



Phase composition and ionic conductivity of zirconia stabilized with scandia and europia

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ABSTRACT

Sintered specimens of zirconia-10 mol% scandia pure and codoped (up to 1.25 mol%) with europium sesquioxide were prepared by solid-state synthesis, aiming to stabilize at room temperature the high-conductivity cubic phase. High-temperature X-ray diffraction and differential scanning calorimetry results reveal that small amounts of the codopant reduce the enthalpy of phase transition, and full stabilization is evidenced for 1 mol% europium sesquioxide. The low-temperature (<600 °C) ionic conductivity increases with increasing codopant content.

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1. Introduction

Over the past half-century a significant effort has been devoted to scientific and technological developments of efficient energy production systems, such as Solid Oxide Fuel Cells (SOFCs). Among the several ceramic components of SOFCs, the solid electrolyte is of primary concern, because it dictates the overall cell performance and the operating temperature [1]. To date, good electrochemical performance has been obtained with SOFC devices containing zirconia-8 mol% yttria (8YSZ) as solid electrolyte, with working temperatures in the high-temperature range (from ~800 to ~1000 °C). In the last years, solid electrolytes with ionic conductivity higher than that of 8YSZ have been thoroughly investigated, envisaging reducing the operation temperature of SOFCs, turning cost-effective that electrochemical device [2–4].

Scandia stabilized zirconia with cubic (c) symmetry is an alternative solid electrolyte with high oxide-ion conductivity (about 2 times that of 8YSZ), wide electrolytic domain and good chemical stability [5]. The complex phase relationship of this system points to ideal compounds those with 10–11 mol% scandia. The stable crystalline phase at room temperature of 10ScSZ (10 mol% scandia-stabilized zirconia) possess rhombohedral symmetry, with $\text{Sc}_2\text{Zr}_7\text{O}_{17}$ stoichiometry (β -phase) and relatively lower ionic conductivity [6].

Room temperature stabilization of the high-symmetry cubic structure in 10ScSZ has been demonstrated by introducing a

second dopant [7–9]. Trivalent rare-earth codopants fit the oxygen-vacancy concentration requirement, in order to obtain high oxide-ion conductivity in the zirconia-scandia system. Previous results with single valence cations such as Gd^{3+} [10], Y^{3+} [11], Sm^{3+} [12] and Dy^{3+} [13] revealed stabilization of the cubic structure at room temperature for different amounts of the codopant. The magnitude of the ionic conductivity was found to be dependent on codopant type and content.

In this work, the effects of small amounts of europium sesquioxide on the β -rhombohedral \rightleftharpoons c phase transition and ionic conductivity of 10ScSZ were investigated by high-temperature X-ray diffraction, differential scanning calorimetry and impedance spectroscopy.

2. Experimental

ZrO_2 : 10 mol% Sc_2O_3 (DKKK) and Eu_2O_3 (99.999%, Aldrich) were used as starting materials. Specimens containing europium sesquioxide were prepared by solid-state synthesis. The additive contents were: 0.25, 0.50, 0.85, 1.00 and 1.25 mol%.

Disc-shaped (ϕ 5 mm, ~2 mm thickness) specimens of pure 10ScSZ and mixed powders were prepared by uniaxial pressing and sintering at 1500 °C for 4 h with 10ScSZ powder bed.

The apparent density of sintered specimens was determined by the immersion method with distilled water. The phase transition was studied by high-temperature X-ray diffraction, HT-XRD, using a diffractometer (D8 Advance, Bruker-AXS) equipped with a Braun position sensitive detector and a heating stage (Anton Paar HTK 1400). Data were collected both during heating and cooling at

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selected temperatures in the 17 to 600 °C range between 47 and 54° 2θ in 0.037° steps. The phase transition was also investigated by differential scanning calorimetry, DSC (404 Pegasus, Netzsch). In these experiments 55 mg of sintered specimens were heated at 10 °C.min⁻¹ from room temperature up to 800 °C and cooled down to 200 °C in atmosphere of synthetic air (20 mL.min⁻¹) with alumina crucible. Spectroscopically pure aluminum was used for DSC calibration. The enthalpy of phase transition was calculated from the area under the peak of the thermal event recorded during heating.

Electrical conductivity measurements of sintered solid electrolytes were carried out by impedance spectroscopy (4192A, HP) in the frequency range of 5 Hz–13 MHz with 200 mV of applied AC signal and in the 300–550 °C range, with silver as electrode.

