Grain boundary Complexion and Transparent Polycrystalline Alumina from an Atomistic Simulation Perspective

Abhishek Tewari, Paul Bowen

*Laboratory of Powder Technology, Institute of Materials Science, École Polytechnique Fédérale de Lausanne EPFL, CH-1015
Lausanne, Switzerland*

Abstract

Transparent alumina is often processed with sintering additives such as, Y, La, Mg, in order to limit its grain growth at high sintering temperatures. Usually, these additives segregate to the grain boundaries due to their larger cationic size than Al and low solubility in bulk α -alumina. The grain boundary excess of these additives plays a key role in determining stable grain boundary complexions and thereby, the grain growth characteristics of the polycrystalline alumina. In the current work, the grain boundary segregation of trivalent (Y, La) as well as bivalent (Mg) dopants on several alumina grain boundaries was simulated using the force field based energy minimization method. Calculated segregation energy plots and atomistic structure analysis, for the case of trivalent dopants, suggest that there is a critical concentration (3-4 atoms/nm²) for achieving the lowest mobility monolayer grain boundary complexion. The bivalent dopant Mg plays a role in grain boundary complexion through creating ordered arrays of oxygen vacancies at the grain boundary and helps create the space for the easier occupation of the grain boundary cationic sites by the trivalent dopants in case of codoping. It was also observed that the twin grain boundaries are more preferable in comparison to general high angle grain boundaries to obtain monolayer complexions, which are necessary for limiting grain growth. The use of atomistic simulations can thus guide the experimentalist towards optimum dopant concentrations to better control ceramic

- 22 microstructures. In a more general sense the possibility of second phase formation or an incipient
- 23 second phase for high grain boundary concentrations >8 cations/nm² is briefly discussed.

1. Introduction

It is well established in the literature that nearly fully dense (>99.99%) alumina ceramics with submicron size grains (<500 nm) are required for obtaining high transparency [1] (i.e with real in-line transmittance (RIT) greater than 80%). Transition element oxides (Y_2O_3 , La_2O_3) are often used as sintering additives for the processing of transparent polycrystalline alumina [2,3] The bigger size cation additives segregate to the grain boundaries and limit the grain growth in the final stages of high temperature sintering due to the solute drag effect.

The aim of the processing experts is to increase the grain boundary excess of the dopants as much as possible in order to maximize the solute drag effect without causing a second phase precipitation, as a second phase will become another source of light scattering at the grain boundaries. The grain boundary excess of the dopants also plays a role in determining the stable grain boundary complexions, which determine the grain boundary mobility [4]. At the dopant levels below the solubility limit, microstructure evolution is strongly dominated by the grain boundary complexions, while it is controlled by second phase precipitation at higher concentrations [5]. According to the Dillon-Harmer complexion experiments [6], monolayer complexions are most effective in reducing the grain boundary mobility in alumina ceramics, and higher order grain boundary complexions (bilayer and above) lead to higher grain boundary mobility and thereby higher grain growth. Therefore, an optimum concentration is required in order to maximize the solute drag effect while maintaining the favorable monolayer complexion.

Lallement et al. [7] reported an optimum Zr and La concentration for minimizing the grain growth and maximizing the real in-line transmittance in polycrystalline alumina. Stuer et al. [3] also showed that the highest transparency is obtained in transparent alumina at an optimum concentrations of Y and La dopants. The optimum concentration has been observed to be dependent on both the valence as well as the ionic size of the dopants [3,7–9].

One of the methods to characterize the grain boundary complexions is to measure the grain boundary segregation layer thickness, which is a characteristic property of grain boundary complexions [10]. Segregation layer thickness is generally of the order of couple of nanometers at the doping levels generally used for transparent polycrystalline alumina [10]. Atomic level resolution is required for the experimental characterization of the grain boundary complexions, which is not a trivial task even with the highly advanced microscopy techniques. Analytical models [11,12] based on the diffuse interface model and the lattice gas model have also been proposed to simulate the grain boundary phase diagrams.

