



Copper and iron precipitates in thermochemically reduced yttria-stabilized zirconia crystals

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ABSTRACT

Thermochemical reduction (TCR) at 2173 K has been performed on nominally pure yttria-stabilized zirconia crystals. After TCR the crystals become opaque owing to a very intense optical absorption band centred at 2.64 eV. Analytical transmission electron microscopy studies have shown that both copper and iron impurity precipitates are present. Colloids with different sizes and shapes are inhomogeneously distributed and both large and small precipitates are observed. Most of the large precipitates are elongated and irregular shaped, with an average dimension of 130 nm × 30 nm; they all contain copper. Exclusively copper and exclusively iron contents can be found in different parts of the same precipitate, an observation that is compatible with the fact that copper and iron are immiscible. Smaller precipitates, with an average size of about 5 nm, are usually iron rich or copper rich.

§ 1. INTRODUCTION

Thermochemical reduction (TCR) of oxides at sufficiently high temperatures causes precipitation of metal impurities which results in broad extinction bands attributed to Mie scattering from precipitates (Jain *et al.* 1974, Narayan *et al.* 1981, 1984, Bunch *et al.* 1985, Ballesteros *et al.* 1988a, 1988b, 1989, 1993, 1997, Savoini *et al.* 1997). Even in nominally pure oxide crystals, precipitation of inherently present impurities has been observed (Ballesteros *et al.* 1988b, 1989, Savoini *et al.* 1997). A necessary condition for colloid formation is the presence of a high concentration of oxygen vacancies. As-grown cubic yttria-stabilized zirconia (YSZ) contains a very large number of anion vacancies created to preserve electrical neutrality when Y³⁺ cations are added in order to stabilize the cubic polymorph (Kingery *et al.* 1959). Therefore, impurity precipitates should not be uncommon. These anion vacancies are distributed randomly in the lattice and are primarily

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responsible for the high ionic conduction exhibited by YSZ (Etsell and Flengas 1970, Catlow 1990, Li and Chen 1994, Li *et al.* 1994a,b, Orliukas *et al.* 1994, Weyl and Janke 1997).

The impurity content in the crystals influences the transport properties of oxygen-ion conductors such as YSZ. However, the defect structure of YSZ crystals is not fully understood and the nature of the interaction between an impurity cation and charge-compensating vacancies to form defect clusters is still a matter of debate. Defect simulation and molecular dynamics (MD) techniques have recently been applied to analyse the diffusion processes in ZrO_2 with different dopants (Khan *et al.* 1998).

In previous work (Savoini *et al.* 1997), copper-rich precipitates were resolved in undoped YSZ single crystals after TCR, with an average size of about 10 nm. Nickel and cobalt precipitates were identified in YSZ crystals doped with nickel and copper respectively. It was found that under identical TCR conditions, the smaller the impurity ionic radius, the lower is the threshold temperature at which the precipitates were formed. Even though the iron concentration was higher than the copper content, no iron precipitates were observed after TCR at 1823 K. Fe precipitates were probably absent in thermochemically reduced YSZ crystals because the reducing temperature was not sufficiently high to induce their precipitation (Savoini *et al.* 1997). In the present study, undoped YSZ crystals from the same boule as that used by Savoini *et al.* (1997) were thermochemically reduced at 2173 K in an attempt to produce iron precipitates. After TCR the samples were characterized by optical absorption measurements and by analytical transmission electron microscopy (TEM). Both copper and iron precipitates were identified.

§ 2. EXPERIMENTAL PROCEDURE

Single crystals of ZrO_2 stabilized with 16 wt% Y_2O_3 were purchased from CERES Corporation (USA). Excellent optical-quality crystals were grown by the skull method. Samples were cut with a diamond saw and polished to optical quality.

TCR was performed in a Thermal Technology graphite furnace, by placing the samples inside an enclosed graphite container surrounded by flowing 'pure' nitrogen gas. Powder X-ray diffraction patterns of the samples were recorded with an X'Pert-MPD Philips diffractometer using $\text{Cu K}\alpha$ radiation. X-ray analysis shows that both as-grown and TCR crystals have a well-crystallized cubic fluorite structure with a lattice parameter of 0.5146 nm, in agreement with previously reported values (Etsell and Flengas 1970).

