Temperature dependence of the internal friction and modulus change in Y_2O_3- and M_gO-doped ZrO_2 polycrystals

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Abstract

Internal friction and frequency measurements were carried out on Y_2O_3- and MgO-doped zirconia polycrystals at low frequencies (1.5–3.5 Hz) in the temperature interval 130–623 K. The results obtained with the first system confirm published data. In the ZrO_2:MgO system two peaks have been observed at 223 and 450 K. The first anneals out at temperatures between 473 and 573 K. The second peak was only detected for high MgO concentrations and increased thereafter. The low temperature peak is associated with oil contamination during sample cutting. The second peak can be ascribed to stress-induced reorientation of oxygen vacancy–magnesium cation pairs in the cubic phase with an activation energy of about 1.17 eV.

1. Introduction

Properties of materials are intimately related to their microstructure and consequently to their fabrication processes. Electronic ceramics are no exception, and to improve their ionic conductivity, they must be doped with heterovalent cations. In this regard special attention must be given to zirconia, since its dopant also acts as a phase stabilizer. Hence it is important to characterize zirconia in terms of phase concentration and point defect distribution. The internal friction (IF) technique is well suited to study zirconia because it is sensitive to point defect diffusion and phase transformation.

Concerning point defects in ZrO_2, several papers have been published where the IF technique has been used [1–12]. In the case of ZrO_2:Y_2O_3, a relatively high dopant concentration is necessary to stabilize the cubic phase (greater than 8 mol%), which makes analysis of the data difficult. In spite of this there is a certain agreement between authors that the oxygen vacancy–yttrium cation pair is responsible for the relaxation peak observed in samples with low concentration (less than 4 mol%) and the agglomeration of these defects at higher concentrations [5]. Other dopants such as CaO [9–12] and CeO_2 [1, 6] have also been used. As far as we know, MgO has not been studied.

The aim of this study is to compare our results with published data on ZrO_2:Y_2O_3 (3 mol%) and to evaluate the influence of MgO concentration (3–13 mol%) on the anelastic properties of ZrO_2.

2. Experimental details

Samples of zirconia partially stabilized with yttria (3 mol%, HSY3) were prepared from coprecipitated powder by uniaxial and isostatic pressing followed by sintering in air for 2 h at 1723 K. Some samples were also obtained by mechanically mixing yttria and zirconia powders. The magnesia-doped zirconia samples were prepared from coprecipitated powder (8.1 mol%, MSZ8) and from mechanically mixed powders of ZrO_2 (DK2) and MgO (Merck P.A.). After uniaxial and isostatic pressing, the samples were sintered in air for 2 h at 1923 K. The compacted specimens at this stage were bars of dimensions $42 \times 7 \times 2$ mm³. In order to make the specimens suitable for the IF apparatus, they were cut to a size of $42 \times 2 \times 2$ mm³. The MgO concentration was measured by neutron activation analysis and found to range between 2.73 and 13.26 mol%. Two samples corresponding to the extreme doping levels were fractured and examined by scanning electron microscopy (SEM).

The IF and frequency measurements were carried out in an inverted torsion pendulum at oscillation frequencies ranging from 1.5 to 3.5 Hz in the temperature interval 130–623 K. The free-decay method was used

and the maximum surface strain amplitude was 5×10^{-5}. The heating rate was 1.5 K min^{-1}.

3. Results and discussion

3.1. ZrO₂:Y₂O₃ system

With an HSY3 sample we have observed a peak located at 373 K (3 Hz). This result agrees well with those reported in refs. 5 and 6 and this peak has been attributed to stress-induced reorientation of oxygen vacancy–yttrium cation pairs.

3.2. ZrO₂:MgO system

Figure 1 shows the IF (Q^{-1}) and frequency spectra as a function of temperature for a coprecipitated sample. Curves a and a' (IF and frequency respectively) were obtained after mounting and curves b and b' after linear annealing at 573 K. In the first ensemble one observes a complex located at approximately 223 K, composed of at least two peaks, with their corresponding modulus defect. They are unstable and practically disappear after annealing at 573 K (curves b and b'). When this sample was sintered at 1923 K for 10 min and remeasured, the complex was no longer observed.

