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On the Extent of Ordering in Stabilized Zirconia

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The structure of crystals of calcia-stabilized zirconia is described in terms of a cubic matrix within which are coherently intergrown both microdomains of $CaZr_4O_9$ structure type and intragranular precipitates of monoclinic ZrO_2. The electrical properties of the material are considered in relation to the proposed microheterogeneous structure.

Introduction

Recently the existence of microdomains of the fluorite-related phase CaM_4O_9 ($M = $ Zr, Hf) in specimens of calcia-stabilized zirconia and hafnia was demonstrated (*1*). The microdomains varied in size from ~30 Å mean dimension upwards depending on their thermal history and, at least in the early stages of growth, were oriented with equal probability along the 12 equivalent $\langle 110\rangle_f$[1] directions of the parent crystal. This work elegantly overtook a contemporary suggestion (*2*) that diffuse scattered intensity from calcia-stabilized zirconia was so oriented within the reciprocal lattice that it probably derived from a short range ordering regime in which the $\langle 111\rangle_f$ directions were of primary significance.

The crystal structure of $CaHf_4O_9$ has subsequently been described (*3*) as a superstructure derived from the defect fluorite type by ordering of the cations and of the anion vacancies. An important feature of the structure is the linking of anion vacancies together into strings with a spacing of $\frac{1}{2}\langle 111\rangle_f$ sub cell vector.

As a result of the studies described in Refs. (*1*) and (*3*) a rather complete description of the structure of the microdomains in calcia-stabilized zirconia and calcia-stabilized hafnia is to hand. However the matrix region between the microdomains is less well characterized even though both parts of the crystal, and the relationship between them must be taken into account when consideration is given to the deterioration in conductivity with ageing (*4*).

The present paper suggests that information from both parts of the crystal (the microdomains and the matrix) is available in the diffraction patterns of stabilized zirconia. In addition the possibility is examined that similar microdomains, albeit with a local structure that must differ from that of $CaHf_4O_9$, may exist in other doped fluorite structure oxides.

Experimental

Specimens were prepared for electron microscopy either by crushing single crystals of calcia-stabilized zirconia or by ion-beam etching polished sections taken from massive polycrystalline ceramic.

All the specimens were air annealed at 1000°C for between 35 and 40 days before observation to reproduce the aged or "ordered" condition described by earlier workers (*4*). A specimen of the sample with lowest CaO content was treated to an additional 24 hours at 1600°C before cooling to room temperature

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[1] Indices used throughout refer to the fluorite substructure and are marked with a subscript f.

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in an hour in order to achieve the disordered state (*4*).

Samples were studied with different compositions within the range 10–20 mol% CaO. Each batch was analyzed for metal ion concentrations by an atomic absorption spectroscopic method (*5*).

Observations

Diffraction micrographs (Fig. 1) contained two distinct features in addition to the fluorite substructure reflections. These were patterns of diffuse scattered intensity and "extra" reflections forbidden by the fluorite structure symmetry. As mentioned previously (*2*) the two features appear coherent with the fundamental diffraction pattern and are believed to represent two additional types of order within a single crystal. Neither of the additional features suffered a positional change through the composition range but the relative intensities altered considerably. The diffuse scattering was weakest for the composition of lowest CaO concentration (Fig. 2a) and increased to its greatest intensity with the specimen of highest CaO concentration (Fig. 2b). The intensity of the "extra" reflections varied in the opposite sense; from a maximum at the lowest concentration of CaO, the intensity fell to a very low level at the highest CaO content (Fig. 2b).

The two features also behaved differently in their response to heat treatment. The specimen of lowest CaO content (and strongest extra reflections) quenched after spending 24 hours at 1600°C lost all trace of extra reflections but retained the diffuse scattering apparently unchanged (Fig. 2c). This is seen as a further indication that the two features derive from separate aspects of the structure.

Details of the specimens examined and a summary of the effects are given in Table I.

The "extra" reflections were always sharper than the diffuse scattering. The sharpness of neither feature altered significantly with composition.

