***Ab Initio* Calculations of Pristine and Doped Zirconia $\Sigma 5$ (310)/[001] Tilt Grain Boundaries**

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The structure of the cubic-ZrO₂ symmetrical tilt $\Sigma 5$ (310)/[001] grain boundary is examined using density functional theory within the local density and pseudopotential approximations. Several pristine stoichiometric grain-boundary structures are investigated and compared with Z-contrast scanning transmission electron microscopy and electron energy loss spectroscopy results. The lowest-energy grain-boundary structure is found to agree well with the experimental data. When Y³⁺ is substituted for Zr⁴⁺ at various sites in the lowest-energy grain-boundary structure, the calculations indicate that Y³⁺ segregation to the grain boundary is energetically preferred to bulk doping, in agreement with experimental results.

I. Introduction

IT is well known that the addition of dopants such as Y₂O₃ allows the cubic polymorph of ZrO₂ to be retained down to room temperature;^{1,2} however, the mechanism by which the stabilization is achieved is not well understood.^{3–20} Consequently, ZrO₂ polymorphs, and yttria-stabilized-zirconia (YSZ), in particular, have been the subject of several experimental^{3–20} and theoretical^{21–35} studies. YSZ is a fast ion-conducting ceramic that is used in a number of applications, such as the electrolyte in oxygen gas separators and solid fuel cells.³⁶ Improvements in YSZ conductivity have been achieved over the last decade by reducing the number of impurities, the size distribution of the starting powders, and the amount of insulating phases formed at the grain boundaries during sintering.³⁷ Even in materials free from grain-boundary interphases, segregation of solute ions to the grain boundary is found to increase the grain-boundary resistivity.³⁸ Much attention has been focused, therefore, on the structure and properties of the grain boundaries in YSZ.

Recently, Dickey *et al.*³⁹ used Z-contrast scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to study the atomic structure and chemistry of the YSZ $\Sigma 5$ (310)/[001] symmetric tilt grain boundary. Cation column positions were obtained directly from the Z-contrast images within an experimental accuracy of ~ 0.02 nm. The EELS data indicated that the oxygen coordination at

the grain boundary is similar to its coordination in bulk YSZ, with O^{2–} ions residing in distorted tetrahedral sites in the grain boundary. Finally, Y³⁺ was shown to segregate to the $\Sigma 5$ grain boundary, in agreement with previous experimental studies on cubic^{38,40,41} and tetragonal^{42,43} YSZ. The spatial distribution of the segregation layer was confined to an area within 1 nm of the boundary plane. An atomic model of the grain boundary, consistent with the experimental data, was proposed, which serves as the basis for the current theoretical investigations. Fisher and Matsubara^{44,45} have previously studied the $\Sigma 5$ (310) YSZ grain boundary using molecular dynamics simulations with empirical potentials. The pure grain-boundary structures were studied at 1273–2673 K. The atomic model of the grain boundary was constructed by joining two (310) surfaces and removing redundant atoms. Relaxation of this structure introduced Schottky defects, both next to and along the grain boundary, resulting in partially filled cation and anion columns. The relaxed grain-boundary energy was calculated to be 0.17–0.18 eV/Å².

In this paper, the $\Sigma 5$ (310)[001] cubic ZrO₂ grain boundary is examined computationally in *ab initio* density functional theory calculations. Several pristine and Y³⁺-doped model structures are considered and compared with the experimental results of Dickey *et al.* and the computational results of Fisher and Matsubara. Grain-boundary energies and site-specific Y³⁺ segregation energies are calculated and the effect of Y³⁺ segregation on the grain-boundary energies is determined.

II. Computational Details

The computational approach is density functional theory using the local density approximation (LDA) combined with nonlocal, norm-conserving pseudopotentials, and plane wave expansions in the CASTEP (CAMbridge Sequential Total Energy Package) program.^{46,47} The calculations use the band-by-band conjugate gradient technique to minimize the total energy with respect to plane wave coefficients. Pseudopotentials of the Kleinman–Bylander^{48–50} representation are generated in real space using a well-established optimization scheme. The oxygen potential uses the reference atomic configuration $2s^2 2p^4$ for s and p angular momentum components. For the d component, $2s^1 2p^{1.75} 3d^{0.25}$ is used and the core radius is 1.8 a.u. The zirconium potential uses a configuration of s and d of $4d^2 5s^2$ and a p component of $4d^2 5s^{0.75} 5p^{0.25}$. Kerker construction⁵¹ is used for the s component and a core radius of 2.7 a.u. is used for s and p , whereas 2.5 a.u. is used for d . The yttrium potential uses $4d^1 5s^2$ for the s and d configurations and $4d^1 5s^{0.75} 5p^{0.25}$ for p . The core radius is 2.9 a.u. for s , 2.8 a.u. for p , and 2.5 for d . Brillouin-zone sampling is done using the lowest-order set of k -points⁵² and the plane-wave cutoff is 600 eV. The atoms in the unit cell are allowed to relax from their initial positions to lower the energy of the system, and the forces on the individual

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atoms, using the Broyden–Fletcher–Goldfarb–Shanno Hessian update method.⁵³ The energy per unit cell is converged to 0.00005 eV/atom and the residual forces to 0.1 eV/Å.