The results obtained with samples prepared by mechanical mixing of the powders are shown in Fig. 2 for the concentrations 2.73, 7.41, 10.27 and 13.26 mol%. Although the intensities are different, the same IF complex appears in all samples at the same temperature. Figures 3 and 4 show micrographs of the fractured surfaces of samples with 2.73 and 13.26 mol% respectively. A predominance of small grains can be observed in the sample shown in Fig. 3, whereas Fig.

Fig. 2. Variation in IF and frequency with temperature for ZrO₂ with various MgO contents.
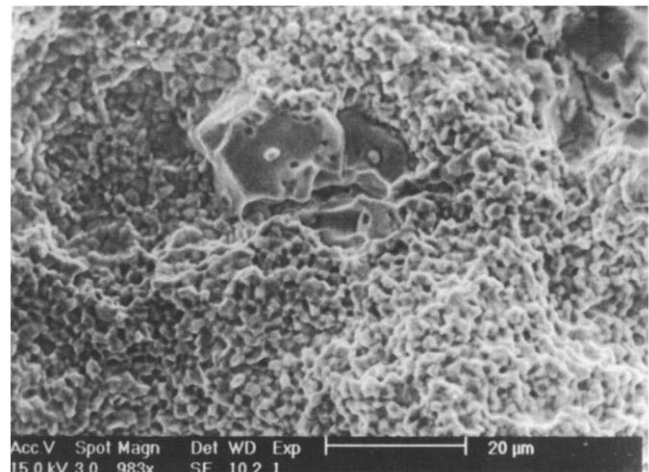
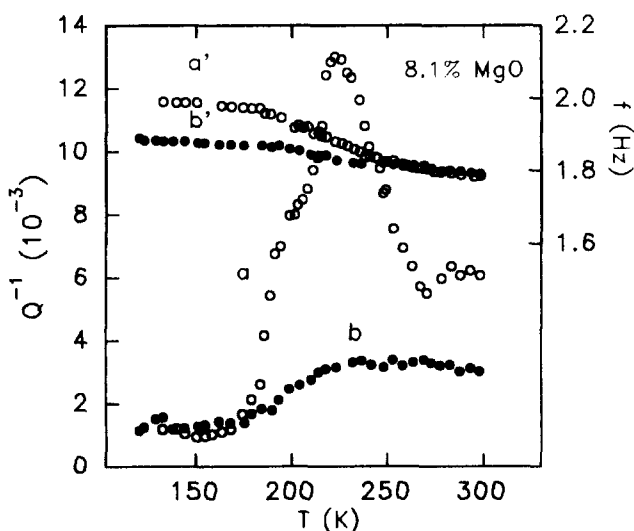Fig. 3. SEM fractograph of a ZrO₂:MgO (2.73 mol%) sample.