With the rapid increase in computational power, the simulation of relatively large groups of atoms like grain boundaries has become possible using atomistic modeling methods. Frolov et al. [13,14] simulated the grain boundary complexion transitions as a function of temperature and defect concentration in the metallic systems using an improvised molecular dynamics method. Sun et al. [15] simulated grain boundary complexions in TiO_2 using first principle energy minimization of grain boundary structures. Although such atomistic simulation approach has not been applied yet in the ceramic systems to study the grain boundary complexions transitions, there are plenty of previous studies which have used atomistic modeling methods to study the grain boundary segregation in alumina systems using both ab-initio methods [16–19] and force field based methods from our group [20–22].

In the present work segregation of single dopants as well as codopants has been simulated using the force field based energy minimization method. The segregation energy plots in combination with the atomistic structure analysis showed the grain boundary complexion transitions as a function of grain boundary excess of dopants for trivalent dopants. Useful insights were also gained on the role of bivalent dopants in the codoped polycrystalline alumina complexions. The sometimes high grain boundary

concentrations observed in the simulations are discussed with reference to possible second phase formation.

2. Computational Method

Born model for solids was used to calculate the zero Kelvin energy of segregated grain boundaries. The inter-atomic potential between the atoms was represented by long range electrostatic potential and short range Buckingham potential. The polarizability of oxygen atoms was taken into account using the core-shell potential proposed by Dick and Overhauser [23]. The potential parameters developed by Lewis and Catlow [24] were used in the present work for energy calculations. The crystal structure of alumina was taken from the work of Liu et al. [25] The current force field has been shown to reproduce atomic positions within 3% error for (01.2) and (00.1) grain boundaries calculated using ab-initio methods[26]. One of the limitations of the energy minimization method is that it does not take into account the segregation entropy, which can play an important role at higher temperatures. But Harding et al. [27] showed that the contribution of vibrational entropy is negligible even at 1200 °C.

The computational method will be described only briefly here due to the space constraints. Readers are requested to refer to our previous papers for the computational details of the segregation energy calculation of single doping [26] and codoping [22] on twin grain boundaries and the general grain boundary [20]. Force field based energy minimization method was used to calculate the energy of the segregated grain boundaries. Segregation energies were calculated for single dopants and codopants on a total of 8 twin grain boundaries. One of the general grain boundary observed in our TEM studies [20] of the Y-La codoped transparent alumina samples was chosen for the simulation of the general grain boundary. General grain boundary cell was simulated using the near coincident site lattice approach [28]. Segregation energies were calculated for ~150 dopant configurations on twin grain boundaries and 30 configurations for general grain boundary. The minimum segregation energy of all the calculated dopant

configurations was taken to plot the segregation energy as a function of dopant concentration. Galmarini et al. [22] also showed in their Monte Carlo based calculations that the average segregation energy at a given concentration lies very close to the minimum segregation energy given by the current energy minimization approach.

3. Results and Discussion

3.1. Trivalent Dopants

3.1.1. Segregation energy curves

Figure 1 shows the La segregation energy plots for low energy and high energy grain boundaries separately, which show two different types of behavior. Segregation energy plots of Y as well as La-Y codoping show a similar behavior [22]. On one hand, the segregation energy reduces continuously at low concentrations for low energy grain boundaries and then slightly increases again before decreasing very slowly. It shows a minimum at a concentration of $\sim 6-8$ atoms/nm². On the other hand, segregation energy of high energy grain boundaries increases at low concentrations and then becomes more or less constant at higher dopant concentrations. We believe the behavior of low energy grain boundaries is due to the close packed nature of these grain boundaries. As the dopants segregate to the grain boundary, they create a disorder in the grain boundary structure and make it easier for the further segregation of dopant atoms, whereas the high energy grain boundaries already have enough disorder for the easier accommodation and thus segregation of larger sized dopants.

The common characteristic of the segregation energy plots of trivalent dopants (La, Y) for high energy grain boundaries, despite a certain amount of noise, is a possible discontinuity in the slope of the curve at an interface dopant concentration of $\sim 3-4$ atoms/nm² before becoming more or less constant at higher concentrations ($\sim 6-8$ atoms/nm²). As shown earlier in the literature [10], a discontinuity in the

slope would suggest a grain boundary complexion transition. To confirm these observations the atomic structures of the minimum energy configurations of the single doped and codoped twin and general grain boundaries were analyzed in more detail and are discussed in the next section.