The effect of different energy cutoffs is tested on a bulk ZrO_2 unit cell. Table I compares the calculated bulk lattice constants and Zr–O distances to experimental values for cubic ZrO_2 . As the table shows, the LDA results are close to the generalized gradient approximation (GGA) results, in agreement with studies⁵⁴ that find that GGA does not give significantly different results for metal oxides such as TiO_2 and SnO_2 . However, other studies³¹ show that GGA must be used to obtain the correct energy differences between the various polymorphs of ZrO_2 , as it is well known that the LDA approach underestimates structural transition pressures.⁵⁵ Because this work focuses on various model grain-boundary structures in cubic ZrO_2 , the LDA approach is taken as it is less computationally expensive than GGA. In our calculations, the LDA results from cutoff energies <1000 eV are very similar to the GGA results at 600 eV, and the difference in energy between the different cutoffs is <0.5%. The calculated values in Table I also show good agreement with available experimental values, although it is recognized that the exact lattice parameter depends on the concentration of Y_2O_3 or other stabilizers² in agreement with Vegard's law.⁵⁶

The approach taken here is almost identical to that used by Christensen and Carter²⁹ in their study of the relaxation of ZrO_2 surfaces. Their study shows that the pseudopotentials used here correctly capture charge transfer in ZrO_2 but overstabilize the cubic phase of pure ZrO_2 relative to the monoclinic and tetragonal phases. As this study focuses only on cubic- ZrO_2 , this overstabilization of one phase relative to the others should not have a significant effect on the results.

III. Model Development

The grain-boundary models used here are constructed from pure cubic ZrO_2 unit cells, which are metastable. In Christensen and Carter's study,²⁹ the surface energy anisotropy was an important key to the detailed understanding of the depression of the tetragonal-monoclinic phase transition temperature in small particles, where surface energetics can dominate bulk stability preferences. Because of the orientational relation between tetragonal and monoclinic phases, stable tetragonal surfaces are forced to transform into less stable monoclinic surfaces, effectively corresponding to a higher surface energy of the monoclinic surfaces. However, in this study the cubic ZrO_2 is in a fully three-dimensional, periodic supercell structure and does not have the ability to transform into a more stable phase.

The Z-contrast STEM imaging technique used in Dickey *et al.*³⁹ directly reveals the projected cation sublattices constituting the interface. However, the positions of the anions are not shown explicitly and the only information available about them, from the EELS data, indicates they are in bulk-like positions. Therefore, the average cation coordinates taken from the experimental Z-contrast STEM images are used as the basis for the theoretical models used in this study. However, as discussed by Dickey *et al.*,³⁹ there is some uncertainty about the positions of the cations within the grain boundary that could be a result of the introduction of Schottky defects at the boundary. Therefore, one of the models has all the cation and anion columns

completely filled, whereas the others have varying arrangements of half-filled cation and anion columns or have combined two columns into one, as discussed later. The oxygen positions are chosen so that they are in environments as close as possible to that of bulk ZrO_2 (tetrahedral coordination).

Similar studies of SrTiO_3 grain boundaries find that the lowest energy structures are not stoichiometric.⁵⁷ There are indications that the YSZ grain boundaries are positively charged,^{57,58} which is further evidence that nonstoichiometric defects are present. However, in this work, stoichiometry is maintained in the grain-boundary models for simplicity, as is done by Dickey *et al.*³⁹ and Fisher and Matsubara.^{44,45} No rigid body translations such as have been examined in other similar grain-boundary systems⁶⁰ are considered in this study because none were observed experimentally. The dimensions of the supercell are set to the case of zero volume expansion normal to the interface, and the atoms are allowed to relax as the dimensions of the supercell remain fixed.

Five initial structures of the pure (310)/[001] ZrO_2 grain boundary are selected for computational studies and are shown in Fig. 1. Every grain-boundary supercell contains two grain boundaries aligned in opposite directions to one another and separated by several Angstroms of bulklike ZrO_2 lattice. In model 1, the grain boundary is constructed in the simplest way by bringing together two (310) surfaces to form the grain boundary and removing the duplicated atoms that overlap one another. This is the coincident site lattice (CSL) model⁶¹ and is the same structure as that considered by Fisher and Matsubara.^{44,45} The obvious problem with this model is that some of the adjacent columns in the grain-boundary core are unrealistically close (the distance between the two closest Zr^{4+} columns is 1.64 Å, whereas, the bulk spacing between Zr^{4+} ions is 3.61 Å).

