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Defects and phase transitions in yttria- and scandia-doped zirconia

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Abstract

Internal friction (IF) experiments were performed on the systems ZrO_2 (8–12 mol%)–Y_2O_3, and ZrO_2 (9–12 mol%)–Sc_2O_3. The following features were found: (i) an IF peak around 500 K in both systems which is assigned to the hopping of trapped oxygen vacancies ($\Delta H=1.2–1.3$ eV); (ii) in polycrystalline materials a high temperature damping background, which is related to cation diffusion; (iii) an order/disorder phase transition at 1450 K in ZrO_2–12 mol%Y_2O_3; and (iv) in ZrO_2–Sc_2O_3 a ferroelastic↔ferroelectric phase transition at 750 K from the rhombohedral to the cubic phase. Cation diffusion experiments in ZrO_2–Sc_2O_3 revealed an activation enthalpy for Zr diffusion of 5.3 eV indicating that short- and long-range cation transport is governed by one type of cation diffusion process.
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1. Introduction

Cubic-stabilized zirconia is widely used as a solid electrolyte in solid oxide fuel cells and oxygen sensors because of its high ionic conductivity at elevated temperatures. Zirconia can be stabilized in its cubic form by doping with lower valent oxides, e.g. CaO, Y_2O_3, or Sc_2O_3 (leading to CSZ, YSZ, or ScSZ). Consequently, oxygen vacancies are introduced as charge compensating defects. From these systems, scandia-doped zirconia exhibits the highest conductivity known for zirconia ceramics. The transport properties of cubic zirconia at elevated temperatures, ionic conduction and diffusion, are widely determined by the defect structure (see, e.g., Refs. [1–4]). Operation at high temperatures leads to degradation of the solid electrolyte. The resulting decrease of the ionic conductivity at prolonged service times (ageing) might be related to a cation diffusion-induced ordering process. Additionally, structural phase transitions may occur, with possible negative influence on the mechanical properties (like crack formation).

Mechanical spectroscopy, based on internal friction measurements, is a non-destructive mechanical method for the study of atomic defects (e.g., Refs. [5,6]) and phase transitions in materials. In this paper, we give a survey of the mechanical loss properties of yttria- and scandia-doped zirconia for doping contents near 10 mol%. The same materials were used in complementary cation tracer diffusion experiments.

2. Experimental

Polycrystalline material of YSZ containing 7.8 mol% Y_2O_3 (YSZ-8) and single crystals containing 10 and 12.4 mol% Y_2O_3 (YSZ-10 and YSZ-12) were investigated. For ScSZ, only polycrystalline material containing 9, 10 and 12 mol% Sc_2O_3 was used. Details of sample preparation and measuring techniques are described in previous papers [6,7]. The specimens for mechanical loss experiments had dimensions of about $40\times5\times0.8$ mm³, while for tracer diffusion and dielectric loss experiments, pieces of $10\times10\times1$ mm³ were prepared. Mechanical loss experiments were carried out with two types of apparatus
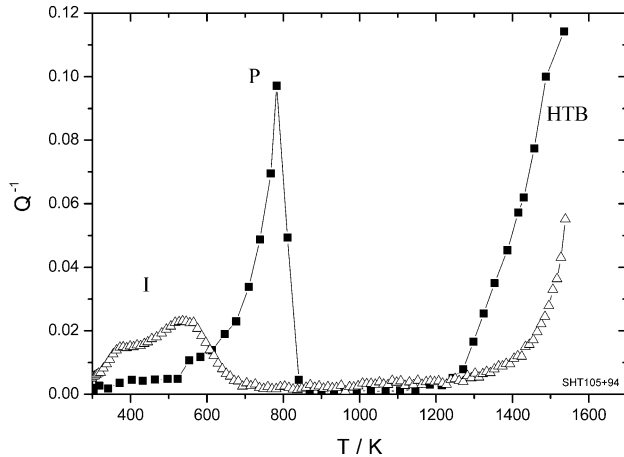
Fig. 1. Mechanical loss spectrum (Q^{-1} vs. temperature) for YSZ-8 ($\triangle$) and ScSZ-9 ($\blacksquare$) at a measuring frequency of 0.1 Hz.

operating in various frequency ranges [8]: (i) Low-temperature loss spectra (300–900K) were measured with an inverted torsion pendulum (frequency range 1–20Hz). (ii) For higher temperatures up to 1600 K a low frequency torsion apparatus (10^{-3} to 10 Hz) was applied.