The possibility of the higher grain boundary concentrations and sometime ordered structures being layers with second phase-like properties has been previously discussed in some detail for both Y [26] and La [21]. For yttrium possible second phases, Y_2O_3 , $AlYO_3$ and $Y_4Al_2O_9$, were analysed with respect to their coordination numbers and mean atomic distances [26] but no close correspondence, in particular with the Y-Y distance were observed. For the La [21] no ordered structures are seen at the grain boundaries studied and segregation energies were grain boundary type dependent and minimum energies were found at quite high dopant concentrations up to 12 cations/nm². Again the coordination numbers and mean atom-atom distances were analysed for probable second phases, namely La_2O_3 , $LaAlO_3$ and $LaAl_{11}O_{18}$, but no clear trends were seen suggesting these layers were closely related to a particular crystal phase.

Figure 1. Segregation energy curves for La segregation at (a) low energy grain boundaries, and (b) high energy grain boundaries.

3.1.2. Complexion Transitions

Figures 2, 3 and 4 show the atomistic structure evolution of grain boundaries with an increasing grain boundary excess of the singly doped Y, La and Y-La codoped, 11.1 twin grain boundaries, respectively. The observed grain boundary complexions are similar to those were observed by Dillon et al. experimentally[29]. Initially the monolayer grain boundary complexion is observed for dopant

concentrations less than 3-4 atoms/nm². At higher dopant concentrations a grain boundary complexion transition occurs from a monolayer to a bilayer complexion. After the dopant concentration of ~6-8 atoms/nm², a grain boundary complexion transition occurs from bilayer to multilayer grain boundary complexion. These grain boundary complexion transitions are also suggested by the segregation energy plots in the form of a change in the slope. As the white rectangles in the figures show, the grain boundary width also increases with increasing dopant concentration, which also suggests a grain boundary complexion transition with the increasing dopant concentration.

Higher order multilayered grain boundary complexions are also observed at very high concentrations (13-14 atoms/nm²) in fig. 2f and fig. 3f. As discussed above, Galmarini et al. [21] showed that the grain boundary saturation concentration of La for high energy grain boundaries was sometimes as high as ~12 atoms/nm². The possibility of second phase precipitation was checked [21,26], and as discussed above the calculated coordination numbers and bond lengths did not confirm any second phase formation. There might, however be a possibility that although these multilayered grain boundary complexions are not due to second phase precipitation, they might be incipient second phases, which could precipitate at higher temperatures during sintering. Since the present simulations are done at 0 K, there is a very high possibility that the second phases will not be visible in these simulations. In the case of codoping the formation of such high concentration grain boundary layered structures with organized interfaces similar to the glassy grain boundary phases of silicate, calcium silicate and calcium alumino-silicates previously studied by molecular dynamics [30–32] is possible. To better characterize these high concentration complexions to see if they are incipient second phases or glassy like structures molecular dynamic simulations at higher temperatures should be carried out using the structures determined by our energy minimization approach.

Figure.2. Grain boundary complexions at the (11.1) twin grain boundary with increasing grain boundary concentration of Y. (a) 1.9, (b) 2.9, (c) 3.9, (d) 4.8, (e) 5.8, and (f) 13.5 atoms/nm². The white rectangles are visual guides to get an idea of the segregation layer width as the grain boundary Y excess increases. All the grain boundaries are viewed parallel to the grain boundary plane. Y: green, O: red, Al: grey.

Figure 3. Grain boundary complexion transition at (11.1) twin grain boundary with increasing grain boundary concentration of La. (a) 1.9, (b) 2.9, (c) 3.9, (d) 4.8, (e) 5.8, and (f) 13.5 atoms/nm². The white rectangles are visual guides to get an idea of the segregation layer width as the grain boundary La excess increases. All the grain boundaries are viewed parallel to the grain boundary plane. La: blue O: red, Al: grey.