3. Results and discussion

All sintered specimens achieved high relative densities ($\geq 94\%$ of the theoretical value).

Fig. 1 shows HT-XRD patterns of pure and codoped 10ScSZ. In this case, only results obtained for pure 10ScSZ and specimens containing 0.50 and 1.00 mol% europium sesquioxide will be shown for the sake of brevity. The heating-cooling cycle is indicated by arrows in these patterns. In the 47 to 54° angular range, the cubic phase displays a single peak at 50.7°, whereas the β -rhombohedral phase shows two peaks at 50.1° and 51.3°, allowing for an easy identification of the characteristic phase at each temperature. The X-ray diffraction patterns of 10ScSZ (Fig. 1a) exhibit the typical peaks of the β -rhombohedral structure from room temperature (17 °C) up to 400 °C. In the 400 to 600 °C, the β -to-c phase transition occurs, and a single diffraction peak is recorded. On cooling down to room temperature, the X-ray diffraction patterns show the peaks of the β -phase. Similar behavior was obtained for 10ScSZ containing, 0.50 (Fig. 1b) europium sesquioxide and with 0.25 and 0.85 mol% Eu₂O₃ (not shown here). In the latter, the reversible phase transition is hardly observed, suggesting that the content

of Eu₂O₃ is close to the limit for full stabilization of the cubic structure. X-ray diffraction patterns of specimen with 1.00 mol% (Fig. 1c) Eu₂O₃ display the single peak corresponding to the cubic phase over the whole thermal cycle. These results evidence that the cubic phase of 10ScSZ may be stabilized at room temperature with about 1 mol% Eu₂O₃.

DSC curves are shown in Fig. 2 for 10ScSZ (a) and Eu₂O₃ doped 10ScSZ (b–f). Pure 10ScSZ exhibits a single endothermic peak during heating and a single exothermic peak during cooling, characteristic of the first-order β -rhombohedral \rightleftharpoons c phase transition. The reversible phase transition occurs in the 500–600 °C range. Similar behavior was obtained for specimens containing 0.25 (Fig. 2b), 0.50 (Fig. 2c) and 0.85 (Fig. 2d) mol% europium sesquioxide. Nevertheless, in these codoped specimens, both the intensity of the endo- and exothermic peaks and the peak temperature (temperature corresponding to the maximum amplitude) are lower than those of 10ScSZ, and steadily decrease with increasing the Eu₂O₃ content, Table 1.

The reversible phase transition was detected (Fig. 2d) in specimens with 0.85 mol% Eu₂O₃ only after increase of the heating rate (20 °C.min⁻¹), due to its low enthalpy. Further increase of the additive to 1.00 (Fig. 2e) and 1.25 mol% (Fig. 2f) reveals no thermal events in the DSC curves, indicating suppression of the phase transition and, therefore, full stabilization of the cubic symmetry at room temperature.

Table 1 summarizes some characteristic features of the β -rhombohedral \rightleftharpoons c phase transition detected by DSC experiments. The hysteresis of the phase transition (ΔT) in 10ScSZ on thermal cycling is about 30 °C, close to that (39 °C) determined for arc-melted ZrO₂: 11 mol% Sc₂O₃ [14]. For Eu₂O₃ doped 10ScSZ, the hysteresis increases gradually with increasing codopant content, evidencing increase of the cell volume and incorporation of the additive into the crystal lattice. The enthalpy for phase transition calculated for 10ScSZ correlates with that of previous report [14], and decreases abruptly with increasing codopant content.

