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Structure and transport properties of zirconia crystals co-doped by scandia, ceria and yttria



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ABSTRACT

This work is a study of the effect of co-doping $(ZrO_2)_{0.9}(Sc_2O_3)_{0.1}$ solid solution with yttria and/or ceria on the phase composition, local structure and transport properties of the crystals. The solid solution crystals were grown using directional melt crystallization in cold crucible. We show that ceria co-doping of the crystals does not stabilize the high-temperature cubic phase in the entire crystal bulk, unlike yttria codoping. Ceria co-doping of the $(ZrO_2)_{0.9}(Sc_2O_3)_{0.1}$ crystals increases their conductivity, whereas the addition of 1 mol.% yttria tangibly reduces the conductivity. Equimolar co-doping of the $(ZrO_2)_{0.9}(-Sc_2O_3)_{0.1}$ crystals with ceria and yttria changes the conductivity but slightly. Optical spectroscopy of the local structure of the crystals identified different types of optical centers. We found that the fraction of the trivalent cations having a vacancy in the first coordination sphere in the ceria co-doped crystals is smaller compared with that in the yttria co-doped crystals.

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1. Introduction

The ionic conductivity of scandia stabilized zirconia-based materials (**ScSZ**) is higher compared with that of the $ZrO_2-Y_2O_3$ system solid solutions [1–3]; this makes the working temperature of the electrochemical devices lower. Zirconia-based materials with high ionic conductivity can be applied in one of the most promising electrochemical systems, which converts chemical energy of hydrocarbon fuel oxidation to electrical and heat energy – solid oxide fuel cells, SOFC [4–7]. Compositions containing (10–12) mol.% Sc₂O₃ have the maximum conductivity in the $ZrO_2-Sc_2O_3$ system. However, the high-conductivity cubic phase transforms to the rhombohedral one in this composition range, this transition causing a significant reduction in the conductivity [1,8]. Furthermore, these materials exhibit a degradation of the electrophysical

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properties after long-term operation. Co-doping of ScSZ with a range of metal oxides such as Y_2O_3 or CeO₂ stabilizes the high-temperature cubic phase at room temperature thus reducing conductivity degradation [2,9–12].

The high oxygen ionic conductivity of the zirconia-based solid electrolytes is caused by the presence of oxygen vacancies in their anion sublattice. These vacancies form due to the heterovalent substitution of the Zr⁴⁺ ions by the R³⁺ ones. Ionic conductivity depends on the type and concentration of the stabilizing oxide, the phase composition and the local crystalline structure of the ZrO₂ base solid solutions. The interaction of the vacancies with stabilizing oxide cations may cause the formation of different types of complexes [13–16]. The formation of these complexes increases the activation energy and hence reduces the conductivity [17,18]. The type of the forming complexes can be characterized by the location of the oxygen vacancies relative to the zirconium and doping impurity cations, i.e., the local structure of the crystalline lattice. One method for studying the local structure of the crystals is selective laser spectroscopy. This method is widely used for studying the defect structure of zirconia-based solid solutions [19,20].

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The aim of this work is to study the effect of 10ScSZ solid solution co-doping with yttria and/or ceria on the phase composition, local structure and transport properties of the crystals grown by directional melt crystallization.

2. Experimental

2.1. Preparation of single-crystalline samples

 $(ZrO_2)_{0.9-x-y}(Sc_2O_3)_{01}(Y_2O_3)_x(CeO_2)_y (x = 0; 0.005; 0.01), y = (0; 0.005; 0.01)$ solid solution crystals were grown by directional melt crystallization in cold crucible [21]. Some compositions were additionally doped with 0.1 mol.% Eu₂O₃ the ions of which were used as a spectroscopic probe for a spectral study.

2.2. Experimental techniques

The chemical composition of the as-grown crystals was examined using a JEOL 5910 LV scanning electron microscope with an INCA Energy dispersion tool. Molten zirconia, scandia and ceria were used as references for crystal composition measurements.

