

BRIEF COMMUNICATIONS

A Cluster-Modeling Study of the Structure of Yttria-Stabilized Zirconias

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The Zr and Y coordination polyhedra, as found in the room-temperature phases of their pure oxides, are used as building blocks in modeling the structures of yttria-stabilized zirconias (YSZ). It is found that, in order to obtain the right coordination geometry, three clusters of four Zr- and Y-based building blocks can be constructed. When Y building blocks are present in a cluster they form a couple, characterized by a common structural vacancy, a neutral defect which can be defined when an oxygen is missing with respect to the case of the Zr seven coordination in monoclinic zirconia. It is shown that this model fairly well justifies the experimental results obtained by others. In conclusion, this kind of cluster modeling is proposed as a general method for solving structural problems in other mixed oxides. © 1992 Academic Press, Inc.

The structure of the technologically important yttria-stabilized zirconia has been the subject of several X-ray, electron, and neutron diffraction studies, and various models for the possible oxygen distributions and corresponding displacements of the oxygen ions from the ideal fluorite sites have been proposed (1–13). All these models do not consider correlations which must exist between the geometries of the Zr- and Y-coordination polyhedra if the stabilizing effect of Y_2O_3 has to be understood. Thus the Zr and Y room-temperature coordination geometries (14) must be used in the generation of the fluorite-type structure, and this is performed in what follows. EXAFS results (5, 6) substantially support the hypothesis that, in YSZ, Zr is seven-coordinated and Y is six-coordinated. Here the basic hypothesis is implicitly made that,

during cooling which follows the preparation of YSZ samples, the presence of Y ions helps the Zr ions in obtaining the coordination number and geometry of the Zr ions in the ZrO_2 phase stable at room temperature (Baddeleyite). Thus, in the present study, coordination polyhedra of Zr and Y in the room-temperature structures of their oxides will be used as building blocks (see Fig. 1) in modeling the YSZ structures.

In Fig. 2 it is shown how coordination polyhedra of Y (I and II, Fig. 1) can generate the right coordination number (seven) for six neighboring Zr "building blocks." The Y_2O_3 content (7.5%), calculated for these models, is therefore the minimum compatible with the above-stated structural hypotheses. This result is in perfect agreement with that obtained experimentally for the lower limit of the stability range of the cubic phase (1, 7).

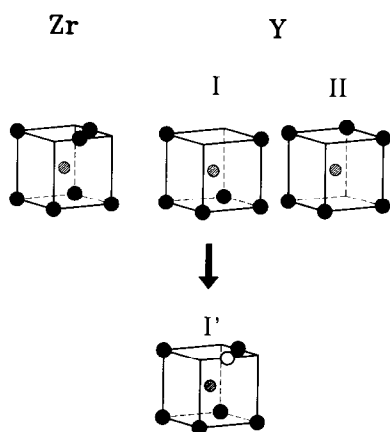


FIG. 1. Zr and Y idealized (with reference to the fluorite structure where the anions are distributed over the cube corners) building blocks as they exist in Baddeleyite for Zr and in the A_2O_3 -C type of structure for Y. In the latter case two possible coordinations exist (I and II) both with coordination number 6. In I two structural vacancies (for the meaning of this term, see the first paragraph) in the fluorite coordination are located at the corners defining the face diagonal of the ideal fluorite coordination cube, while in II two vacancies are located at the corners of the body diagonal (I). I' indicates the hypothesis of deformation of I generating a coordination geometry close to that of Zr in monoclinic ZrO_2 . Black circles represent oxygen ions, while the white circle indicates a structural vacancy.