Figure 4. Grain boundary complexions in La-Y codoped (11.1) twin grain boundary with the increasing dopant concentration. a) 1.93, b) 3.86, c) 5.79, d) 7.72, e) 9.65, and f) 11.58 atoms/nm². The white rectangles are visual guides to get an idea of the segregation layer width as the grain boundary Y excess increases. All the grain boundaries are viewed parallel to the grain boundary plane. La: dark blue, Y: light blue, Al: pink, O: red.

Figure 5 shows the grain boundary complexions with the increasing dopant concentration of a Y-La codoped (01.2) low energy grain boundary. In this case, the monolayer grain boundary complexion is much more clearly defined. Monolayer complexions are the energetically most favorable until a dopant

concentration of ~ 6 atoms/nm², where a minimum in the segregation energy plot is also observed in figure 1. This monolayer to bilayer complexion transition concentration is higher for low energy twin grain boundaries. Therefore, probably the monolayer complexions are more stable at low energy twin grain boundaries in comparison to high energy twin grain boundaries. Bilayer complexions which are formed above this concentration have a layer of original crystal structure sandwiched in between, which are not similar to any of the proposed Dillon-Harmer complexions. To confirm this possible exotic behavior predicted by the simple energy minimization atomistic simulations, more sophisticated molecular dynamics simulations at higher temperatures need to be carried out. These structures could also be the precursors of second phase formation as the grain boundary cation concentrations are high which would again be shown in molecular dynamics simulations. Such special grain boundaries are expected low in numbers in real ceramic systems where they are expected to be about 1-5% of the total [33–36], So finding them experimentally may not be a trivial task - perhaps bi-crystal synthetic grain boundaries are needed if molecular dynamics simulations confirm our preliminary results.

Figure 5. Grain boundary complexions in La-Y codoped (01.2) grain boundary with the increasing dopant concentration. a) 5.7, b) 8.5, c) 11.4, d) 14.2, and e) 17.1 atoms/nm². The squares are visual guides to get an idea of the segregation layer width as the grain boundary Y excess increases. All the grain boundaries are viewed parallel to the grain boundary plane. La: dark blue, Y: light blue, Al: pink, O: red.

Atomistic structures of La-Y codoped general grain boundary are shown in figure 6. Bilayer complexions are formed at the general grain boundary at even lower concentrations, in contrast to the monolayer complexions observed on the twin grain boundaries at similar concentrations. However, these observation need to be confirmed further as the number of configurations simulated for each

concentration were limited to 30 due to the large size of the general grain boundaries and the associated increased computational expense.

Figure 6. Grain boundary complexions observed at the Y-doped general grain boundary (00.1)|| (01.3) with increasing Y concentration. (a) 0.8, (b) 1.6, (c) 2.4, and (d) 3.2 atoms/nm². Top plane is (00.1) and the bottom plane is (01.3). All the grain boundaries are viewed parallel to the GB plane. Y: light blue, Al: pink, O: red.

3.2. Bivalent Dopants

3.2.1. Mg Complexions

Due to the charge neutrality requirement, one oxygen vacancy needs to be introduced in the structure for every two Mg ions, which makes it necessary to put Mg ions only in the multiples of two. Although it was difficult to observe any gradient change in the segregation energy plot due to this limitation, atomistic structure analysis of the lowest energy Mg doped grain boundary configurations shows that the bilayer complexions are formed even at the lower concentrations of the Mg dopants (Figure 7). It suggests that the single doping with bivalent Mg ions may not be beneficial for the grain growth control in transparent ceramics. However, codoping with Mg-La and Mg-Y ions has been reported to be beneficial in comparison to singly doped Y or La doped alumina ceramics for grain growth control [3]. It was observed in our study that Mg plays a different role in the grain growth suppression in transparent polycrystalline alumina, which is discussed in the next section.