The phase composition of the crystals was analyzed using X-ray diffraction on a Bruker D8 instrument in CuK α radiation and using Raman spectroscopy. The excitation source was a 532 nm laser, Raman device was described in details previously [22–24]. The Raman spectra were recorded at multiple points along the crystal for phase composition homogeneity assessment.

The density of the crystals was measured by hydrostatic weighing on a Sartorius hydrostatic weighing device. The microstructure was examined using optical microscopy under a Discovery V12 stereo microscope.

The luminescent spectra were recorded using a Horiba FHR 1000 spectrometer at 300 and 77 K. A Hamamatsu R928 photomultiplier was used as the photodetector. Luminescence was excited at the ${}^{5}D_{1}$ level of Eu³⁺ by second harmonics of YVO₄:Nd ($\lambda_{ex} = 532$ nm) and LiYF₄:Nd ($\lambda_{ex} = 527$ nm) lasers.

The conductivity of the crystals was studied in the 400–900 °C range on heating with a Solartron SI 1260 frequency characteristic analyzer in the 1 Hz to 5 MHz frequency range at a 24 mV current signal amplitude. We used $7 \times 7 \text{ mm}^2$ 0.5 mm thick plates for the measurements. The current contacts were formed by applying platinum paste (burning onto the opposite sides of the crystals at 950 °C for 1 h in air). The impedance spectra were processed using the ZView software (ver. 2.8). The specific conductivity of the crystals was calculated from the data retrieved from the impedance spectra taking into account the dimensions of the specimens.

3. Results and discussion

3.1. Single-crystalline samples

We synthesized $ZrO_2+10\ mol.\%\ Sc_2O_3$ solid solution crystals stabilized with CeO_2 and/or Y_2O_3. Table 1 summarizes the compositions, densities and notations of the crystals to be used hereinafter.

The appearance of the as-grown crystals differed depending on their compositions. The 10ScSZ crystals were semi-transparent; this is an indirect indication of the presence of the second phase in the crystals. Addition of 0.5 and 1 mol% CeO₂ produces an orange-red hue of the crystals the intensity of which grows with increasing ceria concentration, yet the crystals remaining semi-transparent. Addition of 0.5 mol.% Y_2O_3 produces transparent regions, and further increase in the Y_2O_3 concentration to 1 mol% makes the crystals homogeneous and completely transparent. CeO₂ and Y_2O_3 co-doping of the crystals (10Sc0.5Ce0.5YSZ) produced

Table 1

Compositions, densities and brief notations of crystals.

Composition	Notation	Density, g/cm ³
$\begin{array}{l} (ZrO_2)_{0.9}(Sc_2O_3)_{0.1} \\ (ZrO_2)_{0.895}(Sc_2O_3)_{0.1}(CeO_2)_{0.005} \\ (ZrO_2)_{0.895}(Sc_2O_3)_{0.1}(CeO_2)_{0.01} \\ (ZrO_2)_{0.895}(Sc_2O_3)_{0.1}(Y_2O_3)_{0.005} \\ (ZrO_2)_{0.89}(Sc_2O_3)_{0.1}(Y_2O_3)_{0.01} \\ (ZrO_2)_{0.89}(Sc_2O_3)_{0.10}(CeO_2)_{0.005}(Y_2O_3)_{0.005} \\ (ZrO_2)_{0.885}(Sc_2O_3)_{0.10}(CeO_2)_{0.005}(Y_2O_3)_{0.01} \end{array}$	10ScSZ 10Sc0.5CeSZ 10Sc1CeSZ 10Sc0.5YSZ 10Sc1YSZ 10Sc0.5Ce0.5YSZ 10Sc0.5Ce1YSZ	$\begin{array}{c} 5.753 \pm 0.002 \\ 5.748 \pm 0.001 \\ 5.757 \pm 0.002 \\ 5.731 \pm 0.002 \\ 5.744 \pm 0.001 \\ 5.735 \pm 0.001 \\ 5.747 \pm 0.002 \end{array}$

inhomogeneous crystals the bottom parts of which were opaque, and the top parts were transparent. The 10Sc0.5Ce1YSZ crystals were completely transparent and homogeneous. Fig. 1 shows the appearance of crystals for some compositions.