Fig. 1. Variation in IF and frequency with temperature for a coprecipitated ZrO₂:MgO (8 mol%) sample: curves a and a', after mounting; curves b and b', after linear annealing at 573 K.
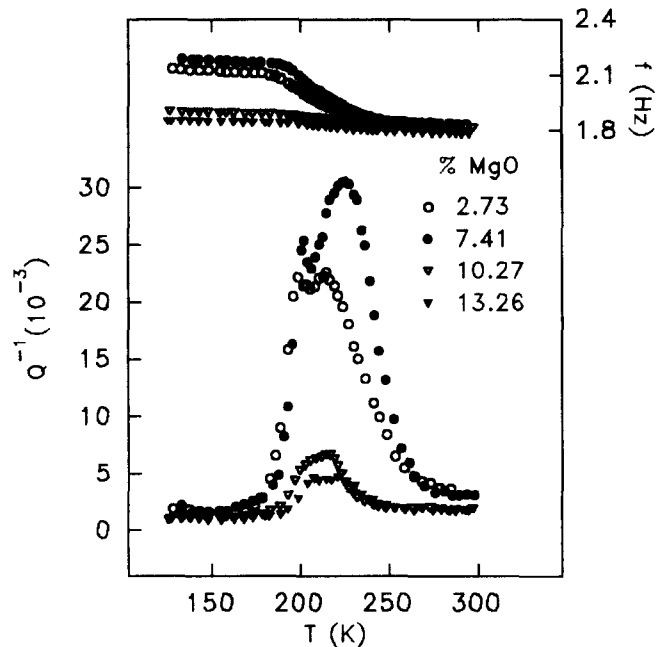
4 shows large grains. This complex has also been observed in yttria-doped zirconia prepared by mechanical mixing and shows the same behaviour after the annealing treatment. The IF complex at 223 K is difficult to analyse because it is composed of more than one peak. However, its elimination with the decrease in frequency at low temperature by the high temperature annealing shows a modification of the defects or an alteration of the microstructure. Chomka and Denga [13] also reported IF peaks in the same temperature range and with identical annealing behaviour. Their samples were metallic alloys covered with mineral paraffin oil and they associated the peaks with the nature of the surface layer. The peak position was related to the melting point of the solidified oil and the peak
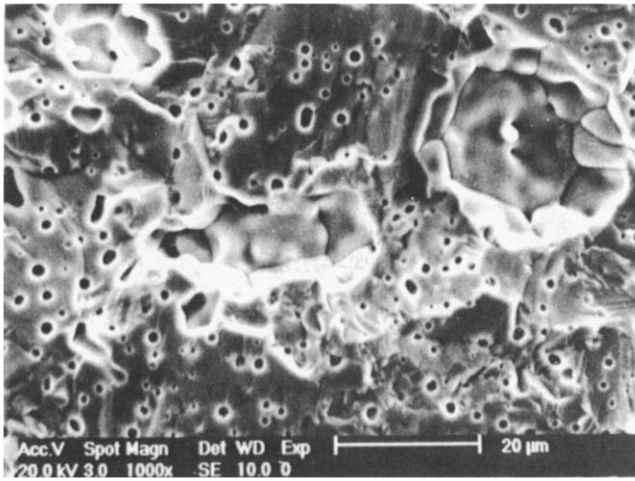
Fig. 4. SEM fractograph of a ZrO_2:MgO (13.26 mol%) sample.

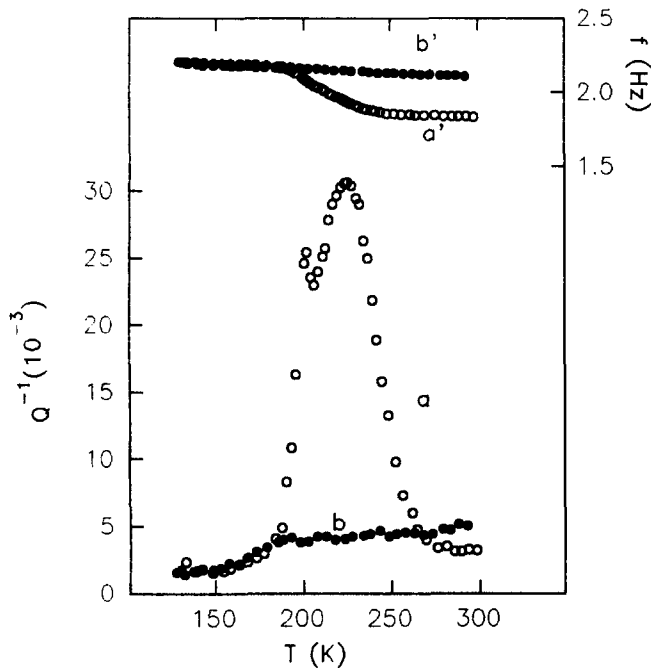Fig. 6. Variation in IF vs. $1/T$ for ZrO_2 with various MgO contents.