Figure 7. Grain boundary complexions at the (11.1) twin grain boundary with increasing grain boundary concentration of Mg. (a) 1.9, (b) 3.9, (c) 5.8, (d) 7.7, (e) 9.7, and (f) 11.6 atoms/nm². All the grain boundaries are viewed parallel to the grain boundary plane. Mg: green, O: red, Al: grey.

3.2.2. Vacancy Structures

The energetic probability of oxygen vacancy formation showed that ordered arrays of oxygen vacancies are more favorable. The oxygen vacancy arrays formed away from the grain boundary showed greater energetic probability. Figure 7 shows schematically the probabilities of different oxygen vacancy sites on 4 different grain boundaries. The oxygen vacancy positions with lighter (or whiter) color and smaller size are the ones with higher probabilities. One of the most prominent features of these probability plots is that the highest probability vacancy sites are not necessarily in the center of the grain boundary region. For (11.1) and (01.2) grain boundaries, the highest probably vacancy sites are located three atomic layers away from the center of the grain boundary region. In the case of (00.1) and (11.3) grain boundaries, the high probability oxygen vacancy sites are more distributed across the grain boundary region. There are a few sites at the grain boundary center which have the highest probability, but there are high probability sites away from the center also. Therefore, it can be concluded that there are high probability sites available away from the grain boundary. Since the creation of the oxygen vacancy provides extra space to accommodate the larger size cations, the presence of higher probability oxygen vacancy sites will mean that the oversized dopants can be accommodated away from the grain boundary also increasing the bulk solubility of the dopants. It provides an explanation to the earlier hypothesis based on the ab-initio study of Elsässer et al. [16] and the experimental observations of Song et al. [37], where they attributed the additional beneficial effect of codoping of alumina with Mg to its ability to redistribute the dopants in the bulk and increase the bulk solubility of dopants due to its charge compensation effect.

Levi-Setti et al. [38,39] also reported enhanced bulk solubility of glass forming impurities in alumina when codoped with Mg in their secondary ion mass spectrometry studies. They attributed the effect to a similar defect complex formation mechanism for the enhanced bulk solubility of glass forming impurities in alumina.

Figure 8. Energetic probabilities of oxygen vacancy formation at the grain boundaries. The sites with smaller and lighter color atoms have higher probability and darkest and largest one have the least possibility. All the grain boundaries are viewed parallel to the GB plane. Vacancies: Grey, Al: pink, O: red.

4. Summary and Conclusions

Combined analysis of the segregation energy plots as well as atomistic structures of the segregated grain boundaries shows that the most favorable monolayer grain boundary complexions are formed at low concentrations, while higher order grain boundary complexions are formed at higher concentrations for all the grain boundaries. The dopant concentration for the monolayer to bilayer complexion transition was observed to be higher for low energy twin grain boundaries (6-8 atoms/nm²) than high energy twin grain boundaries (3-4 atoms/nm²). Higher order grain boundary complexions are formed at even lower concentrations at general high angle grain boundaries in comparison to twin grain boundaries. Therefore, it can be concluded that having higher fraction of twin/special grain boundaries might help in improved grain growth suppression by having lower order grain boundary complexions, which can be further improved by having more low energy twins in the microstructure of transparent polycrystalline alumina. It was observed that codoping with Mg helps in accommodating the higher concentrations of the trivalent dopants in codoped alumina grain boundaries, which could help in producing higher solute drag effect, and thereby smaller grain growth. For higher cation concentrations at grain boundaries studied

there was no correspondence, coordination numbers and atom-atom distances, with probable second phases. However these could be incipient second phase configurations and further higher level simulations such as molecular dynamics need to be carried out to clarify our findings. However the overall trends for complexion seen from our atomistic simulations compare well with experimental observation for the alumina system and we believe can be a rich source of information to help guide the experimentalist towards dopant concentrations with desired grain boundary complexions for desired microstructural and macroscopic properties.

Acknowledgements

The authors would like to thank the Swiss National Science Foundation SNF Project No. 200020_144499 for financial support for part of the current work.