To alleviate the cation crowding in the grain-boundary core, in model 2 two Zr^{4+} columns and two O^{2-} columns at the grain boundary are half filled, which is equivalent to introducing Schottky defects into the structure as observed in the relaxed structure of Fisher and Matsubara.^{44,45} In model 3, different O^{2-} columns, which are closest to the half-filled Zr^{4+} columns, are half filled for evaluation of defect association. In model 4, model 3 is modified by combining the two half-filled Zr^{4+} columns to form a single Zr^{4+} column, as is done by Dickey *et al.*³⁹ Similarly, model 5 is constructed by combining the two half-filled Zr^{4+} columns from model 2. Note that models 4 and 5 are the two that are consistent with the experimental Z-contrast data and are, therefore, predicted to be the lowest energy structures.

To study the effect of grain-boundary/grain-boundary interactions that arise from the periodic boundary conditions, we calculate the energy of the grain boundaries as a function of the separation between them. Figure 2 shows these results for model 2. The figure indicates that the grain-boundary energy increases as the distance between the two grain boundaries increases, which indicates that there is a significant interaction between the grain boundaries that lowers the grain-boundary energy. Therefore, it is necessary to take into account this effect when calculating the grain-boundary energy. Figure 2 also shows that the effect is most significant for separations smaller than 10.43 Å. The need for an adequate separation between the grain boundaries is balanced with the need

Table I. Comparison of Calculated LDA and GGA Results to Each Other and to Experimental Data

Parameter	LDA at 600 eV cutoff	LDA at 800 eV cutoff	LDA at 1000 eV cutoff	GGA at 600 eV cutoff	Experimental data [†]
Lattice parameter (Å)					
Lattice constant	5.15	5.15	5.16	5.16	5.09
Zr–O length	2.23	2.23	2.24	2.24	2.21
Zr–Zr length	3.64	3.64	3.65	3.65	3.60
Energy/ ZrO_2 (eV)	956.39	959.52	961.13	961.07	

[†]Lattice parameters were extrapolated to 0 K in Ref. 35 from data taken from Ref. 62.

Fig. 1. The five grain-boundary models considered in this study are projected along the [001] tilt axis (top) and the orthogonal $[1\bar{3}0]$ axis (bottom). The gray spheres are the Zr^{4+} ions while the white spheres are the O^{2-} ions. See the text for a description of the differences between the models. In models 2–5 the circled atoms in the top view image represent half-filled columns.

Fig. 2. Plot of the grain-boundary energy versus the distance between the grain boundaries in the unit cell.

for a reasonable supercell size to decrease the computational effort involved in the calculations. Therefore, a supercell is used where the separation between the grain boundaries is 10.43 Å, which corresponds to position B in Fig. 2.

IV. Results and Discussion

(1) Pure $\Sigma 5$ (310)/[001] ZrO_2 Grain Boundaries

To select grain-boundary models for further in-depth investigation, we first calculate the energies of the grain boundaries without atomic relaxation. The grain-boundary energies are obtained from the following equation:

$$E_{\text{GB}} = \frac{(E_{\text{tot}} - nE_{\text{Bulk}})}{2A} \quad (1)$$

where E_{tot} is the total energy per grain-boundary supercell, E_{Bulk} is the ZrO_2 bulk energy per formula unit, n is the number of ZrO_2 units in the supercell, and A is the area of the grain-boundary plane in the supercell (the supercell contains two grain boundaries). The results for the five grain-boundary models considered in this study are summarized in Table II.

The calculations indicate that model 1 has the highest grain-boundary energy. Overall, model 2 and model 5, which have the same O^{2-} anion structure, have the lowest grain-boundary energies. The difference between these two structures is that the Zr^{4+} cation positions at the core of the boundary have different arrangements. Model 2 has two half-filled Zr^{4+} columns, whereas model 5 combines these two into a single Zr^{4+} column located midway between the positions of the original two columns. When the atoms in these two structures are allowed to relax, they produce almost the same relaxed geometry, shown in Fig. 3. The grain-boundary energies calculated from both relaxed models are the same within the computational accuracy of the method, as shown in Table II. This result is significant because models 2 and 5 have different starting Zr^{4+} arrangements at the grain boundary, but the average difference between atomic coordinates along the boundary

plane in the final relaxed models is only 2.7% for Zr^{4+} cations and 3.2% for O^{2-} anions. Whereas this is not proof that the relaxed structure shown in Fig. 3 is the global minimum for stoichiometric models of the grain boundary, it is strong evidence that this is a low energy structure.

In the calculations, the positions of the two O^{2-} columns that are half filled to maintain a stoichiometric structure are examined. One set of models (2 and 5) considers vacancies in the oxygen column positions that are closely spaced (1.64 Å) in the unrelaxed grain-boundary model to reduce the anion repulsion. The second set of models (3 and 4) considers oxygen columns adjacent to the partially filled Zr^{4+} columns to simulate possible interactions between the cation and anion vacancies. The calculations show that models 2 and 5 have the lowest energies, indicating that the vacancies prefer to reside in the closely spaced O^{2-} columns and not in the nearest neighbor sites to the cation vacancies.

