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Comment on "Self-diffusion in high-purity α-Al$_2$O$_3$: Comparison of Ti-doped, Mg-doped and undoped single crystals" P. Fielitz, S. Ganschow, K. Klemens, and G. Borchardt, J. Eur. Ceram. Soc., **41**, (2021), 663-668.

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In the article by Fielitz *et al.*, the authors report measurements of oxygen and Al self-diffusion in carefully grown sapphire single crystals, either un-doped or containing 37 or 66 wt. ppm Mg, or 263, 593, or 1100 wt. ppm Ti, using ^{18}O or ^{26}Al isotopic tracers. [1] Surprisingly, the authors found no effect of either aliovalent dopant on oxygen self-diffusion. On the other hand, Mg-doping reduced Al diffusivity compared to un-doped crystals. While it proved difficult to provide a quantitative estimate of the reduction, it was thought to be about two orders of magnitude. Al diffusivity increased with increasing Ti content, up to one order of magnitude for the highest dopant level, 1100 wt. ppm.

In their discussion of the null effect of aliovalent doping

on oxygen diffusivity, the authors appeal to quite old computer simulations of defect formation energies in doped crystals (their refs. [5], [22] and [23], cited here as refs. [2] to [4]) in an effort to rationalize their data and that of others (their refs. [9], [20] and [21], cited here as refs. [5] to [7]). The cited simulations [2-4] are based on classical interatomic potentials; however, they ignore more recent and more accurate DFT simulations of defect formation energies in Al_2O_3 (see refs. [8] to [10]). The 2020 publication of Futazuka *et al.* [10] is particularly relevant, as it reports DFT calculations of point-defect energetics and the charge states of Group II impurities in Al_2O_3, including Mg, for both oxygen-rich and oxygen-poor environments. Based on ref. [10], we have calculated [11] the formation energies and concentrations of point defects at 1400°C in a hypothetical pristine Al_2O_3 crystal and one doped with 252 wt. ppm of Mg (1.8×10^{19}/cm^3). However, whereas ref. [10] provided formation energies for Mg-containing defects under the condition of equilibrium with $MgAl_2O_4$, we treated the chemical potential μ_{Mg} as a control variable in our calculations and varied it until the target concentration of 252 wt. ppm is reached. For the pristine crystal under oxygen-rich conditions, the concentrations of singly charged and doubly charged oxygen vacancies (V_O^{1+} and V_O^{2+}, respectively), Al vacancies (V_{Al}^{3-}), Al interstitials (Al_i^{3+}) and the $(V_O.V_{Al})^{1-}$ vacancy complex are 1.3×10^9/cm^3, 1.0×10^{11}/cm^3, 7.1×10^{10}/cm^3, 2.4×10^8/cm^3 and 1.1×10^9/cm^3, respectively. For the Mg-doped crystal, the concentrations at 1400°C of

isolated defects that could mediate self-diffusion, Al_i^{3+} and V_O^{2+}, are $1.8 \times 10^{17}/cm^3$ and $0.9 \times 10^{17}/cm^3$ respectively. The most numerous defect is actually the Mg substitutional defect (Mg_{Al}^{1-}) at a concentration of $1.2 \times 10^{19}/cm^3$; surprisingly, isolated Al vacancies are present in only miniscule amounts.

The surprising fact that the concentrations of the defects that could mediate self-diffusion in Al_2O_3, namely Al_i^{3+} and V_O^{2+}, are so much smaller than the Mg dopant concentration arises because the increase in negative charge due to Mg ions on Al lattice sites (Mg_{Al}^{-1}) is largely self-compensated by positively charged Mg interstitials (Mg_i^{2+}) at a concentration of 4.7×10^{18} cm^{-3}, which compensates 80% of the negative charge. This constitutes a very effective "buffering" of the point defect population, thereby greatly reducing self-diffusion in Mg-doped Al_2O_3 from what otherwise would be expected. We return to this point below but note that a number of other questions remain concerning self-diffusion in Al_2O_3 – the "corundum conundrum"! [12]

But there is more to be said about self-diffusion kinetics in Al_2O_3. The effects of the aliovalent solutes Mg^{2+} and Ti^{4+} on oxygen lattice diffusion have been studied by one of us in the past [5], and an easily measurable effect of such doping on oxygen diffusivity was found. The technique used was admittedly indirect, but the conclusions that Mg-doping enhances and Ti-doping attenuates oxygen diffusivity compared to that in un-doped crystals appear to be robust. It

is thus appropriate to briefly review the technique used to measure oxygen diffusivity.