References:

- [1] M. Stuer, P. Bowen, M. Cantoni, C. Pecharroman, Z. Zhao, Nanopore Characterization and Optical Modeling of Transparent Polycrystalline Alumina, *Adv. Funct. Mater.* 22 (2012) 2303–2309. doi:10.1002/adfm.201200123.
- [2] N. Roussel, L. Lallemand, J.-Y. Chane-Ching, S. Guillemet-Fristch, B. Durand, V. Garnier, G. Bonnefont, G. Fantozzi, L. Bonneau, S. Trombert, D. Garcia-Gutierrez, Highly Dense, Transparent α -Al₂O₃ Ceramics From Ultrafine Nanoparticles Via a Standard SPS Sintering, *J. Am. Ceram. Soc.* 96 (2013) 1039–1042. doi:10.1111/jace.12255.
- [3] M. Stuer, Z. Zhao, U. Aschauer, P. Bowen, Transparent polycrystalline alumina using spark plasma sintering: Effect of Mg, Y and La doping, *J. Eur. Ceram. Soc.* 30 (2010) 1335–1343. doi:10.1016/j.jeurceramsoc.2009.12.001.
- [4] J. Luo, Developing Interfacial Phase Diagrams for Applications in Activated Sintering and Beyond: Current Status and Future Directions, *J. Am. Ceram. Soc.* 95 (2012) 2358–2371. doi:10.1111/j.1551-2916.2011.05059.x.
- [5] A.K. Lawrence, A. Kundu, M.P. Harmer, C. Compson, J. Atria, M. Spreij, Influence of Complexion Transitions on Microstructure Evolution in Specialty Aluminas, *J. Am. Ceram. Soc.* (2015) n/a–n/a. doi:10.1111/jace.13421.
- [6] S.J. Dillon, M.P. Harmer, Demystifying the role of sintering additives with “complexion,” *J. Eur. Ceram. Soc.* 28 (2008) 1485–1493. doi:10.1016/j.jeurceramsoc.2007.12.018.

299 [7] L. Lallemand, N. Roussel, G. Fantozzi, V. Garnier, G. Bonnefont, T. Douillard, B. Durand, S.
300 Guillemet-Fritsch, J.-Y. Chane-Ching, D. Garcia-Gutierrez, J. Aguilar-Garib, Effect of amount of doping
301 agent on sintering, microstructure and optical properties of Zr- and La-doped alumina sintered by SPS, J.
302 Eur. Ceram. Soc. 34 (2014) 1279–1288. doi:10.1016/j.jeurceramsoc.2013.11.015.

303 [8] N. Roussel, L. Lallemand, B. Durand, S. Guillemet, J.-Y.C. Ching, G. Fantozzi, V. Garnier, G.
304 Bonnefont, Effects of the nature of the doping salt and of the thermal pre-treatment and sintering
305 temperature on Spark Plasma Sintering of transparent alumina, Ceram. Int. 37 (2011) 3565–3573.
306 doi:10.1016/j.ceramint.2011.05.152.

307 [9] S.A. Bojarski, M. Stuer, Z. Zhao, P. Bowen, G.S. Rohrer, Influence of Y and La Additions on Grain
308 Growth and the Grain-Boundary Character Distribution of Alumina, J. Am. Ceram. Soc. 97 (2013) 620–
309 630. doi:10.1111/jace.12669.

310 [10] P.R. Cantwell, M. Tang, S.J. Dillon, J. Luo, G.S. Rohrer, M.P. Harmer, Grain boundary complexions,
311 Acta Mater. 62 (2014) 1–48. doi:10.1016/j.actamat.2013.07.037.

312 [11] M. Tang, W.C. Carter, R.M. Cannon, Diffuse interface model for structural transitions of grain
313 boundaries, Phys. Rev. B. 73 (2006) 024102. doi:10.1103/PhysRevB.73.024102.

314 [12] J. Luo, Grain boundary complexions: The interplay of premelting, prewetting, and multilayer
315 adsorption, Appl. Phys. Lett. 95 (2009) 071911. doi:10.1063/1.3212733.

316 [13] T. Frolov, D.L. Olmsted, M. Asta, Y. Mishin, Structural phase transformations in metallic grain
317 boundaries, Nat. Commun. 4 (2013) 1899. doi:10.1038/ncomms2919.

