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Evidence of induced structural and conduction anisotropy in scandia-stabilized zirconia ceramics

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Evidence of current induced structural and conduction anisotropy was experimentally established in scandia-stabilized zirconia ceramics. It was found that these effects are observed only when the material is in the rhombohedral phase. It was shown using conductivity measurements and X-ray phase analysis that anisotropic behavior of polycrystalline ZrO_2-Sc_2O_3 ceramics is induced by a low-amplitude alternating current in the temperature range corresponding to a rhombohedral-to-cubic phase transition.

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1 Introduction Rare-earth metal oxides are widely used to stabilize cubic phase of zirconia, and it is well known that scandia-stabilized zirconia demonstrates extremely high conductivity as compared with other similar systems [1].

In our prior study of scandia-stabilized zirconia we had first found a low-temperature conductivity anomaly in the ceramics 89 mol.% ZrO_2 + 10 mol.% Sc_2O_3 + 1 mol.% CeO_2 within the temperature range 600–630 K [2]. This anomaly consisted in (i) negligibly small conductivity in the as-sintered condition and the onset of measurable conduction only after high-temperature current passing and (ii) the absence of temperature hysteresis. The latter makes the connection of this anomaly with a phase transition that had induced the assumption about anisotropic behavior of the rhombohedral phase as the main cause of the conductivity anomaly unlikely.

In order to test the above assumption we have analyzed phase composition of nonconductive and conductive specimens at temperatures 290, 560, 680, and 900 K [2]. As-sintered nonconductive ceramics had shown the following phase sequence at these temperatures: cubic → cubic → rhombohedral → cubic. The conductive ceramics had shown a different phase sequence at the same temperatures: rhombohedral → rhombohedral → rhombohedral → cubic. Since in the last case the specimens were predominantly in the rhombohedral phase within the temperature range 290–750 K, it was established that the conductivity anomaly is irrelevant to phase transitions.

It is known that the rhombohedral phase in scandia-stabilized zirconia at Sc_2O_3 concentrations above 9.3 mol.% inherits the anisotropic properties of Sc-O-Sc clusters during formation [3]. This had allowed us to assume anisotropic behavior of such ceramics [2].

The present study was devoted to providing the experimental evidence of anisotropy in scandia-stabilized zirconia with the conductivity anomaly. A ceramics composition of 90 mol.% ZrO_2 + 9.96 mol.% Sc_2O_3 + 0.04 mol.% La_2O_3 was chosen in order to demonstrate the low-temperature conductivity anomaly at different dopant contents. Substitution of cerium oxide with lanthanum oxide pursued the objectives of, on the one hand, better stabilization of the material in the high-temperature range due to larger ionic radius of lanthanum compared with the radii of both zirconium and scandium at close atomic masses, and, on the other hand, increasing the oxygen vacancy concentration and consequently ionic conductivity due to the valence change ($Ce^{4+} \rightarrow La^{3+}$) [4].

2 Experimental Ceramic powder with estimated end composition 90 mol.% ZrO_2 + 9.96 mol.% Sc_2O_3 + 0.04 mol.% La_2O_3 was produced using reverse coprecipitation. Zirconium, scandium, and lanthanum hydroxides were coprecipitated from aqueous solution of the metal chlorides ($ZrOCl_2$, $ScCl_3$, $LaCl_3$) using aqueous ammonium hydrate. Vacuum filtering of the obtained suspension and

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multiple washing with distilled water yielded wet powder, which was twice dried with subsequent grinding in a mortar. A solid solution in the powder particles was synthesized using calcination for 2 h at 1123 K. The residual impurity content in calcined powders was as follows (mol.%): 0.0095 (SiO_2); 0.0057 (Fe_2O_3); 0.0062 (Al_2O_3); 0.0097 (TiO_2); 0.005 (CaO); and 0.01 (MgO). The ceramics was sintered for 2 h at 1820 K. The final chemical composition was determined using the microprobe analysis during scanning electron microscopy. Sintered ceramics had an average grain size of 1.8 μm and a density of 4.3 g/cm^3.

Isostatically pressed, sintered, and polished ceramic specimens for conductivity measurements had cubic shape with the cube edge 4.25 ± 0.50 mm.