All the unrelaxed grain-boundary energies are higher than the grain-boundary energies of Fisher and Matsubara,^{44,45} with the energies of models 2 and 5 showing the best agreement with their data. However, the grain-boundary energies of the relaxed model 2 and relaxed model 5 structures are significantly lower than that of Fisher and Matsubara. This difference is likely because of the fact that Fisher and Matsubara used an empirical potential that excludes self-consistent electronic effects available in *ab initio* calculations.

The distortion of the grain-boundary structure shown in Fig. 3 (from models 2 and 5) as it relaxes occurs mostly along the grain-boundary plane. The agreement with the experimental Z-contrast STEM image is good, as shown in Fig. 4, as the relative Zr^{4+} cation positions match the STEM image perfectly all along the boundary to within the accuracy of the experimental data. Overall, the calculations predict that the atoms along

Fig. 3. Model obtained from relaxing the atoms in models 2 and 5 (both models relax to the same structure shown in this figure). Letters correspond to the five different doping sites where Y^{3+} is substituted for Zr^{4+} .

Table II. Calculated Grain-Boundary Energies of the Five Initial Models of Pure (310)/[001] ZrO_2 Shown in Fig. 1

Model	Number of atoms	Grain-boundary energy (eV/Å ²)	Grain-boundary energy, relaxed (eV/Å ²)
1	144	0.4738 ± 0.0014	
2	132	0.2199 ± 0.0013	0.0449 ± 0.0013
3	132	0.3791 ± 0.0013	
4	132	0.3894 ± 0.0013	
5	132	0.2302 ± 0.0013	0.0449 ± 0.0013

Fig. 4. Overlay of the lowest energy, relaxed grain-boundary structure shown in Fig. 3 on the Z-STEM image obtained by Dickey et al.³⁹

the boundary move to the areas that have more free volume. The average movement is ~ 0.04 Å for Zr^{4+} cations and ~ 0.12 Å for O^{2-} anions at the grain boundaries in model 5 and ~ 0.08 Å for Zr^{4+} cations and ~ 0.12 Å for O^{2-} anions at the grain boundaries in model 2. In model 2, the largest displacements are made by cations in the half-filled Zr^{4+} columns, which move 0.8 Å to a central position.

Table III shows the free volume calculated for the five initial grain-boundary models. The free volume at the grain-boundary core is calculated by determining the volume within the grain-boundary core and subtracting the combined volume of the individual ions within this space, using covalent radii values of 1.42 Å for Zr^{4+} and 0.74 Å for O^{2-} . If the distance between the ions is < 1.5 Å, this space is not counted as part of the free volume. The free volume at the grain boundary is larger than in the bulk material (86.5 Å^3 per unit cell for bulk ZrO_2). In addition, the free volume data indicate that the free volume at the grain-boundary core decreases after relaxation. This is because atoms along the boundary move into the free space within the grain-boundary core to eliminate the strain associated with the grain boundary, because the free volume is associated with the internal strain through the elastic constants. Thus, the potential energy decreases as the free volume decreases. It should be noted that the free volume data correlate with the grain-boundary energies. Except for model 1, the models that have lower grain-boundary energies have lower free volume at the boundaries. In the case of model 1, although it has the lowest free volume compared with the other models, it has more atoms at the grain boundaries. The grain-boundary energy of model 1 is the highest because of the two Zr^{4+} columns that are too close to each other at the grain boundary. As will be discussed later, the free volume also has important consequences for grain-boundary segregation.

(2) Y-Doped $\Sigma 5$ (310)/[001] ZrO_2 Grain Boundaries

The experimental and theoretical evidence is mixed as to whether substituted Y^{3+} and O^{2-} vacancies interact strongly

and/or associate in YSZ. For example, some experimental studies find that O^{2-} vacancies are located at nearest-neighbor sites close to the cation dopants,^{12,14} whereas others find that the O^{2-} vacancies prefer to be near the Zr^{4+} ions, leaving the doping cation fully coordinated.^{13,15,17,19} Some simulations with empirical potentials find that O^{2-} ion vacancies occupy nearest neighbor sites to Y^{3+} dopant ions,²⁵ whereas some recent *ab initio* calculations indicate that vacancies occupy second nearest neighbor sites to the cation dopant ions.³⁰ Because of the small size of the unit cells in this study, doping is accomplished by substituting Y^{3+} for individual Zr^{4+} sites in the unit cell without including the corresponding O^{2-} vacancies needed to achieve electroneutrality. The justification for this is that we are interested in comparing relative substitution energies, and if we included the two Y^{3+} dopants and a corresponding O^{2-} vacancy needed for charge neutrality, the defect concentrations would be excessively high relative to experimental conditions. Furthermore, local electroneutrality need not be, and usually is not, maintained at ionic grain boundaries. However, it is recognized that the calculated segregation and substitution energies would be quantitatively different in the presence of O^{2-} vacancies.