318 [14] T. Frolov, M. Asta, Y. Mishin, Segregation-induced phase transformations in grain boundaries,
319 Phys. Rev. B. 92 (2015) 020103. doi:10.1103/PhysRevB.92.020103.

320 [15] R. Sun, Z. Wang, M. Saito, N. Shibata, Y. Ikuhara, Atomistic mechanisms of nonstoichiometry-
321 induced twin boundary structural transformation in titanium dioxide, Nat. Commun. 6 (2015).
322 doi:10.1038/ncomms8120.

323 [16] C. Elsässer, T. Elsässer, Codoping and Grain-Boundary Cosegregation of Substitutional Cations in
324 γ -Al₂O₃: A Density-Functional-Theory Study, J. Am. Ceram. Soc. 88 (2005) 1–14.
325 doi:10.1111/j.1551-2916.2004.00056.x.

326 [17] I. Milas, B. Hinnemann, E.A. Carter, Structure of and ion segregation to an alumina grain
327 boundary: Implications for growth and creep, J. Mater. Res. 23 (2008) 1494–1508.
328 doi:10.1557/JMR.2008.0188.

329 [18] J.P. Bujan, K. Matsunaga, J. Chen, N. Shibata, W.Y. Ching, T. Yamamoto, Y. Ikuhara, Grain
330 Boundary Strengthening in Alumina by Rare Earth Impurities, Science. 311 (2006) 212–215.
331 doi:10.1126/science.1119839.

332 [19] Z. Wang, M. Saito, K.P. McKenna, L. Gu, S. Tsukimoto, A.L. Shluger, Y. Ikuhara, Atom-resolved
333 imaging of ordered defect superstructures at individual grain boundaries, *Nature*. 479 (2011) 380–383.
334 doi:10.1038/nature10593.

335 [20] A. Tewari, F. Nabiei, M. Cantoni, C. Hebert, P. Bowen, S.C. Parker, M. Stuer, Toward Knowledge-
336 Based Grain-Boundary Engineering of Transparent Alumina Combining Advanced TEM and Atomistic
337 Modeling, *J. Am. Ceram. Soc.* 98 (2015) 1959–1964.

338 [21] S. Galmarini, U. Aschauer, A. Tewari, Y. Aman, C. Van Gestel, P. Bowen, Atomistic modeling of
339 dopant segregation in α -alumina ceramics: Coverage dependent energy of segregation and nominal
340 dopant solubility, *J. Eur. Ceram. Soc.* 31 (2011) 2839–2852. doi:10.1016/j.jeurceramsoc.2011.07.010.

341 [22] A. Tewari, S. Galmarini, M. Stuer, P. Bowen, Atomistic modeling of the effect of codoping on the
342 atomistic structure of interfaces in α -alumina, *J. Eur. Ceram. Soc.* 32 (2012) 2935–2948.
343 doi:10.1016/j.jeurceramsoc.2012.02.056.

344 [23] B.G. Dick, A.W. Overhauser, Theory of the Dielectric Constants of Alkali Halide Crystals, *Phys. Rev.*
345 112 (1958) 90–103. doi:10.1103/PhysRev.112.90.

346 [24] G.V. Lewis, C.R.A. Catlow, Potential models for ionic oxides, *J. Phys. C Solid State Phys.* 18 (1985)
347 1149–1161. doi:10.1088/0022-3719/18/6/010.

348 [25] R.S. Liu, W.C. Shi, Y.C. Cheng, C.Y. Huang, Crystal structures and peculiar magnetic properties of
349 α - And γ -Al₂O₃ powders, *Mod. Phys. Lett. B*. 11 (1997) 1169–1174.

350 [26] S. Galmarini, U. Aschauer, P. Bowen, S.C. Parker, Atomistic Simulation of Y-Doped α -Alumina
351 Interfaces, *J. Am. Ceram. Soc.* 91 (2008) 3643–3651. doi:10.1111/j.1551-2916.2008.02619.x.