The ionic conductivity was measured using a two-electrode circuit. Silver electrodes were applied onto polished specimen surfaces by baking. The total resistance of electrodes and platinum wire leads was less than 1 Ω. The measuring voltages and current densities were within the ranges 10–200 mV and 0–2 mA/cm^2, respectively.

The ionic conductivity was measured simultaneously with X-ray diffraction studies using Cu K$_\alpha$ radiation. The heating and cooling rates were below 2 K/min. The initial X-ray diffraction patterns recorded at room temperature from different faces of ceramic specimens were identical (Fig. 1a).
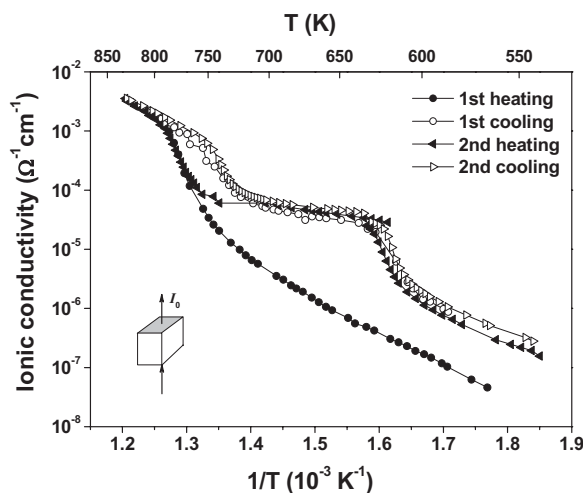
3 Results and discussion Arrhenius plots of ionic conductivity for ceramics 90 mol.% $ZrO_2 + 9.96$ mol.% $Sc_2O_3 + 0.04$ mol.% La_2O_3 during the first two thermal cycles are presented in Fig. 2. These plots reveal all the features observed in previously studied material 89 mol.% $ZrO_2 + 10$ mol.% $Sc_2O_3 + 1$ mol.% CeO_2 [2], namely, a low-temperature conductivity anomaly; high-temperature kinks forming the hysteresis loop caused by the well-known rhombohedral-to-cubic phase transition in the range 750–900 K [5–9], and low-temperature anhysteretic kinks in the range 600–630 K. It can be concluded that both materials show similar behavior and hence the discovered features of ionic conduction are of common nature.

In order to study the material structure anisotropy, one ceramic specimen 90 mol.% $ZrO_2 + 9.96$ mol.% $Sc_2O_3 + 0.04$ mol.% La_2O_3 was first subjected to seven conventional repeated conductivity measurements in the same configuration with heating up to 973 K and cooling down to room temperature in each cycle. After this treatment X-ray diffraction patterns were recorded at room temperature from the specimen faces with normal perpendicular to the electric current direction (Fig. 1b) or parallel to the electric current direction (Fig. 1c). Figure 1 shows that the patterns are essentially different, indicating on structural anisotropy of the specimen, i.e., mutual ordering of grains occurring in rhombohedral phase.

The above-presented evidence of current-induced structural anisotropy implies also possible anisotropy of conductivity. To check this possibility, the specimen subjected to conventional repeated conductivity measurements in one direction (I_0 in inserts of Figs. 1 and 3) was used to measure
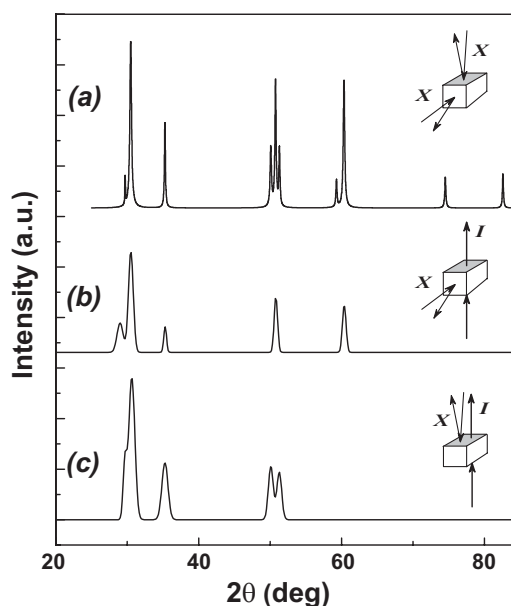