Cation self-diffusion experiments were performed with the ceramic samples ScSZ-12. The ^{96}Zr tracer was applied onto the polished and pre-annealed samples from a nitric acid solution in a thickness of 10–20 nm in a similar way as described elsewhere [7]. The samples were then heated at temperatures between 1500 and 1750 K for appropriate times in air and were thereafter analysed by means of SIMS using a VG SIMSlab machine [7].

3. Results

Mechanical loss spectra of zirconia show various features. They depend on the type of the specimens (polycrystals or single crystals), on the structure (cubic, tetragonal or rhombohedral) and on the kind and content of doping (Sc_2O_3, Y_2O_3).

Fig. 1 shows the mechanical loss spectra, Q^{-1} vs. temperature, for YSZ-8 and ScSZ-9 polycrystals for a measuring frequency of f=0.1 Hz. The spectra show various prominent phenomena designated as I, P, and HTB. In YSZ-8, a doublet peak I appears around 500 K being characteristic for cubic YSZ [6,7]. In ScSZ-9 peak I is only faintly developed (see also Fig. 2) but an additional sharp peak P appears close to 750 K. At high temperatures (>1200 K) both samples show a monotonically increasing damping background HTB.

Fig. 2 depicts measurements of ScSZ-10 for T<900 K with higher resolution obtained with the torsion pendulum. The data were determined for two measuring frequencies (2.1 and 9.8 Hz), for 2.1 Hz during heating and cooling. The temperature position of peak P is independent of the measuring frequency and shows a hysteresis for heating and cooling. The peak height increases with decreasing frequency, which is characteristic for a phase transition. Peak P shows a shoulder on its low-temperature side indicating the presence of a second peak.

The development of the high temperature background is characteristic for polycrystalline specimens. Single crystals, which were only available for yttria-doped zirconia, show another type of behaviour. In YSZ-10, the damping at high temperatures is considerably lower and the HTB prominent
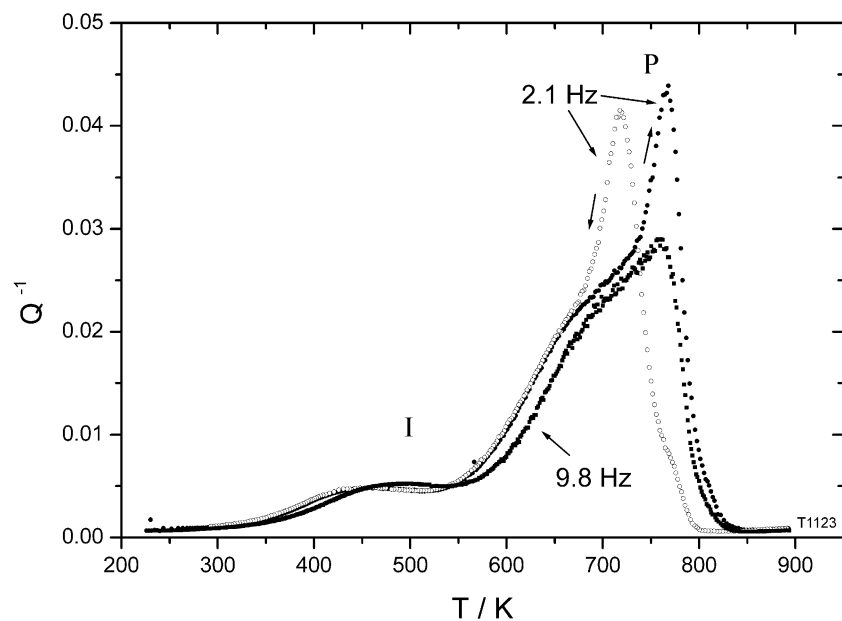