352 [27] P. Masri, P.W. Tasker, J.P. Hoare, J.H. Harding, Entropy of segregation of isovalent impurity
353 cations at the surface of an ionic crystal: MgO(100)Ca²⁺, *Surf. Sci.* 173 (1986) 439–454.
354 doi:10.1016/0039-6028(86)90201-3.

355 [28] T.X.T. Sayle, C.R.A. Catlow, D.C. Sayle, S.C. Parker, J.H. Harding, Computer simulation of thin film
356 heteroepitaxial ceramic interfaces using a near-coincidence-site lattice theory, *Philos. Mag. A*. 68 (1993)
357 565–573. doi:10.1080/01418619308213981.

358 [29] S.J. Dillon, M.P. Harmer, Multiple grain boundary transitions in ceramics: A case study of alumina,
359 *Acta Mater.* 55 (2007) 5247–5254. doi:10.1016/j.actamat.2007.04.051.

360 [30] S. Blonski, S.H. Garofalini, Molecular Dynamics Study of Silica–Alumina Interfaces, *J. Phys. Chem.*
361 100 (1996) 2201–2205. doi:10.1021/jp951798p.

362 [31] S. Blonski, S.H. Garofalini, Atomistic Structure of Calcium Silicate Intergranular Films in Alumina
363 Studied by Molecular Dynamics Simulations, *J. Am. Ceram. Soc.* 80 (1997) 1997–2004.
364 doi:10.1111/j.1151-2916.1997.tb03083.x.

- [32] S. Zhang, S.H. Garofalini, Molecular Dynamics Computer Simulations of the Interface Structure of Calcium–Alumino–Silicate Intergranular Films between Combined Basal and Prism Planes of α -Al₂O₃, J. Am. Ceram. Soc. 88 (2005) 202–209. doi:10.1111/j.1551-2916.2004.00035.x.
- [33] D. Bouchet, F. Dupau, S. Lartigue-Korinek, Structure and chemistry of grain boundaries in yttria doped aluminas, Microsc. Microanal. Microstruct. 4 (1993) 13 pages. doi:10.1051/mm:0199300406056100.
- [34] S. Lartigue, L. Priester, Influence of doping elements on the grain boundary characteristics in alumina, J. Phys. Colloq. 49 (1988) C5–451–C5–456. doi:10.1051/jphyscol:1988555.
- [35] S. Lartigue, L. Priester, Grain Boundaries in Fine-Grained Magnesium-Doped Aluminas, J. Am. Ceram. Soc. 71 (1988) 430–437. doi:10.1111/j.1151-2916.1988.tb05890.x.
- [36] J. Cho, H.M. Chan, M.P. Harmer, J.M. Rickman, Influence of yttrium doping on grain misorientation in aluminum oxide, J. Am. Ceram. Soc. 81 (1998) 3001–3004.
- [37] H. Song, R.L. Coble, Morphology of Platelike Abnormal Grains in Liquid-Phase-Sintered Alumina, J. Am. Ceram. Soc. 73 (1990) 2086–2090. doi:10.1111/j.1151-2916.1990.tb05272.x.
- [38] K.L. Gavrilov, S.J. Bennison, K.R. Mikeska, J.M. Chabala, R. Levi-Setti, Silica and Magnesia Dopant Distributions in Alumina by High-Resolution Scanning Secondary Ion Mass Spectrometry, J. Am. Ceram. Soc. 82 (1999) 1001–1008. doi:10.1111/j.1151-2916.1999.tb01866.x.
- [39] K.L. Gavrilov, S.J. Bennison, K.R. Mikeska, R. Levi-Setti, Role of magnesia and silica in alumina microstructure evolution, J. Mater. Sci. 38 (2003) 3965–3972. doi:10.1023/A:1026206414377.

Figure 1

Figure 2

Figure 3

(a)

(b)

(c)

(d)

(e)

(f)

Figure 4

Figure 5

(a)

(b)

(c)

(d)

(e)

Figure 6

(a)

(b)

(c)

(d)

Figure 7

(a)

(b)

(c)

(d)

(e)

(f)

Figure 8

(11.1)

(01.2)

(00.1)

(11.3)