The EELS data obtained for the experimental system³⁹ indicate that the concentration of Y^{3+} along the grain boundaries is ~ 9 at.% higher than inside the bulk. In the lowest-energy relaxed structure shown in Fig. 3, there are five possible substitution sites to be considered. Four sites reside along the boundary plane, whereas one is outside of the grain-boundary core in a more bulklike region of the unit cell. The positions of these substitution sites are indicated by the letters in Fig. 3. The segregation energy is equal to the difference in energy between this bulk substitution energy and the grain-boundary substitution energy.

The results of the calculations are summarized in Table IV and indicate that the segregation energy is highest (almost zero) in the bulk-like site E and much lower for all the grain-boundary sites. This is indicative of Y^{3+} grain-boundary segregation in YSZ. Within the boundary, site B has the lowest segregation energy relative to all other grain-boundary positions and is therefore the preferred segregation site. The reason for this is that the Y^{3+} ionic radius is 18% larger than Zr^{4+} , providing a driving force for segregation to sites with greater free volume to decrease the strain energy. Because site B has the highest free volume, it is most effective for reducing the strain and thus the total energy of the system. Therefore, these calculations agree with the published experimental results that report segregation of Y^{3+} to ZrO_2 grain boundaries.^{38–43} Any possible space-charge induced segregation, however, would not be captured in the calculations.

The effect of Y^{3+} doping on the grain-boundary structures is also considered. During relaxation of the Y^{3+} -doped structures, the O^{2-} ions nearest the Y^{3+} move the most in response to the substitution, and the average distances moved are listed in Table V. Because the diameter of the Y^{3+} ion is larger than the diameter of the Zr^{4+} ion, the neighboring O^{2-} ions generally move outward from the Y^{3+} -substituted site. This reduces the Zr—O bond lengths near the dopant ion. The O^{2-} ions move the most when Y^{3+} is placed into sites that are bulk-like, such as sites E and D. The O^{2-} ions move a negligible amount when placed in site B because of the free space surrounding the dopant ion.

These results agree qualitatively with the trends reported by Steele and Fender.⁷ However, the amount of movement is smaller

Table III. Free Volume (per Unit Cell) of the 36°ZrO_2 Grain Boundaries[†]

Model	Free volume (Å^3 per unit cell)
1	174.50
2	198.60
3	206.48
4	215.72
5	193.99
Relaxed 2 or 5	156.68

[†]Note: the total volume of the unit cell is 1639.21 Å^3

Table IV. Comparison of Segregation Energies for the Doped and Pristine Grain-Boundary Structures Shown in Fig. 3

Substitution Site	Segregation energy (eV/atom)
Site A	−9.87
Site B	−13.78
Site C	−4.30
Site D	−9.28
Site E	−0.08

Table V. Average Movement of Nearest-Neighbor O^{2-} Ions away from Doping Y^{3+} Ions When They Occupy the Sites Shown in Fig. 3

Site	Movement ($\text{\AA}$)
A	0.024
B	0.000
C	0.025
D	0.034
E	0.039

in the present calculations because they are performed at 0 K. Hence, doping will distort the lattice near the doped sites unless there is significant free volume around the site. For this reason, doping in YSZ occurs preferentially along the grain boundaries because more free volume is available there for the larger Y^{3+} ions. These results imply that when vacancies are introduced, the free volume of neighboring sites will also increase, thus stabilizing the doping of these neighboring sites. Stefanovich *et al.*²⁴ found that lattice distortion around vacancies is important to the stabilization of ZrO_2 by dopants. Thus, we conclude that including vacancies at the grain boundaries will increase the segregation of dopants to the grain boundary.

VI. Conclusions

In this paper density functional theory, using the local density approximation, is used to investigate the structure and energetics of the $\Sigma 5(310)/[001]$ grain boundary. Five pure grain-boundary models are constructed and the most energetically favorable model determined. The lowest energy models are relaxed and the resulting structures are found to compare extremely well with experimental Z-contrast image data. The segregation energies at the grain boundaries after Y^{3+} doping are also determined. The calculations indicate a preferred doping site that has the lowest segregation energy. Doping along the grain boundary is predicted to be preferred because there is more free volume there to accommodate the larger Y^{3+} cations than is available in the bulk.