Pletka, Mitchell and Heuer in 1982 [13] made a detailed TEM study of the dislocation debris in un-doped, Mg-doped, Cr-doped and Ti-doped sapphire deformed by basal slip at temperatures of 1500–1520°C. The features of interest to the present discussion are small prismatic dislocation loops, which form from breakup of dislocation dipoles, themselves formed by trapping of edge dislocations on parallel glide planes. The loops so produced then annihilate at a rate controlled by the self-diffusion kinetics.

The evolution of the debris structure for the *isovalent* Cr^{3+} and Ti^{3+} dopants was similar to that for un-doped crystals, whereas that for samples doped with the *aliovalent* Mg^{2+} and Ti^{4+} solutes was distinctly different. In particular, very few loops were present in the Mg^{2+}- doped samples, whereas prominent strings of loops were present in the Ti^{4+}-doped crystals but only at small strains. Lagerlöf, Mitchell and Heuer in 1989 [5] then determined the diffusivities of the rate controlling species, assumed to be oxygen, as revealed by the loop shrinkage data in un-doped, Mg^{2+}-doped, and Ti^{4+}-doped crystals. (There is universal agreement in the ceramic science community [14] that oxygen, rather than Al, is the slower diffusing species in single crystals and thus rate controlling for any high temperature diffusion-controlled process in single crystals, such as shrinkage of prismatic dislocation loops.)

TEM foils prepared from crystals deformed at 1400°C to about 5% plastic strain were annealed *ex situ* in the temperature range 1200-1500°C. [5] The shrinkage rates of individual loops sequentially annealed were then used to determine the rate-determining (oxygen) diffusivities. The oxygen diffusivities for the un-doped crystals were in general agreement with tracer self-diffusion data (see Fig. 9a in ref. [9]), while the Mg-doped (Ti-doped) crystal showed an increase (decrease) in oxygen diffusivity by a factor of about 100 (50).

Heuer, in 2008 [14], surveyed the available literature on oxygen and Al diffusion in Al_2O_3 and concluded that there were eight major questions and issues that would constitute fitting subjects for additional research. Some of these have been resolved in the intervening years but several remain troublesome and are still worth exploring. More to the point, he pointed out that essentially all tracer studies of oxygen diffusion involve penetration depths ($x=(Dt)^{1/2}$) of 0.1 - 0.6 μm. They are thus susceptible to the extent of machining damage incurred during specimen preparation. Further, the issue of possible evaporation of MgO during the diffusion anneal was suggested to be responsible for the null result reported by Reddy and Cooper [6]. Unfortunately, this issue has not been considered in any detail in any of the oxygen tracer diffusion studies of Mg-doped crystals.

Neither the question of machining damage or of MgO evaporation should have been an issue in the loop annealing

experiments of Lagerlöf *et al.* [5]. They were able to determine the very small values of the diffusion depth x (=$(Dt)^{1/2}$) because of the good resolution of TEM. And by employing relatively low annealing temperatures they could assume that when a dislocation loop emitted a vacancy (or absorbed an interstitial), point defect equilibrium was readily reestablished in times short compared to the duration of the diffusion anneal.

Lagerlöf *et al.* attempted, unsuccessfully, to use traditional point defect notions to rationalize their activation energy data – 6.1 (± 0.2) eV, 5.8 (± 0.4) eV, and 7.0 (± 0.4) eV for un-doped, Mg^{2+}-doped, and Ti^{4+}-doped crystals, respectively. They therefore suggested that some form of solid state "buffering" must be present to rationalize their data, and as already discussed, it now seems clear that buffering arises in the case of Mg-doping from self-compensation due to Mg interstitials.