3.2. X-ray diffraction analysis

The chemical composition and the distribution of the solid solution components along the crystals were analyzed using energy dispersion X-ray diffraction.

Ceria doping of 10ScSZ with 0.5 mol.% (10Sc0.5CeSZ) produced a homogeneous CeO₂ distribution, while for 1 mol.% CeO₂ (10Sc1CeSZ) an enrichment of the top part of the crystal with cerium was observed. The optically homogeneous 10Sc1YSZ crystals (Fig. 1b) had a homogeneous longitudinal component distribution, their composition corresponding to the raw charge composition. The transparent regions of the optically inhomogeneous 10Sc0.5Ce0.5YSZ crystals exhibited a slight increase in the ceria and yttria concentrations. The 10Sc0.5Ce0.5YSZ crystals had no sharp boundary between the transparent and the opaque regions. At a higher Y_2O_3 concentration (1 mol.%, 10Sc0.5Ce1YSZ) the visually homogeneous crystals had a homogeneous longitudinal component distribution.

Table 2 shows X-ray diffraction data on the phase composition of the $(ZrO_2)_{0.9-x-y}(Sc_2O_3)_{0.1}(Y_2O_3)_x(CeO_2)_y$ crystals.

As can be seen from Table 2, the 10ScSZ crystal was a mixture of two phases, i.e., the cubic and the rhombohedral zirconia modifications. Addition of 0.5 and 1 mol% ceria to 10ScSZ does not increase the quantity of the cubic phase in the crystals. However, the lattice parameter of the cubic phase increases with ceria concentration. Yttria doping of the 10ScSZ crystals has a greater effect on the phase composition of the crystals compared with cerium doping. Addition of 0.5 mol.% Y₂O₃ to 10ScSZ increase the quantity of the cubic phase, while at 1 mol% Y₂O₃ the high-temperature cubic phase stabilizes in the entire crystal bulk. The lattice parameter of the cubic phase also increases with yttria concentration. For co-doping of 10ScSZ with ceria and yttria to 0.5 mol.%, the



Fig. 1. Appearance of (a) 10ScSZ, (b) 10Sc1YSZ and (c) 10Sc0.5Ce1YSZ crystals.

Table 2 Phase composition and lattice parameters of $(ZrO_2)_{0.9-x-y}(Sc_2O_3)_{0.1}(Y_2O_3)_x(CeO_2)_y$ crystals.

Sample	Phase	Weight Fraction, %	Lattice parameters	
			a, nm	c, nm
10ScSZ	c	65	0.5091(1)	0.9010(2)
	r	35	0.3562(2)	
10Sc0.5CeSZ	с	65	0.5092(1)	0.9008(2)
	r	35	0.3561(2)	
10Sc1CeSZ	с	70	0.5093(1)	0.9007(2)
	r	30	0.3560(2)	
10Sc0.5YSZ	с	80	0.5092(1)	0.9007(2)
	r	20	0.3560 (2)	
10Sc1YSZ	с	100	0.5093(1)	
10Sc0.5Y0.5CeSZ	с	80	0.5092(1)	0.9008(2)
	r	20	0.3560(2)	
10Sc1Y0.5CeSZ	с	100	0.5093(1)	

quantity of the cubic phase in the 10Sc0.5Ce0.5YSZ crystal was comparable to that in the 10Sc0.5YSZ crystal. Thus, we did not observe high-temperature cubic phase stabilization as a result of cerium doping to 0.5 mol.%.

Data for crystals' phase composition in Table 2 do not agree with the results of numerous studies of ceramic samples. In particular, it was reported that ceramic samples of 10Sc1CeSZ have single-phase cubic structure [10,15,25,26]. The phase composition and properties of the zirconium based materials strongly depend on thermal history. For ceramic technologies the materials are typically sintered at up to 1600 °C. We synthesized the crystals by directional melt crystallization beginning from temperatures above the melting point (approx. 2800 °C). This difference in the synthesis conditions may alter the phase formation mechanisms occurring in the material and eventually lead to different phase compositions of the synthesized specimens in spite of their similar chemical composition.