Figure 3 is a bright field image of a grain from the 15 mol% CaO specimen showing structure (~50 Å features) similar to that observed during the microdomain study (*1*). Figure 4 is a dark field image of a crystal from the specimen containing 16 mol% CaO

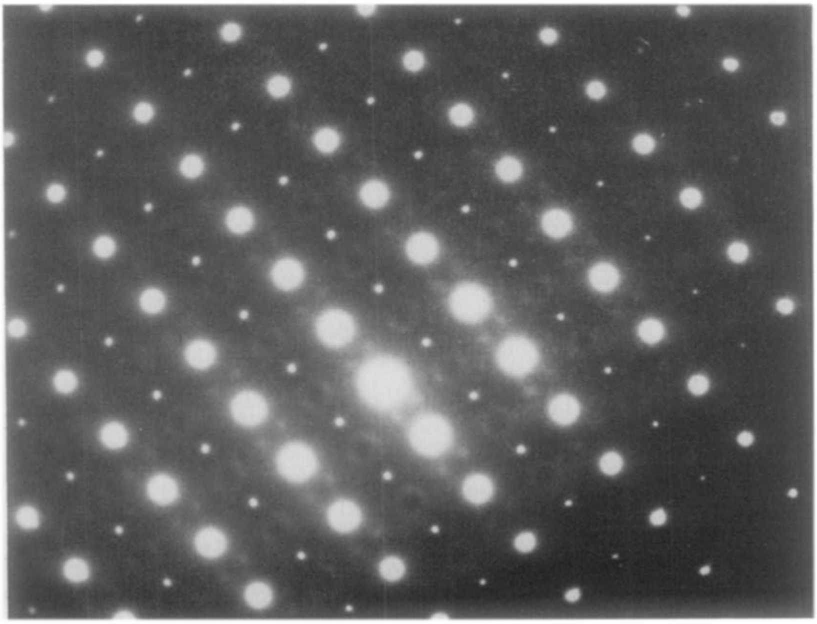

FIG. 1. $\langle 11\bar{2} \rangle_f$ diffraction pattern from specimen containing 15 mol% CaO showing both diffuse scattering and reflections forbidden by the symmetry of the fluorite structure.

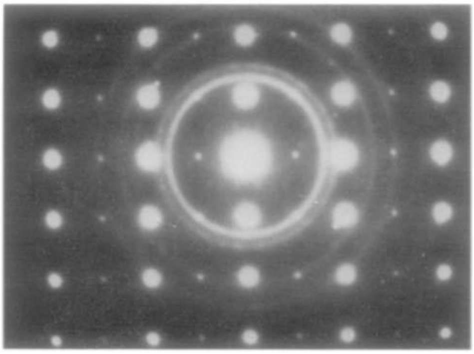

FIG. 2a. $\langle 11\bar{2}\rangle_f$ diffraction pattern from specimen containing 10 mol% CaO. Diffuse scattering weak. (Ring pattern due to carbon coated grid.)

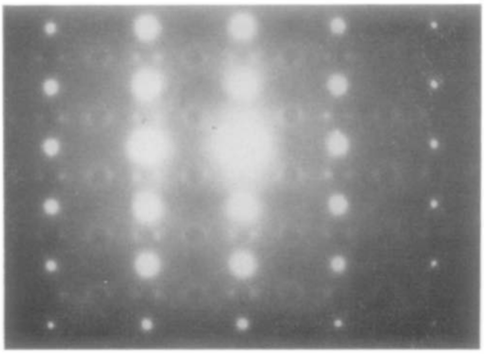

FIG. 2b. $\langle 11\bar{2}\rangle_f$ diffraction pattern from specimen containing 18 mol% CaO. Extra reflections no longer visible. Diffuse scattering strong.

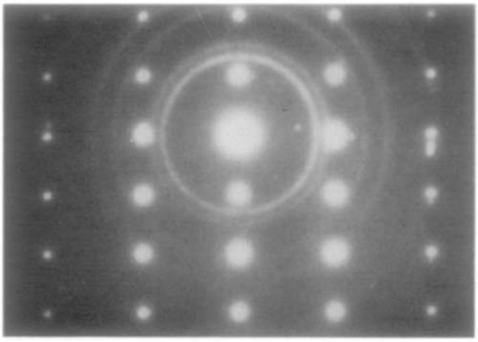

FIG. 2c. $\langle 11\bar{2}\rangle_f$ diffraction pattern from specimen containing 10 mol% CaO after quenching. Superlattice disappeared. Diffuse scattering visible on original. (Ring pattern due to carbon coated grid.)