Modeling of the latter structure can be performed by proper packing of the basic models in Fig. 2, as indicated in Fig. 3 for the case of Fig. 2a. Further increase of the Y_2O_3 content leads to local situations where two Y polyhedra are necessarily next neighbors, forming with two Zr blocks anyone of the three four-block clusters of Fig. 4a. The couple of Y building blocks is characterized by a common structural vacancy, a neutral defect which can be defined when an oxygen atom is missing with respect to the case of the Zr seven coordination in monoclinic zirconia. This common structural vacancy has already been proposed as a hypothesis by Steele and Fender (1) to justify their results of neutron scattering experiments and by Orera *et al.* (15). Figure 4b shows a structure

of composition intermediate between that of Fig. 3 (with the minimum Y_2O_3 content for cubic YSZ) and that of Fig. 4c (with a maximum Y_2O_3 content for our model). In the model of Fig. 4c, Zr and Y ions are located in the regular cation fluorite sites. The anions are distributed in layers of different structural types separated by $a/2$. In a first type the distribution is the same as that of CaF_2 , while the second type is constituted by a less dense distribution containing structural vacancies. It is worthwhile to note that also in other fluorite-related structures, as, e.g., that of Baddeleyite (9) and that of the vernier phases (16), the same sequences of layers of different density is present. Indeed, in the case of the latter phases, it is to these sequences of periodicity higher than that of the fluorite lattice that the appearance of superlattice peaks in the diffraction patterns was attributed (16). It is interesting that Suzuki *et al.* (8), after thermal treatment of a YSZ sample, found superlattice reflections in their electron diffraction patterns. The main feature of these models is that, independently from the composition, one has the same geometry for the distribu-

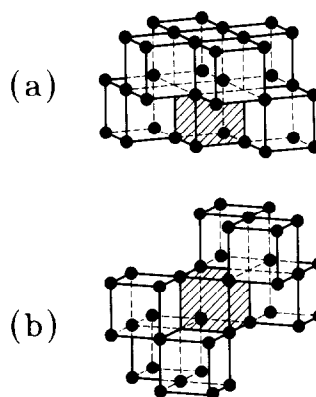


FIG. 2. Generation of coordination number seven for six neighboring Zr "building blocks" by polyhedra I and II of Y (Fig. 1). In (a) a model (C_{2v} symmetry) based on Y polyhedron I is shown and in (b) the model (C_{3v} symmetry) based on II is represented. In both (a) and (b) the Y polyhedra are dashed.

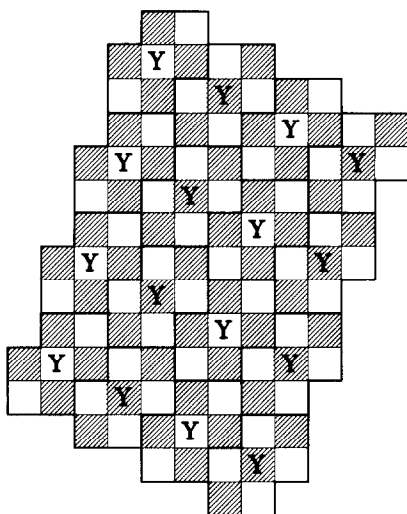


FIG. 3. Model of the Y_2O_3 7.5 mole% structure ($Zr_{0.86}Y_{0.14}O_{1.93}$) obtained by the packing of units of the basic model in Fig. 2a. While arbitrary, this choice is suggested by the fact that in the structure of Y_2O_3 (1) three-fourths of the coordination polyhedra are of the type shown in Fig. 2a.

tion of oxygen ions and structural vacancies inside each cluster (Fig. 4a). In the cluster three oxygen ions and one structural vacancy define a square centered at the internal corner of the cluster. Morinaga *et al.* (2, 3) studied the structure of these systems by X-ray diffraction methods. Note that our model fairly well justifies the difference electron density map obtained by them for $z = \frac{1}{4}$ and characterized by four peaks forming a square about the ideal anionic fluorite site. Those authors suggest that the observed effects are due to static displacements, as we propose with our models.

