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

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A R T I C L E  I N F O
Article history:
Received 29 October 2018
Received in revised form 4 February 2019
Accepted 12 February 2019
Available online 14 February 2019

Keywords:
Single crystals
Solid oxide fuel cell
Solid solutions
Ionic conducting materials
ZrO2-Sc2O3-CeO2-Y2O3

A B S T R A C T
This work is a study of the effect of co-doping (ZrO2)0.9(Sc2O3)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 co-doping. Ceria co-doping of the (ZrO2)0.9(Sc2O3)0.1 crystals increases their conductivity, whereas the addition of 1 mol.% yttria tangibly reduces the conductivity. Equimolar co-doping of the (ZrO2)0.9(Sc2O3)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 ZrO2-Y2O3 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 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+ ions. 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 metal oxides such as Y2O3 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+ ions. 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 metal oxides such as Y2O3 or CeO2 stabilizes the high-temperature cubic phase at room temperature thus reducing conductivity degradation [2,9–12].

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 properties after long-term operation. Co-doping of ScSZ with a range of metal oxides such as Y2O3 or CeO2 stabilizes the high-temperature cubic phase at room temperature thus reducing conductivity degradation [2,9–12].

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].

https://doi.org/10.1016/j.jmat.2019.02.004
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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

\((\text{ZrO}_2)_{0.9-x-y} (\text{Sc}_2\text{O}_3)_x (\text{CeO}_2)_y (\text{Y}_2\text{O}_3)_y\) (\(x = 0; 0.005; 0.01\), \(y = 0; 0.005; 0.01\)) solid solution crystals were grown by directional melt crystallization in cold crucible [21]. Some compositions were additionally doped with 0.1 mol.% Eu\(_2\)O\(_3\) 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 JSM 5910 LV scanning electron microscope with an INCA Energy dispersion system. 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 Cu\(K\alpha\) 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 Eu\(^{3+}\) by second harmonics of YVO\(_4\):Nd 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 × 7 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\(_2\)O\(_3\) solid solution crystals stabilized with CeO\(_2\) and/or Y\(_2\)O\(_3\). 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.% CeO\(_2\) 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\(_2\)O\(_3\) produces transparent regions, and further increase in the Y\(_2\)O\(_3\) concentration to 1 mol.% makes the crystals homogeneous and completely transparent. CeO\(_2\) and Y\(_2\)O\(_3\) co-doping of the crystals (10Sc0.5Ce0.5YSZ) produced 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 CeO\(_2\) distribution, while for 1 mol.% CeO\(_2\) (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 ytrria concentrations. The 10Sc0.5Ce0.5YSZ crystals had no sharp boundary between the transparent and the opaque regions. At a higher Y\(_2\)O\(_3\) concentration (1 mol.%, 10Sc0.5Ce1YSZ) the visually homogeneous crystals had a homogeneous longitudinal component distribution.

Table 1

| Composition | Notation | Density, g/cm\(^3\) | Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>Notation</th>
<th>Density, g/cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ZrO(<em>2))(</em>{0.9-2x} (\text{Sc}_2\text{O}_3)_x (\text{CeO}_2)_y (\text{Y}_2\text{O}_3)_y</td>
<td>10ScSZ</td>
<td>5.753 ± 0.002</td>
</tr>
<tr>
<td>(ZrO(<em>2))(</em>{0.9-2x} (\text{Sc}_2\text{O}_3)_x (\text{CeO}_2)_y (\text{Y}_2\text{O}_3)_y</td>
<td>10Sc0.5CeSZ</td>
<td>5.748 ± 0.001</td>
</tr>
<tr>
<td>(ZrO(<em>2))(</em>{0.9-2x} (\text{Sc}_2\text{O}_3)_x (\text{CeO}_2)_y (\text{Y}_2\text{O}_3)_y</td>
<td>10Sc1CeSZ</td>
<td>5.757 ± 0.002</td>
</tr>
<tr>
<td>(ZrO(<em>2))(</em>{0.9-2x} (\text{Sc}_2\text{O}_3)_x (\text{CeO}_2)_y (\text{Y}_2\text{O}_3)_y</td>
<td>10Sc0.5YSZ</td>
<td>5.731 ± 0.002</td>
</tr>
<tr>
<td>(ZrO(<em>2))(</em>{0.9-2x} (\text{Sc}_2\text{O}_3)_x (\text{CeO}_2)_y (\text{Y}_2\text{O}_3)_y</td>
<td>10Sc1YSZ</td>
<td>5.744 ± 0.001</td>
</tr>
<tr>
<td>(ZrO(<em>2))(</em>{0.9-2x} (\text{Sc}_2\text{O}_3)_x (\text{CeO}_2)_y (\text{Y}_2\text{O}_3)_y</td>
<td>10Sc0.5Ce1YSZ</td>
<td>5.735 ± 0.001</td>
</tr>
<tr>
<td>(ZrO(<em>2))(</em>{0.9-2x} (\text{Sc}_2\text{O}_3)_x (\text{CeO}_2)_y (\text{Y}_2\text{O}_3)_y</td>
<td>10Sc0.5Ce0.5YSZ</td>
<td>5.747 ± 0.002</td>
</tr>
</tbody>
</table>