References

- C. Pascual and P. Duran, "Subsolidus Phase Equilibria and Ordering of the System $\text{ZrO}_2\text{-Y}_2\text{O}_3$," *J. Am. Ceram. Soc.*, **66**, 23–27 (1983).
- A. Heuer and L. Hobbs, *Science and Technology of Zirconia*. American Ceramics Society, Westerville, Ohio, 1981.
- J. Howard, R. J. Hill, and B. E. Reichert, "Structures of the ZrO_2 Polymorphs at Room Temperature by High-Resolution Neutron Powder Diffraction," *Acta Crystallogr., Sect. B: Struct. Sci.*, **B44**, 116–20 (1988).
- H. Horiuchi, A. J. Schultz, P. C. W. Leung, and J. M. Williams, "Time-of-Flight Neutron Diffraction Study of a Single Crystal of Yttria-Stabilized Zirconia, $\text{Zr}(\text{Y})\text{O}_{1.862}$, at High Temperature and in an Applied Electric Field," *Acta Crystallogr., Sect. B: Struct. Sci.*, **B40**, 367–72 (1984).
- J. Faber, M. H. Mueller, and B. R. Cooper, "Neutron-Diffraction Study of $\text{Zr}(\text{Ca,Y})\text{O}_{2-x}$: Evidence of Differing Mechanisms for Internal and External Distortions," *Phys. Rev. B: Condens. Matter*, **17**, 4884–88 (1978).
- M. Morinaga, F. Frey, and H. Schultz, "X-ray Diffraction Study of $\text{Zr}(\text{Ca,Y})\text{O}_{2-x}$," *Acta Crystallogr., Sect. A: Found Crystallogr.*, **36**, 520 (1979).
- D. Steele and B. E. F. Fender, "The Structure of Cubic $\text{ZrO}_2\text{:YO}_{1.5}$ Solid Solutions by Neutron Scattering," *J. Phys. C: Solid State Phys.*, **7**, 1–11 (1974).
- W. L. Roth, R. Wong, A. I. Goldman, E. Canova, Y. H. Kao, and B. Dunn, "Structure of Additives in Beta Alumina and Zirconia Superionic Conductors," *Solid State Ionics*, **18–19**, 1115–19 (1986).
- N. Argyriou, M. M. Elcombe, and A. C. Larson, "A Neutron Scattering Investigation of Cubic Stabilized Zirconia (CSZ). I. The Average Structure of Y-CSZ ," *J. Phys. Chem. Solids*, **57**, 183–93 (1996).
- H. Morikawa, Y. Shimzugawa, F. Marumo, T. Harasawa, H. Ikawa, K. Tohji, and Y. Udagawa, "Local Structures around Y Atoms in Y_2O_3 -Stabilized Tetragonal ZrO_2 ," *J. Ceram. Soc. Jpn.*, **96**, 253 (1988).
- M. H. Tuilier, J. Dexpert-Ghys, H. Dexpert, and P. Lagarde, "X-Ray Absorption Study of the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ System," *J. Solid State Chem.*, **69**, 153–61 (1987).
- M. Weller, "Atomic Defects in Yttria- and Calcia-Stabilized Zirconia," *Z. Metallkd.*, **84**, 381–86 (1993).
- C. R. A. Catlow, A. V. Chadwick, G. N. Greaves, and L. M. Moroney, "EXAFS Study of Yttria-Stabilized Zirconia," *J. Am. Ceram. Soc.*, **69**, 272–77 (1986).