Fig. 2. High resolved mechanical loss spectra (Q^{-1} vs. temperature) for ScSZ-10 as a function of the measuring frequency (2.1 and 9.8 Hz). For 2.1 Hz, the measurements were obtained during heating and cooling.
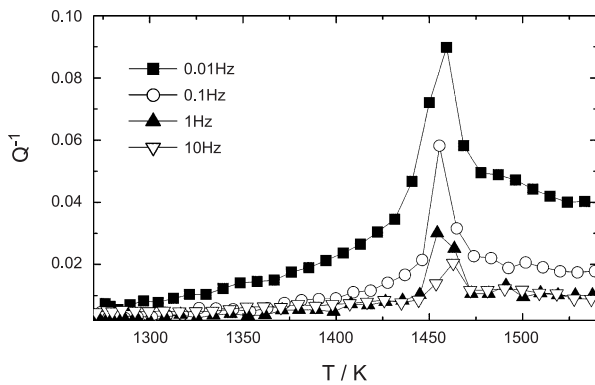
Fig. 3. Mechanical loss spectrum (Q^{-1} vs. temperature) for single crystalline YSZ-12 for different measurement frequencies.

for polycrystals is not observed (see Ref. [6]). Experiments with single crystals with slightly higher Y_2O_3 contents show a new phenomenon. Fig 3 shows, as an example, measurements on YSZ-12. A sharp internal friction peak appears around 1450 K with the characteristic features of a phase transition: frequency-independent temperature position and peak height decreasing with increasing measuring frequency.

In Fig. 4, cation self-diffusion coefficients for the tracer diffusion of ^{96}Zr in ScSZ containing 12 mol% Sc_2O_3 are shown. They follow a linear Arrhenius-like behaviour with an activation enthalpy of 5.3 eV. The pre-exponential factor is relatively high, roughly 10^{+2} cm^2 s^{-1}, equivalent to an activation entropy of $10k_B$. (Calculation: $\Delta S/k_B = \ln[8D_0/(a^2 f \nu_0)]$; a=513 pm is the lattice constant of YSZ, f=0.65 is the correlation factor, $\nu_0 = 1.3 \times 10^{13}$ s^{-1} is the Debye frequency [9] and k_B is the Boltzmann constant).

Measurements of dielectric loss ($\tan\Phi$) and permittivity ε' are shown in Fig. 5a and b. The dielectric loss spectra (Fig. 5a) show two overlapping peaks P around 700 K. This correlates with a decrease in ε' (superimposed on a steeply increasing background). The temperature position of both effects is independent of the measurement frequency. A smaller peak I occurs between 550 and 650 K which shifts towards higher temperatures with increasing measurement frequency (0.1–1 kHz).

4. Discussion

The various phenomena appearing in the mechanical loss spectra of zirconia can be classified in three different categories and are discussed accordingly in the following.

4.1. Low-temperature loss peak I

As was already described and analysed in preceding papers [6,10], the low-temperature loss peaks I in YSZ are related to local jumps of oxygen vacancies, which are associated with dopant cations forming elastic (and electric) dipoles with [111] oriented dipole axis corresponding to a

trigonal defect symmetry. The activation enthalpy for reorientation jumps of these associated oxygen vacancies (1.3 eV) is slightly higher than for ionic conduction, which is based on freely migrating (dissociated) oxygen vacancies, where 1.1 eV was found [11].

The mechanical loss peak I in scandia-doped zirconia is assigned according to the same defect model. The smaller peak height in the scandia system can be explained with the smaller dipole shape factor. From the ionic radii in the fluorite lattice coordination (Sc^{3+}: 87 pm; Y^{3+}: 102 pm; Ca^{2+}: 112 pm; Zr^{4+}: 84 pm; Refs. [4,12]) we expect a much lower misfit parameter for Sc in zirconia. The activation enthalpy obtained from the frequency shift of the peak is 1.2 eV, i.e., close to that in yttria-doped zirconia. Additional evidence for the interpretation of peak I in ScSZ as being due to a point defect relaxation (i.e., reorientation of dipoles) comes from dielectric loss measurements. The dielectric loss peak I around 550 K shifts toward higher temperatures with increasing measurement frequency and can therefore be assigned to reorientation of electric dipoles consisting of oxygen vacancies and scandium cations.

