⁸ on the effects of domains on piezoelectric ceramics. More recently, the discovery by Seidel et al¹⁰⁹ that domain walls in ferroelectrics can form highly-conducting paths with nanometre width in an otherwise-insulating matrix has led to the concept of domain wall nanoelectronics (Catalan et al¹¹⁰) in which domain walls can form circuits and semiconducting components that can be actively rewritten. Improper ferroelectrics, in which the dielectric polarization is not the order parameter, are of particular interest here. Examples in which charged domain walls show enhanced conductivity include the hexagonal ErMnO_3 and related rare-earth manganites¹¹¹ and copper chlorine boracite ($\text{Cu}_3\text{B}_7\text{O}_{13}\text{Cl}$)^{112,113}. There are a number of papers relevant to this concept in this collection. Salje¹¹⁴ gives a perspective on the use of ferroelectric and ferroelastic domain walls in neuromorphic computing, whereby walls take the role of mimicking synapses and defect clusters neurons. Roede et al¹¹⁵ demonstrate the use of focussed ion and electron beams to charge the surface and reversibly switch improper ferroelectric domains in ErMnO_3 . McCartan et al¹¹⁶ discuss the properties of the improper ferroelectric CsNbW_2O_9 as being the first material outside the manganite family to show similar meandering six-fold domain wall patterns with the potential for charged domain walls that may ultimately show enhanced domain wall conduction. Moore et al¹¹⁷ review the use of aberration-corrected, sub-atomic resolution STEM to study the changes in polarization, chemical composition, charge density and strain at ferroelectric domain wall boundaries and vortices and map the 3D nature of ferroelectric polar skyrmions. Domains are also of considerable interest in antiferroelectric

materials and An et al¹¹⁸ discuss the hierarchical nature of the domains in PZT crystals with only 2 at% Ti, close to the antiferroelectric PbZrO₃ composition, showing how this forms in the intermediate ferroelectric state and have a significant impact on the materials' physical properties. Also in the collection, crystallographic investigations of antiferroelectric crystals of PbZr_{1-x}Sn_xO₃ with 0.05<x<0.3 by Jankowska-Sumara et al¹¹⁹ reveal new incommensurate phase structures and correlated disorder of the octahedral tilts.

The study of ferroelectricity started 100 years ago with Rochelle salt, sodium potassium tartrate, and continued with KDP and its isomorphs until the discovery of ferroelectricity in the perovskite oxides and their relatives. While there has been a strong emphasis since the early 1950's on the science and technology of materials like BaTiO₃ and PZT, there has also been a continuous interest in hybrid metal organic and molecular ferroelectrics which is now undergoing something of a renaissance. Ferroelectricity was demonstrated at low temperatures in tetramethylammonium cadmium tribromide by Gesi in 1960¹²⁰ and at ambient temperatures in the tetramethylammonium mercury trihalides^{121,122} in 1962. Subsequently there has been shown to be a wide range of metal organic complex ferroelectrics, as reviewed by Hang et al¹²³. In this collection, we have an overview by Yao et al¹²⁴ of the potential for bandgap engineering in hybrid organic-inorganic perovskite (HOIP) ferroelectrics such as (MDABCO)(NH₄)I₃ (MDABCO = N-methyl-N'-diazabicyclo(222)octonium), with the potential for linking the excellent characteristics of the new perovskite materials for solar cells, such as methylammonium lead iodide (MAPbI₃)¹²⁵ with the photovoltaic effects seen in ferroelectrics. Bie et al¹²⁶ report on theoretical predictions for how the Curie temperature can be increased to >500K (from 448K) in (MDABCO)(NH₄)I₃ by replacing the NH₄⁺ ion with metal ions such as K⁺ or Rb⁺. The molecular ferroelectrics solid solution system, (TMFM)_x(TMCM)_{1-x}CdCl₃ (TMFM = trimethylfluoromethyl ammonium; TMCM = trimethylchloromethyl ammonium, 0 ≤ x ≤ 1), has been shown by Liao et al¹²⁷ to possess a piezoelectric $d_{33} > 1500$ pC/N, which is much larger than PZT. Guo et al¹²⁸ describe high pressure synchrotron XRD experiments on another HOIP ferroelectric, TMCM-CdCl₃ (TMCM = trimethylchloromethyl ammonium), which indicate that while the material has piezoelectric coefficients comparable with BaTiO₃¹²⁹, it has significantly-lower acoustic impedance, indicating promise for energy recovery and sonar applications. Ye et al¹³⁰ describe two new molecular hexagonal perovskite ferroelectrics (R)-3-OH-(C₄H₉N)[CdCl₃] and (R)-3-OH-(C₄H₉N)[CdCl₃], both with significantly-higher Curie temperatures than the parent compound, while Xiong et al¹³¹ discuss two further new hybrid ferroelectric perovskites: [(CH₃)₂SO][RE(HCOO)₃] with RE = Lu³⁺ and Y³⁺. Harada et al¹³² give a perspective on plastic molecular ferroelectrics such as quinuclidinium perchlorate which have interesting spontaneous polarisations at room temperature. Lang et al¹³³

present the results of density functional theory studies of the ferroelectric properties of the Preyssler-type polyoxometalates, while Hu and Ren¹³⁴ present their theoretical studies of the electro-resistance and electro-optic properties of molecular ferroelectrics. Recently, intriguing topological vortex domain structure have been observed in organic ferroelectrics and organic-inorganic hybrid perovskite ferroelectrics^{37,135,136}, showing great potential as a reconfigurable electronic element for soft robotics, flexible and wearable devices and biomachines. Xiong et al¹³⁷ have proposed a concept of “ferroelectrochemistry” that focuses on the chemical design and performance optimization of molecular ferroelectrics. In this collection, Mu et al¹³⁸ present a brief summary of the design strategies and phenomenological theories behind this concept, which set a new trend for rational chemical synthesis over the next 100 years for ferroelectrics.

The science and technology of ferroelectric materials has undergone enormous development in the last 100 years, leading to huge diversity of material forms and types, a wide variety of useful properties and a world-market for materials and devices that is expected to reach close to US\$100 billion in this decade. The papers in this collection offer a fascinating snapshot of the topic and an invaluable perspective on where the subject is going. The editors hope that the readers of this collection will agree that the topic of ferroelectric materials is as interesting and exciting as it has ever been over the last 100 years and shows no signs of running out of steam.

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