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

### Table 2

Phase composition and lattice parameters of (ZrO2)0.9-x-y(Sc2O3)x(1−y)(Y2O3)y(0.5CeO2)y crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Weight Fraction, %</th>
<th>Lattice parameters</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>a, nm</td>
</tr>
<tr>
<td>10ScSZ</td>
<td>c</td>
<td>65</td>
<td>0.5091(1)</td>
</tr>
<tr>
<td>10Sc0.5CeSZ</td>
<td>c</td>
<td>65</td>
<td>0.5092(1)</td>
</tr>
<tr>
<td>10Sc1CeSZ</td>
<td>c</td>
<td>70</td>
<td>0.5092(1)</td>
</tr>
<tr>
<td>10Sc0.5YSZ</td>
<td>c</td>
<td>80</td>
<td>0.5092(1)</td>
</tr>
<tr>
<td>10Sc1YSZ</td>
<td>c</td>
<td>100</td>
<td>0.5093(1)</td>
</tr>
<tr>
<td>10Sc0.5YSZ0.5CeSZ</td>
<td>c</td>
<td>100</td>
<td>0.5092(1)</td>
</tr>
<tr>
<td>10Sc1Y0.5CeSZ</td>
<td>c</td>
<td>100</td>
<td>0.5093(1)</td>
</tr>
</tbody>
</table>

3.5. Luminescence spectroscopy analysis

We used optical spectroscopy to study the local structure of the...
10Sc1YSZ and 10Sc1CeSZ crystals doped with 0.1 mol.% Eu₂O₃ which was used as a spectroscopic probe. Similar studies were carried out earlier for (ZrO₂)₁₋ₓ(Y₂O₃)ₓ solid solution crystals over a wide range of Y₂O₃ 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, but one is present in the second coordination sphere. Type III optical centers have three oxygen vacancies at the diagonal positions of the cube, i.e., Eu³⁺ 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 Eu³⁺ 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 (ZrO₂)₁₋ₓ(Y₂O₃)ₓ crystals. Fig. 6 shows the luminescence spectra of the 10Sc1YSZ and 10Sc1CeSZ crystals for the ⁵D₀ → ⁷F₁ transitions of the Eu³⁺ ions during excitation of the ⁵D₁ (λex = 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 Y₂O₃ concentration was comparable with the overall concentration of the stabilizing oxides in the crystals studied in this work.

The luminescence spectra for the ⁵D₀ → ⁷F₁ transition of the Eu³⁺ ions in the 10Sc1YSZ crystal recorded after excitation of the ⁵D₁ 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 Eu³⁺ ions in the 10Sc1YSZ crystal recorded after excitation of the ⁵D₁ 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 Eu³⁺ 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 ⁵D₀ → ⁷F₁ 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
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 $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$ transitions of Eu$^{3+}$ ions during excitation of the $^5D_0$ ($\lambda_{ex} = 532$ nm) level at (a) 300 and (b) 77 K. Numbers show types of Eu$^{3+}$ optical centers.

Fig. 6. Luminescence spectra of 10Sc1YSZ, 10Sc1CeSZ and 12YSZ crystals caused by $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$ transitions of Eu$^{3+}$ ions during excitation of the $^5D_0$ ($\lambda_{ex} = 532$ nm) level at (a) 300 and (b) 77 K. Numbers show types of Eu$^{3+}$ optical centers.

4. Conclusions and future perspectives

Scandia stabilized zirconia-based solid solution crystals co-doped 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$_2$O$_3$ to the crystals increases the quantity of the cubic phase, while addition of 1 mol.% Y$_2$O$_3$ 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/\% Eu$_2$O$_3$ 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.

Acknowledgements

Financial support from the Russian Science Foundation (Project 17-79-30071 “Scientifically grounded optimization of performance and mass-dimensional characteristics of planar SOFC stacks and development of fuel processor for highly-efficient transport and stationary power plants”) is gratefully acknowledged. A part of experimental facilities used for this research were developed in framework of Project 14.B25.31.0018 funded by the Russian Ministry of Education and Science.

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