Crystal density depends on type and concentration of stabilizing oxide as well as on phase composition of the crystal, it growth when on adds ceria. Density of single-phase cubic crystal 10Sc0.5Ce1YSZ is slightly above the density of 10Sc1YSZ because we additionally introduced the heavier cerium ion in a crystal composition. Density of two-phase (c + r) crystals is mainly governed by two factors. Introduction of yttria and ceria, which are heavier than Sc₂O₃, has to lead to growth of crystal density, meanwhile increase of rhombohedral phase content leads to decrease of crystal density, as rhombohedral phase has lower density than cubic phase. That is why there is no obvious dependence of two-phase crystal density.

3.3. Raman spectroscopy analysis

The Raman spectra of the as-grown crystals are shown in Fig. 2. The phase composition data retrieved from the Raman spectra suggest that the Raman spectra of the homogeneous and transparent 10Sc1YSZ and 10Sc0.5Ce1YSZ crystals are typical of the t⁺ phase [27]. The Raman spectra of the two-phase 10ScSZ, 10Sc0.5CeSZ and 10Sc0.5Ce0.5YSZ crystals contain bands typical of the rhombohedral phase, but these bands are quite broadened. The Raman spectra of the 10Sc1CeSZ resembles that of the cubic phase but is strongly broadened in the region of the rhombohedral phase bands.

Thus, the Raman spectroscopy data are generally in agreement with the X-ray diffraction data. One should however note that, according to X-ray diffraction data, the Raman spectra of the single-phase cubic crystals have a peak near 480 cm^{-1} which is attributed to the tetragonal t[°] phase [27].



Fig. 2. Raman spectra of $(ZrO_2)_{0.9-x-y}(Sc_2O_3)_{0.1}(Y_2O_3)_x(CeO_2)_y$ crystals (**top of the crystal,*bottom of the crystal).

3.4. Impedance spectroscopy analysis and temperature dependence of conductivity

Typical impedance spectra of two crystals are shown at Fig. 3: for single-phase cubic crystal 10Sc1YSZ (a) and for 10Sc0.5CeSZ (b), which consist of cubic and rhombohedral phases. These spectra consist of arc in high-frequency part of the spectrum, which corresponds to bulk conductivity, as well as low-frequency arc, which present polarization resistance of electrodes. Intermediate arc, which corresponds to grain boundary conductivity, is absent. Thus, despite of two-phase structure of 10Sc0.5CeSZ crystal its impedance spectrum has no peculiarities in comparison to impedance spectrum of single-phase cubic 10Sc1YSZ crystal.

Fig. 4 shows the conductivity as temperature functions of the $(ZrO_2)_{0.9-x-y}(Sc_2O_3)_{0.1}(Y_2O_3)_x(CeO_2)_y$ crystals in Arrhenius coordinates. The temperature functions of the conductivity of the 10ScSZ, 10Sc0.5CeSZ and 10Sc0.5Ce0.5YSZ crystals have a clear break in the low-temperature region indicating the presence of the rhombohedral to cubic phase transition. The absence of that break in the temperature function of the electrical conductivity of the 10Sc1CeSZ specimen which also contains the rhombohedral phase can be attributed to the inhomogeneity of the crystal. This crystal contains large areas of rhombohedral phase, which are non-uniformly placed in cubic matrix.