TABLE I

SUMMARY OF OBSERVATIONS

Specimen:	1	2	3	4	5[a]
Analysis[b] (CaO-mol%)	18	16	15	10	10
Diffuse scattering	— Decreasing intensity →				Present
Extra reflections	— Increasing intensity →				Absent

[a] Specimen heated to 1600°C for 24 hr and quenched.

[b] All specimens contained approximately 1w/o HfO_2.

recorded with an "extra" reflection in the objective aperture showing grosser features (~800 Å).

A specimen of 10 mol% yttria stabilized zirconia yielded a $\langle 11\bar{2}\rangle_f$ diffraction pattern with diffuse scattering features of similar dimensions and location to those found for calcia-stabilized zirconia. The scattering was less sharp than that shown in Fig. 1 and there were no extra reflections.

Structure and Ageing of Calcia-Stabilized Zirconia

Although the diffuse scattering and the extra reflections react differently to composition and temperature changes the diffraction patterns suggest that the two features arise from a coherent single crystal which is substantially of the fluorite structure type. It has already been shown (*1*) how the diffuse scattering can arise from microdomains of an ordered structure (probably $CaZr_4O_9$) residing coherently within the cubic parent crystal. It is evident therefore that the composition of all other parts of the crystal (the matrix) must contain substantially less CaO than the overall composition of the material.

The diffraction observations made above are consistent with a second form of coherent intergrowth (*6*), this time of monoclinic zirconia within the cubic crystal, giving rise to the extra reflections. Although there is a small mismatch between the monoclinic and cubic cells involved (Fig. 5) several authors (*7*, *8*) have cited evidence for intragranular

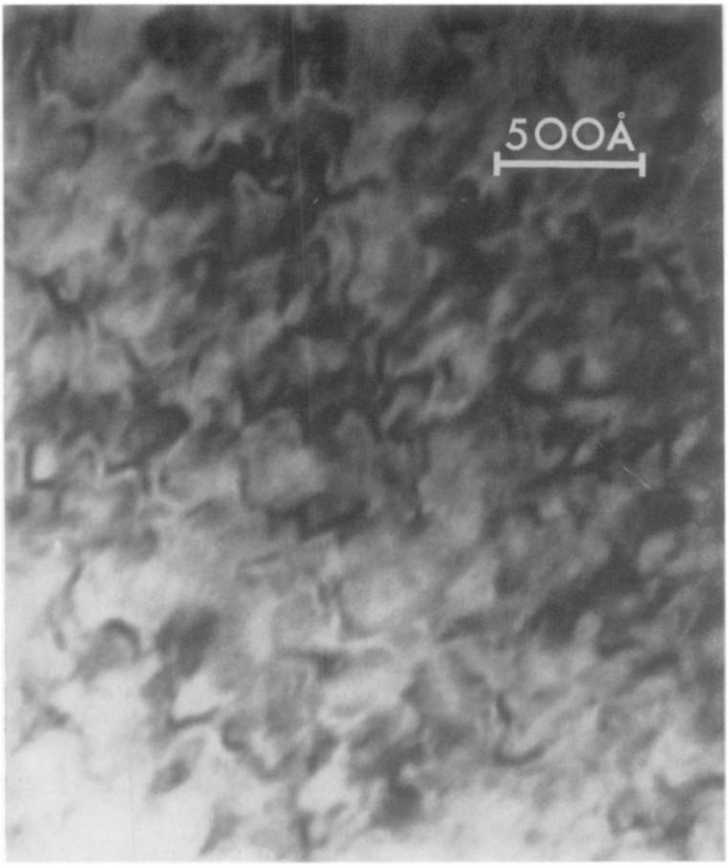

FIG. 3. Bright field micrograph of a grain from specimen containing 15 mol% CaO showing contrast features approx. 50 Å across.