Inspection of the models in Figs. 3, 4b, and 4c gives the possibility of finding correlations between their structures and the conductivity properties of the materials having the same compositions. Note that, in order to keep the right coordination geometry in all the Zr blocks, it is necessary that any additional Y polyhedron (in Fig. 4b) share a structural vacancy with an already existing

(Fig. 3) Y building block, thus generating a cluster within which only small mobility is left to the oxygen ions. Indeed any O^{2-} shift from the positions indicated in the clusters (Fig. 4a) leads to a change in the Zr coordination geometry and thus to a decrease in local stability. The model in Fig. 3, containing no clusters, is the most open of the

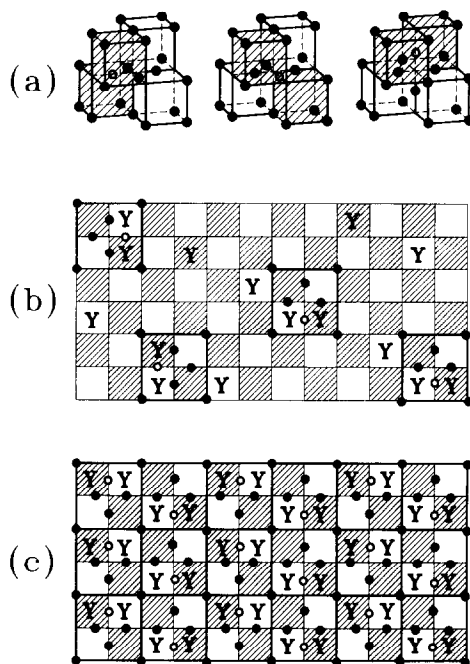
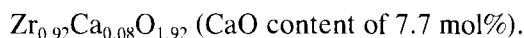


FIG. 4. (a) Three possible clusters of four Zr and Y building blocks (see Fig. 1). Black circles represent oxygen ions, while the white circle indicates a structural vacancy. The Y polyhedra are dashed. (b) Section, containing the less dense oxygen layer, for a structural model of composition intermediate between that of Fig. 3 and that represented in the following Fig. 4c. These model represents a situation in which four-block clusters (Fig. 4a) are formed when additional Y-blocks come close to others already existing in the structure of Fig. 3. (c) Section, containing the less dense oxygen layer, for a model obtained for a Y_2O_3 content of 33 mole%, when the criteria for the formation of clusters, as stated in the text, are taken into consideration. In building this model, for the sake of simplicity, we used only one type of cluster and therefore one can foresee that in the material with the same Y_2O_3 content the degree of order will be lower.

three models shown. It is interesting to note that, indeed, Ikeda *et al.* (4) found for this composition the highest value of conductivity for temperatures up to 1000°C. The results obtained by these authors indicated for the conductivity a monotonically decreasing behavior from the above-mentioned maximum value to the much smaller values observed for increasing Y₂O₃ content, in very good agreement with our predictions. Indeed, for the model in Fig. 4c we have a very closed structure and one may foresee for the corresponding YSZ material a very small value of the ionic conductivity.

In the case of CaSZ, analogous reasoning leads to the definition of different Ca coordination polyhedra. If the Ca ions are located in the cation fluorite sites their coordination number will be four instead of eight. Therefore a reasonable building block in this case will have vacancies located at the end of face diagonals. In this hypothesis the 12 Zr polyhedra surrounding the Ca building block will have seven coordination. The minimum Ca content consistent with this hypothesis is represented by the formula



This can be compared with the minimum Ca content experimentally found (2) in Zr_{1-x}Ca_xO_{2-x} for x = 0.1.

While in the case of Y₂O₃ there is only one face available for satisfying the Zr coordination requirements, in the case of CaO, all the faces have an equal opportunity of inducing the right coordination geometry for Zr, thus making modeling more difficult. However, in view of the difference electron density map obtained for CaSZ by Morinaga *et al.* (2), the oxygen distribution about the regular fluorite anion site should be very close to that already shown (Fig. 4) for YSZ.

In conclusion, this kind of cluster modeling may be used as a general method for

solving structural problems in other mixed oxides, especially in the presence of variable valency ions. This may be the case for HfO₂-Y₂O₃, showing very similar electron diffraction patterns (8).

Acknowledgments

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