4.2. High-temperature damping background (HTB)

The mechanical loss spectra of polycrystalline yttria- and scandia-doped zirconia show a monotonic increase of the damping above about 1000 K, which is shifted with increasing frequency towards higher temperatures indicating a viscoelastic relaxation process. From an analysis of the
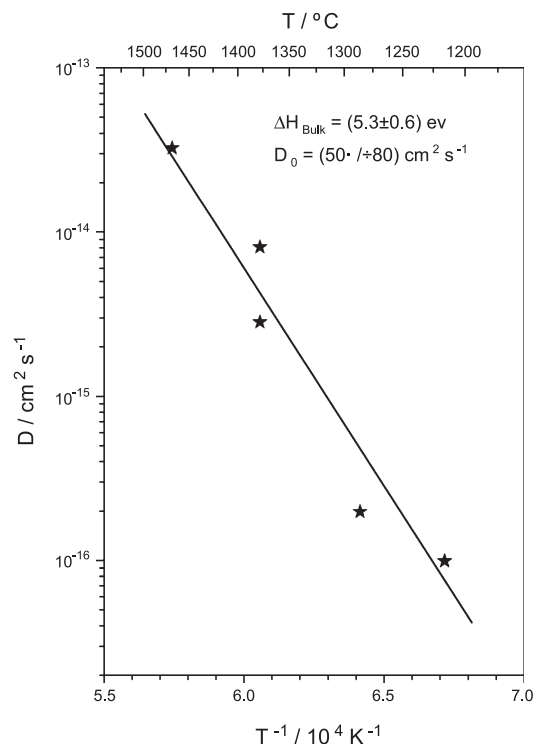

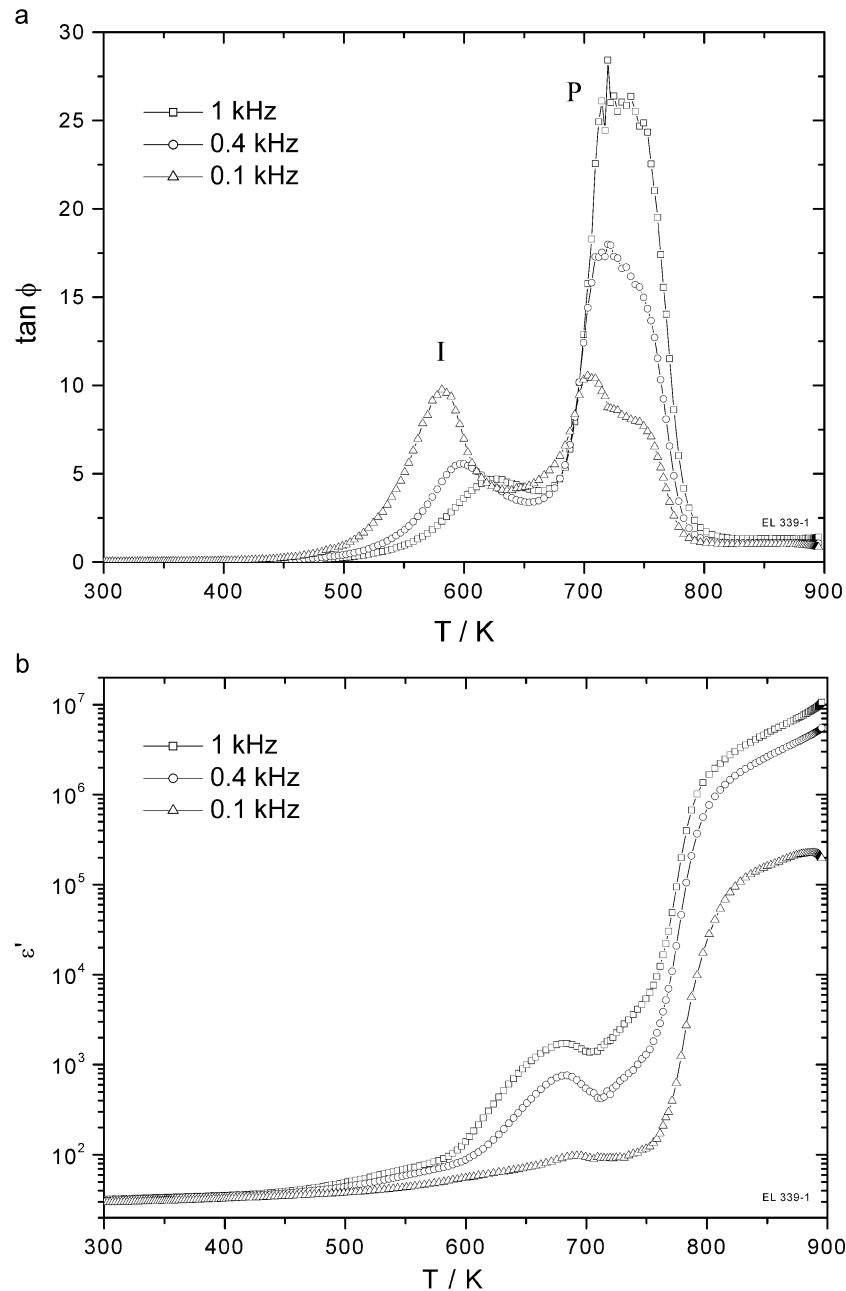Fig. 4. ^{96}Zr bulk tracer diffusion in ScSZ-12.