Fig. 5 shows effect of dopant content on the electrical conductivity of 10ScSZ crystals doped with ceria and yttria and co-doped with these oxides at 1173 K. Ceria doping of the 10ScSZ crystals increases their conductivity, with the highest conductivity occurring at 0.5 mol.% ceria. Same maximum of conductivity at 0.5 mol.% of ceria was also detected in samples of ScSZ–xCeO₂ (x = 0.5, 1.0, 5.0 mol.%), which were prepared at 1600 °C from nano-sized powders [28]. Yttria doping to 1 mol.% significantly reduces the conductivity. Equimolar co-doping of the 10ScSZ crystals changes their conductivity but slightly, and further increasing the yttria concentration to 1 mol.% leads to a decrease in the conductivity. Interestingly, the 10Sc1YSZ and 10Sc0.5Ce1YSZ crystals have close conductivities, i.e., in this case ceria doping to 0.5 mol.% has but minor effect on the conductivity.

3.5. Luminescence spectroscopy analysis

We used optical spectroscopy to study the local structure of the



Fig. 3. Impedance spectra of the 10Sc1YSZ $({\rm a})$ and 10Sc0.5CeSZ $({\rm b})$ crystals at 653 and 719 K respectively.



Fig. 4. Electrical conductivity as temperature functions of the crystals (**top of the crystal,*bottom of the crystal).

10Sc1YSZ and 10Sc1CeSZ crystals doped with 0.1 mol.% Eu₂O₃ which was used as a spectroscopic probe. Similar studies were carried out earlier for $(ZrO_2)_{1-x}(Y_2O_3)_x$ solid solution crystals over a wide range of Y_2O_3 concentrations (x = 0.027–0.38) [20]. It was shown that in this concentration range there are four main types of optical centers of Eu³⁺ ions having different crystalline neighborhood. Type I optical centers are Eu³⁺ cations surrounded by oxygen seven-vertex and characterized by the presence of an oxygen vacancy in the first coordination sphere. Type II optical centers form if an Eu³⁺ cation is in the center of an oxygen eight-vertex, i.e., there is no oxygen vacancy in the first coordination sphere. Type III optical centers



Fig. 5. Effect of dopant content on the electrical conductivity of 10ScSZ, 10Sc xCeSZ 10Sc1YSZ and 10Sc0.5Ce xYSZ crystals at 1173 K.

have three oxygen vacancies at the diagonal positions of the cube, i.e., Eu^{3+} is in the center of an oxygen six-vertex, i.e., two oxygen vacancies are present in the first coordination sphere. Type IV optical centers are characterized by an eightfold coordination and the absence of oxygen vacancies in the nearest crystalline neighborhood. The presence of a specific type of Eu^{3+} optical centers depends on the concentration of the stabilizing oxide and the crystalline structure of the material.

We analyzed the luminescence spectra of the 10Sc1YSZ and 10Sc1CeSZ crystals taking into account the results obtained for $(ZrO_2)_{(1-x)}(Y_2O_3)_x$ crystals. Fig. 6 shows the luminescence spectra of the 10Sc1YSZ and 10Sc1CeSZ crystals for the ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions of the Eu³⁺ ions during excitation of the 5D_1 ($\lambda_{ex} = 532$ nm) level at 300 and 77 K. For comparison Fig. 6 also shows the luminescence spectra of the 12YSZ crystal [16] in which the Y_2O_3 concentration was comparable with the overall concentration of the stabilizing oxides in the crystals studied in this work.

The luminescence spectra for the ${}^5D_0 \rightarrow {}^7F_1$ transition of the Eu³⁺ ions in the 10Sc1YSZ crystal recorded after excitation of the 5D_1 level of the Eu³⁺ ions at 300 and 77 K have the same spectral bands as for the 12YSZ crystal. However, there are differences in the intensity ratios of the spectral bands corresponding to different Eu³⁺ optical centers in the 10Sc1YSZ and 12YSZ crystals. For example, in the 300 K luminescence spectra of the 10Sc1YSZ crystals (Fig. 5a) the intensity of the bands corresponding to type II optical centers is higher than the intensity of the band corresponding to type I optical centers, whereas in the luminescence spectra of the 12YSZ crystals the intensity ratio of these bands is contrary.