Optical absorption measurements in the ultraviolet–visible–infrared were made with a Perkin–Elmer Lambda 19. For TEM, specimens were first cut into discs 3 mm thick, dimpled to a thickness below 30 μm , and then argon milled with a convergent beam with an acceleration voltage of 5 kV and an incidence angle of 10°. TEM, X-ray microanalysis and electron diffraction studies of the individual precipitates were carried out with a Philips CM200 field emission analytical electron microscope operated at 200 kV, equipped with a beryllium specimen holder.

§ 3. RESULTS AND DISCUSSION

X-ray fluorescence analyses of nominally pure YSZ crystals show that all the crystals inadvertently contain copper and iron in concentrations of the order of 250 and 400 cationic ppm respectively.

After thermochemical reduction at 2173 K, YSZ crystals become opaque. In order to measure the optical absorption spectrum, a sample was thinned down to a thickness of 200 μm . Figure 1 shows the optical spectra before and after TCR. In the reduced crystal, a strong composite band appeared at 2.64 eV (470 nm). Previously, this absorption band had tentatively been assigned to electrons trapped at oxygen vacancies nearest to zirconium cations and to oxygen ions with trapped holes adjacent to yttrium cations (Orera *et al.* 1990). This composite band is responsible for the colouration of the crystals. A less intense band is observed at 1.2 eV (1030 nm).

Precipitates were not found in as-grown YSZ crystals. To determine whether TCR at 2173 K induces iron precipitation, analytical TEM was performed on thermochemically reduced samples. Precipitates with different sizes and shapes were observed, some of which were associated with voids (figure 2). The larger precipitates are elongated and are inhomogeneously distributed.

X-ray microanalysis indicates that most of these precipitates are rich in copper. However, a few precipitates (such as that indicated with an arrow in figure 3) were found to contain either exclusively copper or exclusively iron in different regions in

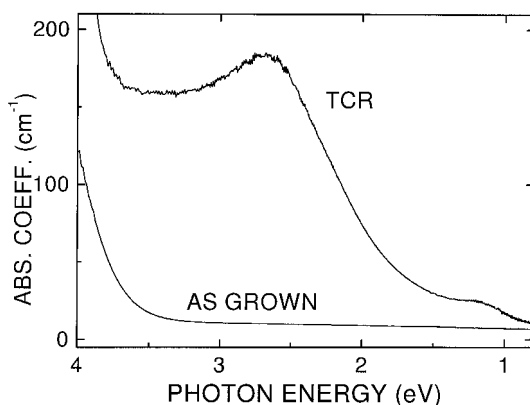


Figure 1. Optical absorption spectra of an undoped YSZ crystal before and after TCR at 2173 K for 1 h.

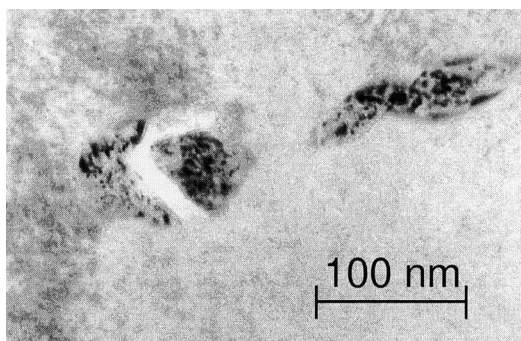


Figure 2. Transmission electron micrograph showing precipitates in a YSZ specimen. A void is also observed.

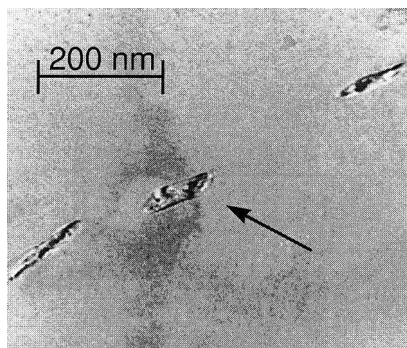


Figure 3. Transmission electron micrograph of precipitates. The left region of the precipitate indicated with an arrow is composed of copper; the right region is composed of iron.