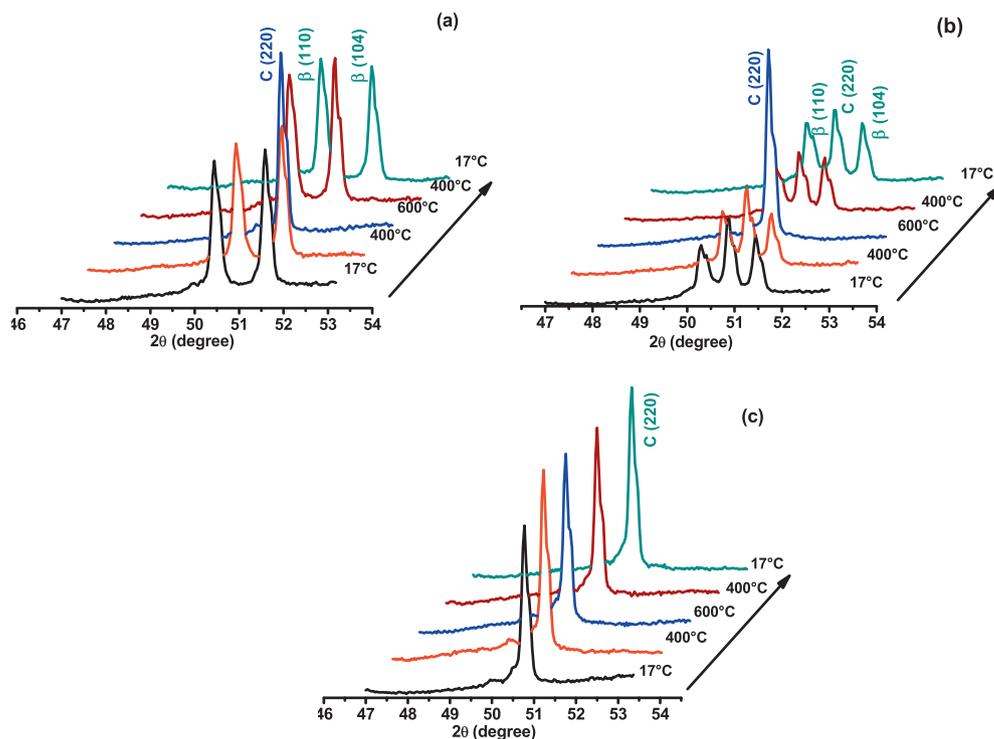


Fig. 1. HT-XRD patterns of (a) pure and Eu₂O₃ codoped 10ScSZ with (b) 0.50 and (c) 1.00 mol% during a heating-cooling cycle.