precipitates of monoclinic ZrO_2 (including micrographs (*7*) resembling our Fig. 4) in partially stabilized zirconia (typically approx. 3w/o CaO) and the lower symmetry forms of ZrO_2 are known (*9*) to give rise to the "symmetry forbidden" reflections under consideration here. Further, these reflections appear to be the same ones that Carter and Roth correlated with the ordering (ageing) process (*4*) in which the ionic conductivity fell as a function of time of annealing at ~1000°C. The ageing phenomenon is readily understood if it involves the growth of intragranular volumes of pure ZrO_2 and if we make the assumption that the ionic conductivity of the disordered matrix > the ionic conductivity of $CaZr_4O_9 \geqslant$ that of pure ZrO_2 then we have at least a qualitative understanding of the observed maximum (at approx. 15 mol% CaO). Starting from pure ZrO_2 and increasing the oxygen ion vacancy concentration will increase the oxygen ion mobility until a balance is reached due to growth of the ordered $CaZr_4O_9$ phase.

To summarize, our model for calcia-stabilized zirconia has a fundamental matrix with the fluorite structure and contains small (30–100 Å) microdomains of $CaZr_4O_9$. Freshly quenched, the disordered structure of the matrix exhibits maximum ionic conductivity but annealing at ~1000°C allows the coherent precipitation of monoclinic ZrO_2 together with further nuclei of $CaZr_4O_9$ and the decay of the conductivity.

Previous observations do not appear to be at odds with this model. The result of Carter

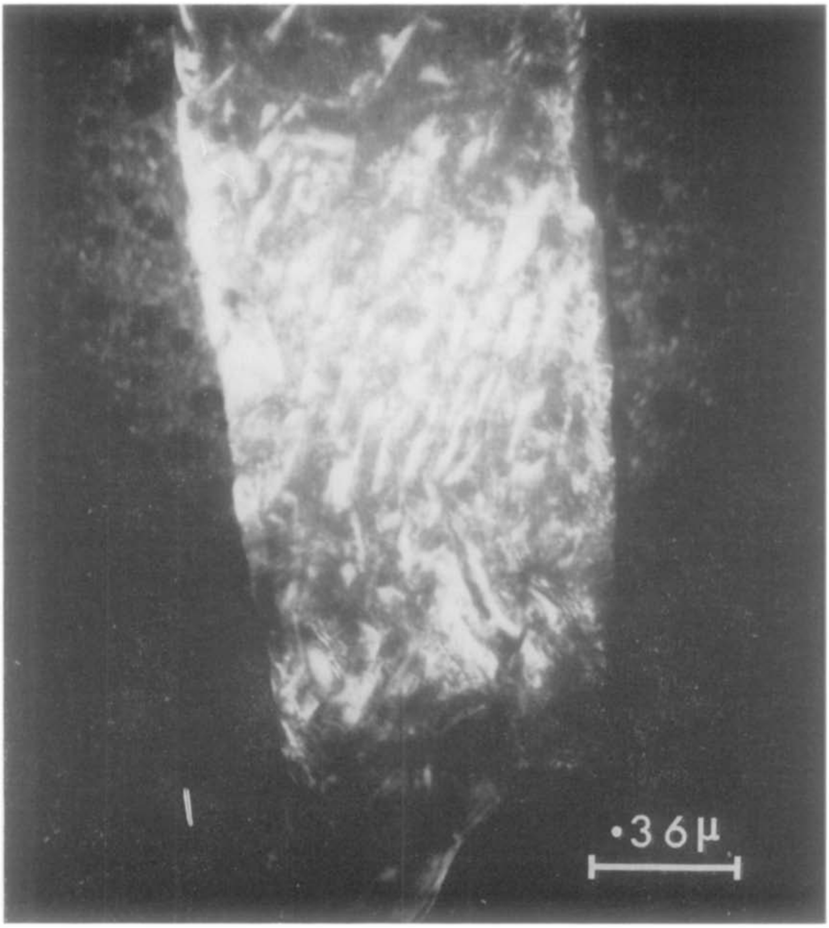

FIG. 4. Dark field micrograph of grain from specimen containing 16 mol% CaO showing contrast features approx. 800 Å across. ("Extra" reflection in the objective aperture.)

and Roth's structural refinement of the disordered material (*4*) is not statistically different from the microdomain model that allows vacancies (and small local atomic shifts) to be distributed equally along the four cubic $\langle 111 \rangle_f$ directions. Allpress and Rossell (*1*) did not observe the extra reflections apparently because the specimens they subjected to long anneals were of the 20 mol% CaO composition. The intragranular precipitation of ordered phases and of slightly distorted ZrO_2 have been reported separately in the papers of other workers. The present evidence suggests that the two features can coexist within a single grain.