the same precipitate. This observation is compatible with the fact that copper and iron are immiscible. Small iron-rich precipitates with an average size of 5 nm were also identified. Figure 4 is a high-resolution image of two precipitates. The large precipitate with a diameter of 8 nm is a copper-rich precipitate, and the smaller precipitate, 2 nm in diameter, is iron rich. Figure 5 shows an X-ray fluorescence spectrum of the latter, exhibiting the Fe $L\alpha$ line at 0.71 keV, the Fe $K\alpha$ line at 6.4 keV and the Fe $K\alpha$ line at 7.05 keV. Owing to their small sizes and elongated shapes, microdiffraction patterns were not obtained.

We propose that the small absorption at 1.2 eV (figure 1) is an extinction band due to Mie scattering from copper precipitates. The Mie theory (Schulman and Compton 1962, Skilman and Berry 1968, Jain and Arora 1974, Fuchs 1975, Hughes and Jain 1979) predicts that the peak wavelength of an extinction band shifts towards longer wavelengths as the precipitate radius increases. In a previous study (Savoini *et al.* 1997) we showed that TCR at 1823 K resulted in an extinction band at 1.8 eV, which was attributed to small copper precipitates with an average

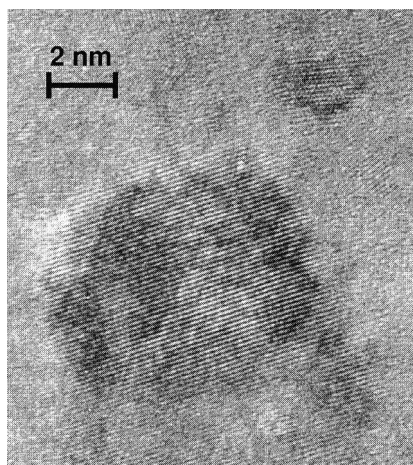


Figure 4. High-resolution transmission electron micrograph showing a copper precipitate (larger) and an iron precipitate (smaller).

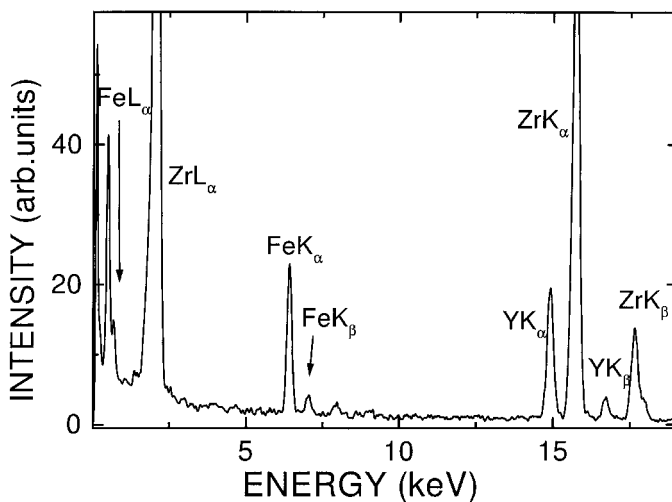


Figure 5. Energy-dispersive X-ray fluorescence spectrum from an iron precipitate showing the Fe L α , Fe K α and Fe K β lines.

size of 10 nm. In the present study, the copper precipitates are significantly larger (about 130 nm \times 30 nm), resulting from TCR at 2173 K. (The concentration of iron precipitates is much lower than that of copper and can effectively be ignored.) We therefore attribute the shift from 1.8 to 1.2 eV to the change in dimensions from 10 to approximately 100 nm. After the anneal at 2173 K (this temperature is significantly higher than the threshold temperature for iron precipitation estimated in the next paragraph), an extinction band related to iron precipitates is not observed because the concentration of these precipitates is very low. Thus, it is not feasible to monitor the iron precipitation as a function of reducing temperature.