Fig. 5. Variation in IF and frequency with temperature for two ZrO_2:MgO (7.41 mol%) samples cut with different coolants: curves a and a', oil; curves b and b', water.
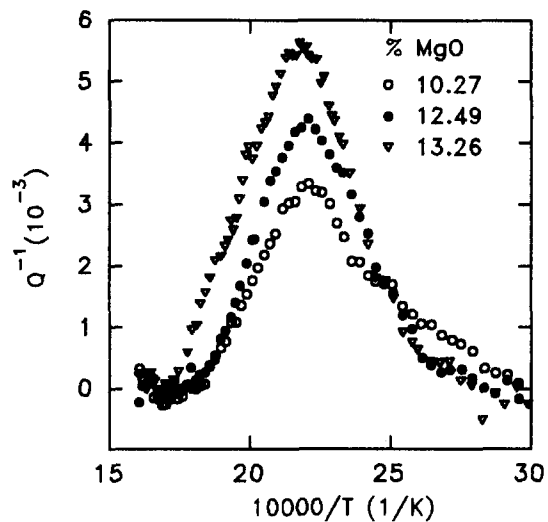
Fig. 7. Variation in IF (without background) vs. $1/T$ for ZrO_2 with various MgO contents.

height to the annealing temperature. In order to verify the influence of the liquid utilized as coolant, we decided to use water instead of oil. Figure 5 shows the spectra of IF and frequency as a function of temperature for two samples with the same MgO content (7.41 mol%) cut with oil (curves a and a') and with water (curves b and b'). In the last curve the complex is not observed. This result shows that the 223 K complex is associated with the penetration of oil in the samples.

Figure 6 shows the IF spectra as a function of temperature from 330 to 623 K for four samples with higher concentrations. Samples with lower concentrations are partially stabilized and the others fully sta-
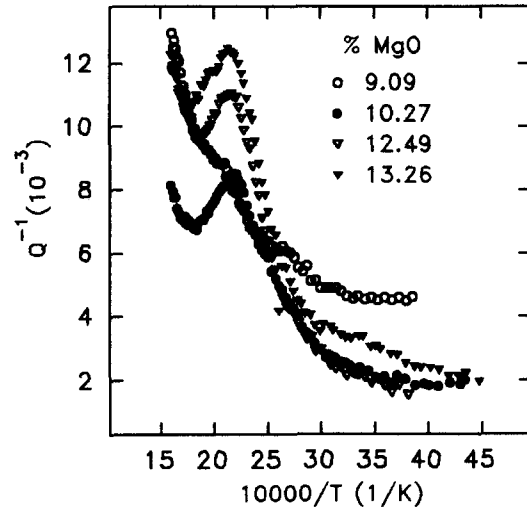
bilized. The curves presented in Fig. 7 have been obtained from those of Fig. 6 by subtraction of an exponential background ($r^2 > 0.997$), with the exception of the lower concentration curve which did not fit this function. One can observe a peak at 450 K, the height of which increases with concentration. This behaviour can be attributed to the presence of Mg ions and/or oxygen vacancies. If one assumes a point defect relaxation ($\tau_0 \approx 10^{-14}$ s), the activation energy of this process would be about 1.17 eV, which is consistent with reorientation of the Mg cation–oxygen vacancy pair in the cubic phase [14], because its binding energy is 1.19 eV [15] and the oxygen migration energy in ZrO_2 is 0.65 eV [16]. Assuming this energy, the peaks are at least 2.8 times broader than a Debye peak.

4. Conclusions

IF measurements carried out on Y_2O_3-doped ZrO_2 confirm data from the literature for 3 mol% Y_2O_3. For the ZrO_2:MgO system with concentrations ranging from 2.73 to 13.26 mol% MgO two main complexes were observed. The first at 223 K was unstable and disappeared after linear annealing at 573 K. It has been attributed to the penetration of oil during sample cutting. The second at 450 K is only observed for high MgO content and increases with MgO content. This can be attributed to stress-induced oxygen vacancy–magnesium cation pair reorientation in the cubic phase.

Acknowledgments

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