The situation with regard to Ti^{4+}-doping is more complex. The possible charge-compensating isolated defects for the aliovalent Ti^{4+} dopant are Al vacancies, V_{Al}^{3-}, and oxygen interstitials, O_i^{2-}. The overwhelming belief in the ceramic science community when considering Ti-doping, usually citing simulations based on classical interatomic potentials, including that in ref. [1], is that it is the Al vacancy. Further, the most recent DFT-based study of isolated defects and defect complexes in Ti-doped Al_2O_3 only considered systems containing Al vacancies [15]. However, Phillips,

Mitchell and Heuer in 1980 [16], studied the precipitation of TiO_2 precipitates in Ti-doped Al_2O_3 (star sapphire), in particular the chemical effects accompanying precipitation. Their atomic "bookkeeping" showed, surprisingly, that the charge-compensating defect accompanying Ti^{4+}-doping had to be an oxygen interstitial-type defect, rather than Al vacancies or defect complexes containing Al vacancies, in spite of the larger energy penalty associated with oxygen interstitials. They also provided precision lattice parameter data for an un-doped and a Ti^{4+}-doped crystal, and found that the lattice expansion for the relatively dilute Ti-doped crystal was much greater along the c-axis than along the a-axis. Phillips *et al.* thus suggested [16] that Ti^{4+}-doped crystals must contain Ti-oxygen interstitial defect complexes, elongated along the c-axis. We have not discovered any computer simulations exploring this possibility.

We now turn to the origin of the null effect of Mg- or Ti-doping on oxygen diffusivity reported by Fielitz *et al.* [1] They performed a 1650°C pre-annealing for 9 hrs. to remove polishing damage, a further 1650°C pre-anneal for 48 hrs., appreciably longer than the duration of the tracer diffusion experiments, and the 1650°C $^{18}O_2$ 24 hr. tracer diffusion anneals themselves. We suggest that these heat treatments may have caused near-surface dopant evaporation, and thus the null result for dopant effects on oxygen diffusivity.

In summary, we still believe that Mg-doping enhances oxygen diffusivity by a factor of about 100 and retards Al

diffusivity by a like amount. On the other hand, Ti-doping attenuates oxygen diffusivity by a factor of about fifty and enhances Al diffusivity by a factor of about ten. How should these dopant effects be understood?

Firstly, the Al diffusion depth in the Mg-doped crystal, although less than the Al diffusion depths in the Ti-doped crystals, must have been sufficiently large that it included the region where the Mg dopant had not been depleted by evaporation. What then is the cause of the reduction of Al diffusivity by Mg-doping? Fielitz *et al.,* in a prior study [17], assumed the presence of Al interstitials as a dominant defect species, injected at the solid- liquid interface during crystal growth because of the low $p(O_2)$ present. In ref. [1], they speculate that the trapping of such Al interstitials into $(Mg_{Al}.Al_i)^{2+}$ defect clusters attenuate Al self-diffusion. However, a relevant observation, first reported by Reddy and Cooper [6] and further discussed by Heuer [14], is that non-Fickian oxygen diffusion was observed in a number of crystals of varying provenance. Such non-Fickian behavior could be eliminated by annealing prior to the ^{18}O diffusion exchange, and was not sensitive to the dislocation content of the crystals used for these experiments. We suggest that the non-equilibrium defects posited by Fielitz *et al.* [1, 17] may be the cause of the non-Fickian diffusion reported by Reddy and Cooper in their as-received crystals. However, the extensive annealing prior to the $^{18}O_2$ diffusion anneals would have restored point defect equilibria, in which case the proposed formation of $(Mg_{Al}.Al_i)^{2+}$ defect clusters due to a

non-equilibrium concentration of Al_i^{3+} point defects could not be the cause of the reduced Al diffusivity on Mg-doping. What then is the correct explanation?

Chemical analysis of the un-doped crystal reported in Table 2 in ref. [1] reveals a slight excess of Si and P compared to K and Ca. (Na and Cl are present in equal amounts.) This crystal thus has a slight excess of positively charged impurities which will enhance the concentration of V_{Al}^{3-}, and thus enhance Al diffusivity, compared to what might be observed in a pristine crystal. The attenuation of Al diffusivity on Mg-doping follows naturally.

Regarding the effect of Ti-doping on Al diffusivity, we note that the effect is quite modest, an order of magnitude increase for a dopant level of about 1100 wt. ppm. [1] Clearly, some type of buffering must also be occurring in the case of Ti-doping but the exact buffering mechanism must still be elucidated. There clearly is much still to be learned about aliovalent dopant effects in Al_2O_3.

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