Next, we shall address the ability of substitutional copper, nickel, cobalt and iron ions to precipitate on the basis of their ionic sizes. The ionic radii of Cu $^{2+}$, Ni $^{2+}$ and Co $^{2+}$ ions are 0.69, 0.72 and 0.74 Å respectively. To precipitate, the impurity ions must diffuse and aggregate with oxygen vacancies. The smaller the ionic radius, the lower is the diffusion temperature. We know from a previous study that the threshold temperatures for copper, nickel and cobalt ions to precipitate are 1425, 1600 and 1750 K respectively (Savoini *et al.* 1997). A linear behaviour is observed by plotting T^{-1} versus ionic radius (figure 6). Extrapolation of the threshold temperature for precipitation of Fe $^{2+}$ ions (ionic radius, 0.76 Å) yields a value of 1925 K. The present study confirms that iron precipitates are formed during TCR at 2173 K.

The binding energies (with respect to isolated defects) of several dopant–vacancy pair clusters were obtained by computer simulation (Khan *et al.* 1998). For the Cu $^{2+}$ ion as a dopant with an oxygen vacancy, the binding energy is -0.58 eV. For Ni $^{2+}$, Co $^{2+}$ and Fe $^{2+}$ as dopants with an oxygen vacancy, the binding energies are -0.49 , -0.48 and -0.47 eV respectively. (The negative binding energies indicate that these clusters are bound.) In general the vacancy is more mobile than the impurity. These results, in conjunction with our findings, suggest that, the more stable the dopant–vacancy pair, the easier it is for the impurity to diffuse and the lower is the threshold temperature for precipitation. Anion vacancies first associate themselves with impurity ions and eventually cluster to form the precipitates.

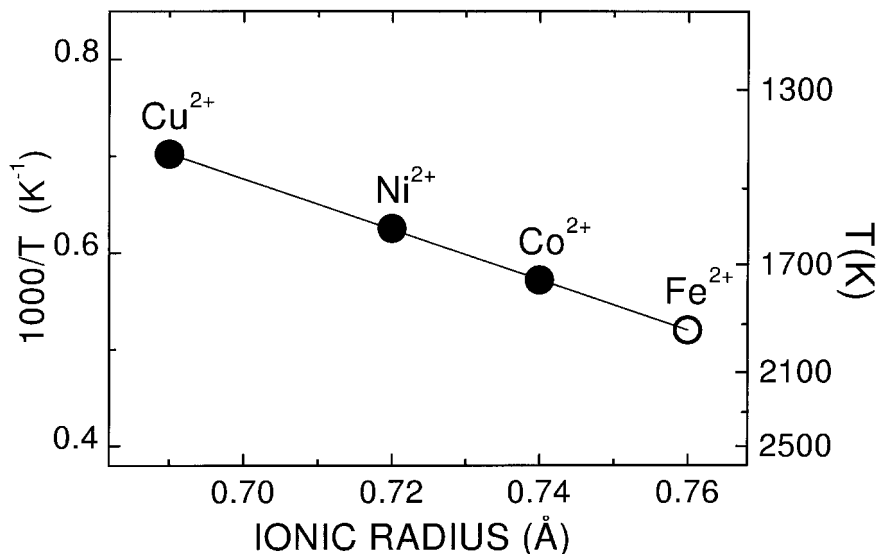


Figure 6. Reciprocal of the precipitation threshold temperature versus ionic radius.

§ 4. SUMMARY AND CONCLUSIONS

Undoped YSZ crystals containing several inherent impurities were thermochemically reduced at 2173 K. After TCR the crystals become opaque. Optical absorption measurements show the presence of a strong composite band at 2.64 eV, which is responsible for the colouration of the crystals, and a less intense band at 1.2 eV. The former band has been tentatively assigned to electrons trapped at oxygen vacancies nearest to zirconium cations and to oxygen ions with trapped holes adjacent to yttrium cations (Orera *et al.* 1990). The 1.2 eV band is attributed to an extinction band due to copper precipitates produced during TCR. Analytical TEM studies show that both copper and iron impurities precipitate. Colloids of different sizes and shapes were inhomogeneously distributed, and occasionally associated with voids. Large elongated precipitates with average dimensions of 130 nm × 30 nm contain primarily copper, although some contain copper and iron in different regions of the same precipitate. Small iron-rich precipitates were also found with an average size of about 5 nm. Our results, in conjunction with previous (Khan *et al.* 1998) defect simulations and MD studies, suggest that the more stable the dopant–vacancy pair, the easier it is for the impurity to diffuse.

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