- B. W. Veal, A. G. McKale, A. P. Paulinkas, S. J. Rothman, and L. J. Nowicki, "EXAFS Study of Yttria Stabilized Cubic Zirconia," *Physica B+C (Amsterdam)*, **150**, 234–40 (1988).
- D. Komyoji, A. Yoshiasa, T. Moriga, S. Emura, F. Kanamaru, and K. Koto, "EXAFS Study of the Fluorite-Type Compounds in the Systems $(1-x)\text{ZrO}_{2-x}\text{YbO}_{1.5}$ ($0.18 \leq x \leq 0.5$) and $\text{Zr}_2\text{Ln}_2\text{O}_7$ ($\text{Ln} = \text{Tb, Dy, Ho, Er, and Yb}$)," *Solid State Ionics*, **50**, 291–301 (1992).
- P. Li, W. Chen, and J. E. Penner-Hahn, "X-Ray-Absorption Studies of Zirconia Polymorphs. I. Characteristic Local Structures," *Phys. Rev. B: Condens. Matter*, **48**, 10063–73 (1993).
- P. Li, W. Chen and J. E. Penner-Hahn, "X-Ray-Absorption Studies of Zirconia Polymorphs. II. Effect of Y_2O_3 Dopant on ZrO_2 Structure," *Phys. Rev. B: Condens. Matter*, **48**, 10074–81 (1993).
- P. Li, W. Chen, and J. E. Penner-Hahn, "X-Ray-Absorption Studies of Zirconia Polymorphs. III. Static Distortion and Thermal Distortion," *Phys. Rev. B: Condens. Matter*, **48**, 10082–89 (1993).
- P. Li, W. Chen, and J. E. Penner-Hahn, "Effects of Dopants on Zirconia Stabilization: An X-Ray Absorption Study. I. Trivalent Dopants," *J. Am. Ceram. Soc.*, **77**, 118–28 (1994).
- Z. R. Dai, Z. L. Wang, Y. R. Chen, H. Z. Wu, and W. X. Liu, "Local Ordering of Oxygen Vacancies in Cubic Zirconia (ZrO_2) Stabilized with Yttria (Y_2O_3) and Magnesia (MgO). I. Electron Diffuse Scattering Study," *Philos. Mag.*, **73**, 415–30 (1996).
- B. Sobolev, A. N. Varaksin, O. A. Keda, and A. P. Khaimenov, "Electronic Structure and Charge State of Oxygen Vacancies in Perfect ZrO_2 Crystals," *Phys. Status Solidi B*, **162**, 165–71 (1990).
- F. Shimojo, T. Okabe, F. Tachibana, M. Kobayashi, and H. Okazaki, "Molecular Dynamics Studies of Yttria-Stabilized Zirconia. I. Structure and Oxygen Diffusion," *J. Phys. Soc. Jpn.*, **61**, 2848–57 (1992).
- S. E. Kul'kova and O. N. Murzyzhnikova, "The Calculation of the Electronic Structure of Zirconium Dioxide in Cubic and Tetragonal Phases," *Physica B*, **192**, 284–90 (1993).
- V. Stefanovich, A. L. Shluger, and C. R. A. Catlow, "Theoretical Study of the Stabilization of Cubic-Phase ZrO_2 by Impurities," *Phys. Rev. B: Condens. Matter*, **49**, 11560–71 (1994).
- X. Li and B. Hafskjold, "Molecular Dynamics Simulations of Yttrium-Stabilized Zirconia," *J. Phys.: Condens. Matter*, **7**, 1255–71 (1995).
- G. A. Ol'kovic, I. I. Naumov, and O. I. Velikokhatnyi, "Band Structure of Cubic- ZrO_2 Containing Oxygen Vacancies and Calcium Ions," *J. Phys.: Condens. Matter*, **7**, 1273–82 (1995).
- H. Brinkman, W. Briels, and H. Verweij, "Molecular Dynamics Simulations of Yttria-Stabilized Zirconia," *Chem. Phys. Lett.*, **247**, 386–90 (1995).
- H. Okazaki, H. Suzuki, and K. Ihata, "A Possibility of the Oxygen Diffusion Enhancement in YSZ: A Molecular Dynamics Study," *Phys. Lett. A*, **188**, 291–95 (1994).
- A. Christensen and E. Carter, "First Principles Study of the Surfaces of Zirconia," *Phys. Rev. B*, **58**, 8050–64 (1998).
- G. Stapper, M. Bernasconi, N. Nicoloso, and M. Parrinello, "Ab Initio Study of Structural and Electronic Properties of Yttria-Stabilized Cubic Zirconia," *Phys. Rev. B*, **59**, 797–810 (1999).
- G. Jomard, T. Petit, A. Pasturel, L. Magaud, G. Kresse, and J. Hafner, "First-Principles Calculations to Describe Zirconia Pseudopolymorphs," *Phys. Rev. B*, **59**, 4044–52 (1999).
- K. Suzuki, M. Kubo, Y. Oumi, R. Miura, H. Takaba, A. Fahmi, A. Chatterjee, K. Teraishi, and A. Miyamoto, "Molecular Dynamics Simulation of Enhanced Oxygen Ion Diffusion in Strained Yttria-Stabilized Zirconia," *Appl. Phys. Lett.*, **73**, 1502–504 (1998).
- M. W. Finnis, A. T. Paxton, M. Methfessel, and M. v. Schilfgaarde, "Crystal Structures of Zirconia from First Principles and Self-Consistent Tight-Binding," *Phys. Rev. Lett.*, **81**, 5149–52 (1998).
- S. Fabris, A. T. Paxton, and M. W. Finnis, "Free Energy and Molecular Dynamics Calculations for the Cubic-Tetragonal Phase Transition in Zirconia," *Phys. Rev. B*, **63**, 94101 (2001).
- P. K. Schelling, S. R. Phillpot, and D. Wolf, "Mechanism of the Cubic-to-Tetragonal Phase Transition in Zirconia and Yttria-Stabilized Zirconia by Molecular-Dynamics Simulation," *J. Am. Ceram. Soc.*, **84**, 1609–19 (2001).
- N. Minh, "Ceramic Fuel Cells," *J. Am. Ceram. Soc.*, **76**, 563 (1993).
- D. Bingham, P. W. Tasker, and A. N. Cormack, "Simulated Grain-Boundary Structures and Ionic Conductivity in Tetragonal Zirconia," *Philos. Mag.*, **60**, 1–14 (1989).
- M. Aoki, Y. Chiang, I. Kosacki, L. Lee, H. Tuller, and Y. Liu, "Solute Segregation and Grain-Boundary Impedance in High-Purity Stabilized Zirconia," **79**, 1169–80 (1996).
- E. C. Dickey, X. Fan, and S. J. Pennycook, "Structure and Chemistry of Yttria-Stabilized Cubic-Zirconia Symmetric Tilt Grain Boundaries," *J. Am. Ceram. Soc.*, **84**, 1361–68 (2001).
- A. Winnubst, P. Kroto, and A. Burggraaf, "AES/STEM Grain Boundary Analysis of Stabilized Zirconia Ceramics," *J. Phys. Chem. Solids*, **44**, 955–60 (1983).
- L. Merkle, G.-R. Bai, Z. Li, C.-Y. Song, and L. J. Thompson, "High-Resolution Studies of Grain Boundary Structure in Yttria-Stabilized Cubic Zirconia Thin Films Grown by MOCVD," *Phys. Status Solidi A*, **166**, 73–89 (1998).
- M. R. Boutz, A. J. A. Winnubst, and A. J. Burggraaf, "Yttria-Ceria Stabilized Tetragonal Zirconia Polycrystals: Sintering, Grain Growth and Grain Boundary Segregation," *J. Eur. Ceram. Soc.*, **13**, 89–102 (1994).
- H. Ogawa, A. Yasuda, N. Shibata, Y. Ikumura, and T. Sakuma, "Segregation of Yttrium Ions to Domain Boundaries of Tetragonal Zirconia," *Philos. Mag. Lett.*, **77**, 199–203 (1998).
- J. Fisher and H. Matsubara, "Oxide Ion Diffusion along Grain Boundaries in Zirconia: A Molecular Dynamics Study," *Solid State Ionics*, **113–115**, 311–18 (1998).