In the 77 K luminescence spectra (Fig. 6b) the intensity ratio of the bands corresponding to the type I and II optical centers in the 10Sc1YSZ crystals is lower compared with that ratio for the 12YSZ crystals. The differences in the luminescence spectra of Eu^{3+} ions in the 10Sc1YSZ and 12YSZ crystals suggest that the fraction of the type I optical centers having an oxygen vacancy in the first coordination sphere in the 10Sc1YSZ crystals is lower compared with that in the 12YSZ crystals.

The most significant differences are between the luminescence spectra of the 10Sc1CeSZ and 12YSZ crystals. The luminescence spectra of the 10Sc1CeSZ crystals for the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition of the Eu³⁺ ions at 300 K have an intense band in the 586–589 nm region (type II optical centers). A band peaking at 585.5 nm and corresponding to type I optical centers is weakly resolved against the short-wave side of that band. Thus, the fraction of the type I optical



Fig. 6. Luminescence spectra of 10Sc1YSZ, 10Sc1CeSZ and 12YSZ crystals caused by ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions of Eu³⁺ ions during excitation of the ${}^{5}D_{1}$ ($\lambda_{ex} = 532 \text{ nm}$) level at (a) 300 and (b) 77 K. Numbers show types of Eu³⁺ optical centers.

centers is even lower in 10Sc1CeSZ than in the 10Sc1YSZ and 12YSZ crystals.

There are more differences in the luminescence spectra, e.g. for the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transitions of Eu³⁺ the origin of which requires further investigation. Thus, spectroscopic studies of the 10Sc1YSZ and 10Sc1CeSZ crystals suggest that the fraction of Eu³⁺ ions with a vacancy in the first coordination sphere (type I optical centers) is lower in the 10Sc1CeSZ crystals than in the 10Sc1YSZ crystals. Influence of local crystal lattice structure on ionic transport of oxygen was studied in a series of works [17,18,29–32]. It was shown that conductivity of materials based on zirconia is governed not only by quantity of vacancies, but also by their position in crystal lattice. Computation results showed that oxygen vacancies situated in a first coordination sphere of dopant ion are not active for oxygen diffusion. Increase of relative ratio of such vacancies leads to the decrease of ionic conductivity [18].

One can therefore conclude that the mobility of the oxygen ions and hence the conductivity of the 10Sc1CeSZ crystals should be higher compared with the 10Sc1YSZ crystals which is in agreement with the data on the transport parameters of these crystals.

4. Conclusions and future perspectives

Scandia stabilized zirconia-based solid solution crystals codoped with ceria and/or yttria were grown by directional melt crystallization in cold skull.

Study of the phase composition of the crystals with X-ray diffraction and Raman spectroscopy showed that addition of 0.5 and 1 mol.% ceria to 10ScSZ does not stabilize the high-temperature cubic phase in the entire crystal bulk. Addition of 0.5 mol.% Y_2O_3 to the crystals increases the quantity of the cubic phase, while addition of 1 mol.% Y_2O_3 leads to the formation of single-phase cubic single crystals.

Ceria doping of the 10ScSZ crystals increases their conductivity, the maximum conductivity occurring at 0.5 mol.% ceria. Addition of 1 mol.% yttria notably reduces the conductivity. The conductivity of the 10Sc0.5Ce0.5YSZ crystals is close to that of the 10ScSZ ones, while the conductivity of the single-phase cubic 10Sc0.5Ce1YSZ crystals is comparable with that of the 10Sc1YSZ crystals.

Optical spectroscopic study of the local structure of the 0.1 mol/ % Eu₂O₃ doped 10Sc1YSZ and 10Sc1CeSZ crystals allowed us to identify different types of optical centers. We found that the fraction of trivalent cations having a vacancy in the first coordination sphere (type I optical centers) is lower in the 10Sc1CeSZ crystals than in the 10Sc1YSZ crystals.

Zirconia-based crystals stabilized by Scandia and co-doped with ceria and/or yttria can find their application in the most promising high-temperature electrochemical devices, which convert chemical energy of fuel oxidation into electrical power and heat, solid oxide fuel cells, SOFC.

Conflicts of interest

Authors declare no conflict of interest.

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