Figure 1 X-ray diffraction patterns recorded at room temperature from different faces of one ceramic specimen 90 mol.% $ZrO_2 + 9.96$ mol.% $Sc_2O_3 + 0.04$ mol.% La_2O_3: (a) from any face in the as-sintered condition; (b) from the face with a normal perpendicular to the electric current direction during seven prior conventional repeated conductivity measurements in the same configuration with heating up to 973 K; and (c) from the face with a normal parallel to the prior electric current direction.

Figure 2 Arrhenius plots of ionic conductivity in ceramics 90 mol.% $ZrO_2 + 9.96$ mol.% $Sc_2O_3 + 0.04$ mol.% La_2O_3 during the first two thermal cycles.

the conductivity in a perpendicular direction (I_1 in insert of Fig. 3). The results are presented in Fig. 3.

On first heating to 665 K, the temperature lying between two kinks in Arrhenius plots (see Figs. 2 and 3), and then cooling down to room temperature yielded virtually

Phys. Status Solidi A **209**, No. 4 (2012)

729

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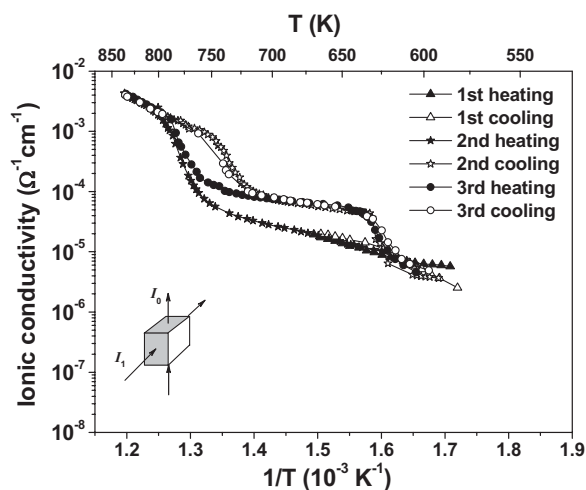
Figure 3 Arrhenius plots of ionic conductivity in ceramics 90 mol.% ZrO_2 + 9.96 mol.% Sc_2O_3 + 0.04 mol.% La_2O_3 in the direction (I_1) perpendicular to prior conventional conductivity measurements (I_0).

coinciding curves similar to first heating in the as-sintered condition (Fig. 2) but with a much higher ionic conductivity. As opposed to Fig. 2, the low-temperature conductivity anomaly is absent here. A second cooling and all subsequent heating and cooling cycles give identical curves with kinks and low-temperature conductivity anomaly similar to the curves of the second cycle in Fig. 2.

As a result, on heating to above 800 K the specimen laterally connected to the measurement circuit inverted the total picture of ionic conductivity. Namely, a low-temperature conductivity anomaly again appeared in the lateral direction (I_1) while in the initial direction (I_0) this anomaly was absent and the low-temperature conductivity values were lower.

It can be concluded therefore that the ionic conductive properties of the material can be made anisotropic and "switchable" by changing the current leading faces and heating under current flow at temperatures within the rhombohedral phase stability range.

4 Conclusions The analysis of above-presented experimental data suggests that the observed ionic conduction anisotropy is caused by ordering of crystallites due to the instability of the crystalline lattice in the vicinity of the rhombohedral-to-cubic phase transition. Lattice instability and initiation of soft modes in the phonon spectrum essentially facilitate rearrangement of the lattice by cooperative ordered movement of foreign scandium ions in a weak electric field.

It should be underlined that the induced anisotropic properties in polycrystalline ceramic specimens are quite stable. We had found experimentally that ionic conductivity values as well as the appearance of Arrhenius curves remain the same within measurement error after storage of specimens for 10 days at room temperature. However, the induced anisotropy completely disappeared after storage for one year or more. Nevertheless, anisotropy in such degraded specimens can be restored by electric measurements during heating up to 873–973 K.

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