The lack of equilibrium implied by the structure proposed here for calcia stabilized zirconia is consistent with the observed thermal behavior of the material. The progress of the intragranular transformations is doubtless influenced by the interfacial energies at microdomain boundaries and hence we would expect that other systems (e.g., ZrO_2–Y_2O_3, ZrO_2–Sc_2O_3) for which the $CaZr_4O_9$ structure is not available would behave differently in the matter of ageing.

The observation of diffuse scattering in diffraction patterns of yttria stabilized zirconia resembling the diffuse scattering in diffraction patterns of calcia stabilized zirconia encourages the notion that related microdomain structures might occur in a range of

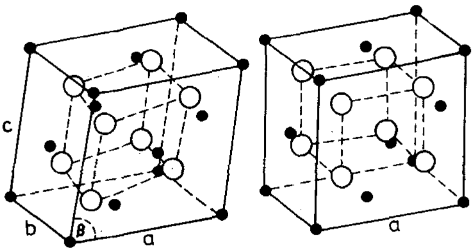

FIG. 5. Unit cell of monoclinic ($a = 5.145$, $b = 5.208$, $c = 5.311$ Å, $\beta = 99°14'$) and cubic ($a = 5.07$ Å) modifications of ZrO_2. Dark circles represent zirconium atoms, open circles represent oxygen atoms.

"solid solution" fluorite systems. The study of fluorite related crystal structures has led earlier workers (*10*) to predict the existence of microdomains in such systems where the degree of misfit across the domain boundaries is not prohibitive.

Radius ratio considerations suggest that the small size of the zirconium (IV) ion is particularly well suited to the formation of structures such as that represented by Fig. 6 (*11*) in which one of the cations must be six coordinated. However, when the atoms do not depart far from the fluorite structure sites larger atoms might be accommodated so that a search for microdomains in other defective fluorite structure oxides could well prove fruitful. It will be interesting to discover whether or not microdomains of future ordered structures in which vacancies align along $\langle 111 \rangle_f$ directions give rise to similar ring-like diffuse scattering to that mentioned herein regardless of the identity of the aliovalent ions responsible.

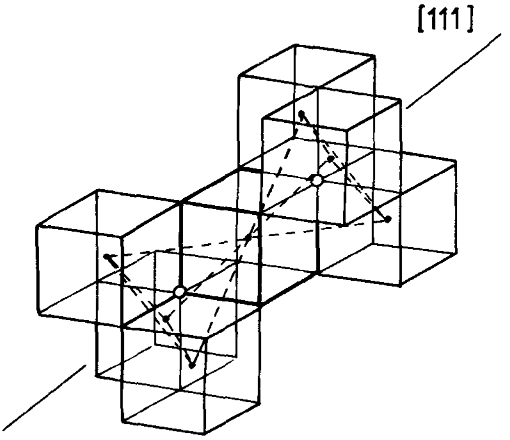

FIG. 6. The "Bevan Cluster" (*11*) of two oxygen vacancies (open circles) aligned along the cubic [111] direction. The central cation is six coordinate and the remaining six cations are seven coordinate. All the cations are represented by dark circles.

Although the diffuse scattering observed in these materials is geometrically quite similar to that observed in VC and TiO (*12*, *13*), our previous assertion (*2*) that a Fermi surface could not be responsible for the diffuse scattering in stabilized zirconia is vindicated by the present analysis.

It has already been pointed out (*14*) that information about microdomain type heterogeneities in crystals can be obtained by the lattice image method only where order is nearly perfect in at least one direction; when order is limited in every direction the information must be sought via a close study of the diffraction pattern (reciprocal space).

Acknowledgments

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