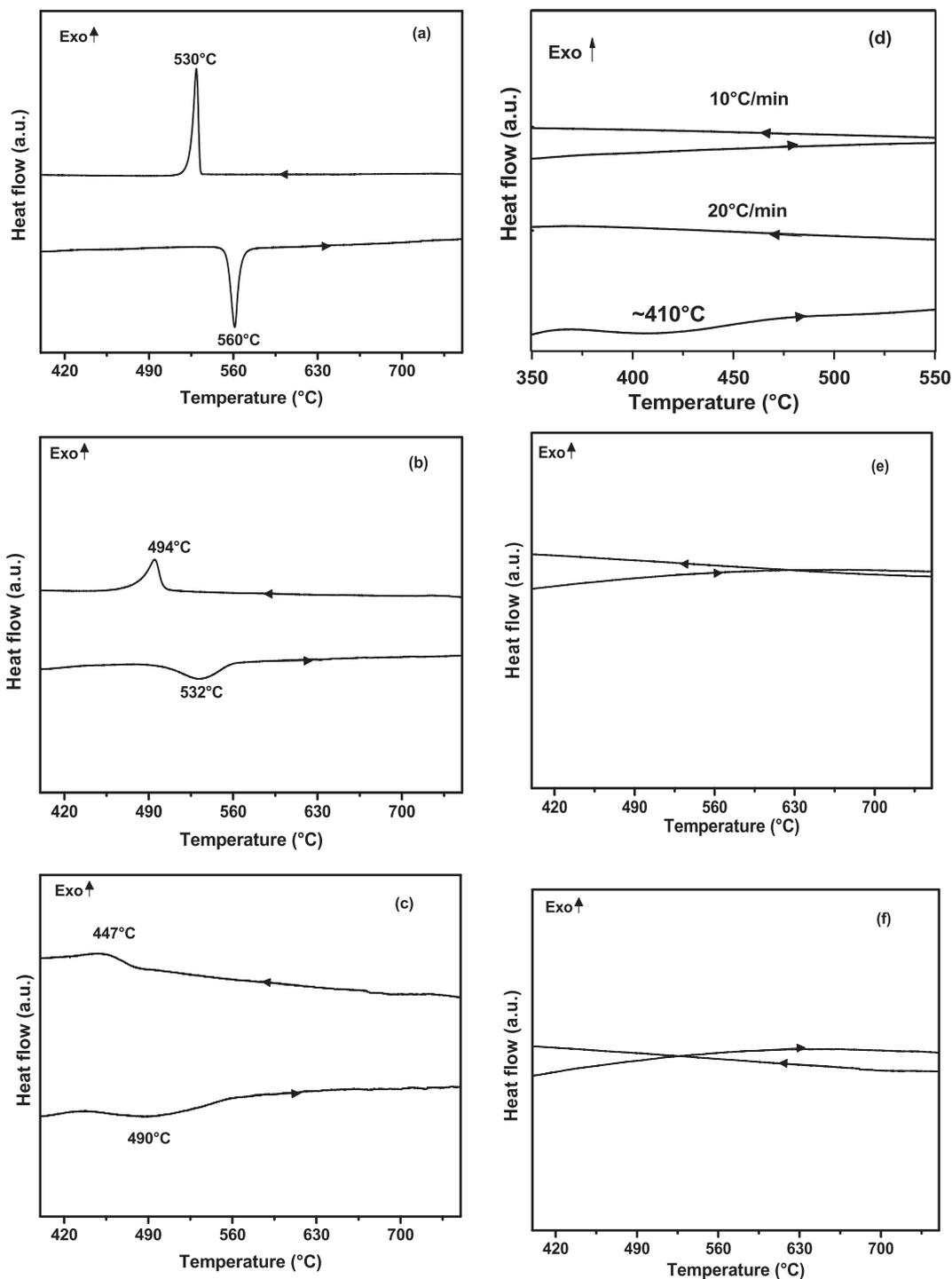


Fig. 2. DSC curves of (a) pure and Eu_2O_3 codoped 10ScSZ. (b) 0.25, (c) 0.50, (d) 0.85, (e) 1.00 and (f) 1.25 mol%.

Table 1

Peak temperature (T) and enthalpy (ΔH) of the β -rhombohedral \rightleftharpoons c phase transition determined during heating pure and codoped 10ScSZ specimens.

Specimen	T (°C)	ΔT (°C)	ΔH (J.g ⁻¹)
10ScSZ	560	30	17.66
0.25 mol% Eu_2O_3	532	38	12.31
0.50 mol% Eu_2O_3	490	43	5.75
0.85 mol% Eu_2O_3	~410	-	-

The $-Z''(\omega)$ versus $Z'(\omega)$ impedance spectroscopy diagrams of codoped 10ScSZ specimens consist of two overlapping arcs due

to grain and grain boundary electric responses (Fig. S1). The imaginary ($-Z''$) and the real (Z') components of the impedance were normalized for specimen dimensions for comparison purposes. Numbers in these plots stand for the logarithm of the relaxation frequency. In pure as well as in codoped specimens the contribution of grain boundaries to the overall ionic conductivity of the solid electrolytes is marginal. Then, in a typical operation temperature (600–750 °C) of intermediate-temperature SOFCs the contribution of grain boundaries may be neglected.

Fig. 3 shows the Arrhenius plots of the overall (grain and grain boundaries) ionic conductivity (σ_{τ}) of pure and Eu_2O_3 doped

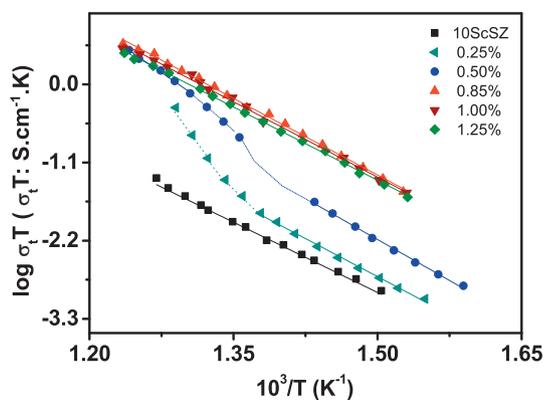


Fig. 3. Arrhenius plots of the ionic conductivity of pure and Eu_2O_3 codoped 10ScSZ specimens.

10ScSZ. Europium sesquioxide promoted a substantial increase of the magnitude of σ_t . At 500 °C, for example, σ_t amounts 0.039 and 2.0 $\text{mS}\cdot\text{cm}^{-1}$ for pure 10ScSZ and 1.00 mol% Eu_2O_3 codoped solid electrolytes, respectively.

4. Conclusions

Small amounts (less than 1 mol%) of Eu_2O_3 added to zirconia-10 mol% scandia lead to a reduction of the temperature and the enthalpy associated to the β -rhombohedral to cubic phase transition, and promoted partial stabilization of the cubic structure. Full stabilization of the high-symmetry cubic phase at room temperature was obtained with 1 mol% europium sesquioxide, with consequent increase of the ionic conductivity.

The zirconia-scandia-europia is a potential candidate for application as solid electrolyte in electrochemical devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.matlet.2018.06.091>.

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