Fig. 5. Dielectric loss spectra, tanφ vs. *T* (a) and dielectric permittivity ε′ vs. *T* (b) for ScSZ-10 obtained at measurement frequencies from 0.1 to 1 kHz.

frequency dependence of the HTB in YSZ-8, an activation enthalpy of ΔH=5.5 eV was obtained [13,14]. This value correlated well with results from tracer diffusion experiments in this same material. Using the same method, the tracer diffusivity of Zr in ScSZ was determined similarly by measuring the depth distribution of the stable tracer [96]Zr in ScSZ-12. The activation enthalpy of ΔH=5.3 eV is like in YSZ-8 close to the results of the mechanical spectroscopy. This indicates that the HTB is in both systems related to the cation diffusion. The activation entropy of $10k_B$ is indicative for a diffusion mechanism going via lattice vacancies. In YSZ and CSZ, Zr has a lower diffusivity than the dopant elements [14]. It is therefore likely that also in ScSZ the diffusion of Zr might be the slowest transport process. Regarding the similarity in the activation enthalpies, both phenomena, high temperature viscoelastic relaxation and tracer diffusion, can be attributed to the same transport process. The HTB is based on local cation jumps, tracer diffusion monitors long-range cation diffusion. The activation enthalpies for the two processes are the same, which means that the long-range diffusion is not affected by further interacting processes as was observed in perovskites [15]. Since the HTB is only observed in polycrystals, the underlying deformation mechanism is assigned to grain boundary sliding by intergranular cation diffusion corresponding to Nabarro–Herring creep (see also Ref. [22]).

4.3. Phase transitions effects

Both in yttria- and scandia-doped zirconia, we observe at higher temperatures a sharp peak with the characteristic features of a phase transition: (i) the temperature position of the peak is independent of the measuring frequency; and (ii) the intensity is inverse proportional to the frequency f. In YSZ-12 single crystals, the peak around 1450 K (see Fig. 3) is assigned to a structural phase transition occurring in zirconia with higher yttria contents (12–18 mol%) (see also Refs. [6,14]). This structural phase transition corresponds to an order↔disorder phase transition, which was also observed in complementary measurements of the ionic conductivity in the same samples [11]. Here, it is found to be sensitive to the thermal history of the samples.

The phase transition peak P in ScSZ around 750 K, observed both with mechanical loss and dielectric loss spectroscopy, is assigned to another type of phase transition. Scandia-stabilised zirconia can form at least three different rhombohedral phases, which are quite unique for this system and are not known in the low-pressure phase diagrams of other doped zirconias like yttria-doped zirconia. Due to these rhombohedral phases, the phase diagram of the system ZrO_2–Sc_2O_3 is still controversially discussed; both the detailed structure of the different rhombohedral phases and the width of the phases are not clear [16–19]. The structure of the ordered rhombohedral phase was very recently solved and found to consist of a very big unit cell [21]. Peak P around 750 K is thus related to the phase transition from the rhombohedral β-phase to the non-ordered cubic phase.

Preliminary high-temperature X-ray studies performed in the same material confirmed this phase transition, and there was a similar temperature hysteresis between heating and cooling [20]. The rhombohedral β-phase is considered as a ferroelastic phase, and there is also some evidence for the existence of a second, less-ordered phase within the rhombohedral phase about 50–100 K below the cubic-rhombohedral phase transition [18]. This could explain the substructure of peak P in the mechanical loss spectra (Fig. 2) as well as the formation of a double peak P in the dielectric loss spectra (Fig. 5). The dielectric peak is connected with a decrease in electrical permittivity ε' (the steeply increasing ε'-values at high temperatures are assigned to space charge polarisation arising from increasing ionic conductivity, see Ref. [23]). We conclude that the underlying phase transition related to peak P is of ferroic nature and both ferroelastic and ferroelectric.

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