- ⁴⁵J. Fisher and H. Matsubara, "Molecular Dynamics Investigations of Grain Boundary Phenomena in Cubic Zirconia," *Comput. Mater. Sci.*, **14**, 177–84 (1999).
- ⁴⁶M. Payne, R. Teter, D. Allan, T. Arias, and J. Joannopoulos, "Iterative Minimization Techniques for *Ab Initio* Total-Energy Calculations: Molecular Dynamics and Conjugate Gradients," *Rev. Mod. Phys.*, **64**, 1045–97 (1992).
- ⁴⁷V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatkaya, and R. H. Nobes, "Electronic Structure, Properties, and Phase Stability of Inorganic Crystals: A Pseudopotential Plane-Wave Study," *Int. J. Quantum Chem.*, **77**, 895–910 (2000).
- ⁴⁸L. Kleinman and D. M. Bylander, "Efficient Form for Model Pseudopotentials," *Phys. Rev. Lett.*, **48**, 1425–28 (1982).
- ⁴⁹J. S. Lin, A. Qteish, M. C. Payne, and V. Heine, "Optimized and Transferable Nonlocal Separable *Ab Initio* Pseudopotentials," *Phys. Rev. B*, **47**, 4174–80 (1993).
- ⁵⁰D. C. Langreth and M. J. Mehl, "Beyond the Local-Density Approximation in Calculations of Ground-State Electronic Properties," *Phys. Rev. B: Solid State*, **28**, 1809–34 (1983).
- ⁵¹G. P. Kerker, "Non-Singular Atomic Pseudopotentials for Solid State Applications," *J. Phys. C*, **13**, L189–L194 (1980).
- ⁵²H. J. Monkhorst and J. D. Pack, "Special Points for Brillouin-Zone Integrations," *Phys. Rev. B: Solid State*, **13**, 5188–92 (1976).
- ⁵³W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes: The Art of Scientific Computing*. Cambridge University Press, Cambridge, U.K., 1989.
- ⁵⁴J. Goniakowski, J. M. Holdender, L. N. Kantorovich, M. J. Gillan, and J. A. White, "Influence of Gradient Corrections on the Bulk and Surface Properties of TiO₂ and SnO₂," *Phys. Rev. B: Solid State*, **53**, 957–60 (1996).
- ⁵⁵J. E. Jaffe, J. A. Snyder, Z. Lin, and A. C. Hess, "LDA and GGA Calculations for High-Pressure Phase Transitions in ZnO and MgO," *Phys. Rev. B: Solid State*, **62**, 1660–65 (2000).
- ⁵⁶S. P. Terblanche, "Thermal-Expansion Coefficients of Yttria-Stabilized Cubic Zirconias," *J. Appl. Crystallogr.*, **22**, 283–84 (1989).
- ⁵⁷M. Kim, G. Duscher, N. D. Browning, K. Sohlberg, S. T. Pantelides, and S. J. Pennycook, "Nonstoichiometry and the Electrical Activity of Grain Boundaries in SrTiO₃," *Phys. Rev. Lett.*, **86**, 4056–59 (2001).
- ⁵⁸X. Guo, "Physical Origin of the Intrinsic Grain-Boundary Resistivity of Stabilized Zirconia: Role of the Space Charge Layers," *Solid State Ionics*, **81**, 235–42 (1995).
- ⁵⁹S.-L. Hwang and I.-W. Chen, "Grain Size Control of Tetragonal Zirconia Polycrystals Using the Space Charge Concept," *J. Am. Ceram. Soc.*, **73**, 3269–77 (1990).
- ⁶⁰S. B. Sinnott, R. F. Wood, and S. J. Pennycook, "*Ab-Initio* Calculations of Rigid-Body Displacements at the $\Sigma 5$ (210) Tilt Grain Boundary in TiO₂," *Phys. Rev. B: Solid State*, **61**, 15645–48 (2000).
- ⁶¹S. Ranganathan, "On the Geometry of Coincidence-Site Lattices," *Acta Crystallogr.*, **21**, 197 (1966).
- ⁶²P. Aldebert and J.-P. Traverse, "Structure and Ionic Mobility of Zirconia at High Temperature," *J. Am. Ceram. Soc.*, **68**, 34–40 (1985). □