ORIGINAL PAPER



lonic conductivity, phase composition, and local defect structure of ZrO₂-Gd₂O₃system solid solution crystals

Ekaterina A. Agarkova¹ · Mikhail A. Borik² · Tatiana V. Volkova³ · Alexey V. Kulebyakin² · Irina E. Kuritsyna¹ · Elena E. Lomonova² · Filipp O. Milovich⁴ · Valentina A. Myzina² · Polina A. Ryabochkina³ · Nataliya Yu. Tabachkova^{2,4}

Received: 27 April 2019 / Revised: 14 July 2019 / Accepted: 27 July 2019 © Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

The crystalline structure, ionic conductivity, and local structure of ZrO_2 -Gd₂O₃solid solution crystals have been studied for a wide range of compositions. The $(ZrO_2)_{1-x}(Gd_2O_3)_x$ crystals (x = 0.03-0.33) have been grown by directional melt crystallization in cold crucible. The phase composition of the crystals has been studied using X-ray diffraction and transmission electron microscopy. The transport parameters have been studied using impedance spectroscopy in the 400–900 °C range. The local structure of the crystals has been studied by optical spectroscopy with Eu³⁺ ion probe. The maximum conductivity at 900 °C (0.047 S/cm) has been observed in the crystals containing 10 mol% Gd₂O₃. This composition is close to the cubic/tetragonal phase boundary. The compositions corresponding to the single-phase cubic region exhibit a decrease in the ionic conductivities with an increase in the Gd₂O₃ concentration. Studies of the local structure of the ZrO₂-Gd₂O₃ system solid solutions have revealed specific features of the formation of optical centers which characterize the localization of oxygen vacancies in the lattice parameter with those calculated using various models has shown that the best fit between these data is provided by the model of inequiprobable distribution of oxygen vacancies. We have discussed the correlation between the crystalline and local structures and the transport parameters of the crystals. Analysis of the results allows us to identify the Gd₂O₃ concentration ranges in which the ionic conductivity of the crystals is mainly determined either by the phase composition or by the regularity of oxygen vacancy localization in the crystal lattice.

Keywords Single crystals · Solid oxide fuel cell · Solid solutions · Ionic conducting materials · ZrO₂-Gd₂O₃

Introduction

Zirconia-based materials exhibit high ionic conductivity at high temperatures and are therefore widely used as solid electrolytes for

Filipp O. Milovich philippmilovich@gmail.com

- ¹ Institute of Solid State Physics, Russian Academy of Sciences, Academician Osip'yan str. 2, Chernogolovka, Moscow District, Russia 142432
- ² Prokhorov General Physics Institute, Russian Academy of Sciences, Vavilov Str. 38, Moscow, Russia 119991
- ³ Ogarev Mordovia State University, 68 Bolshevistskaya Str, Saransk, Republic of Mordovia, Russia 430005
- ⁴ National University of Science and Technology (MISIS), Leninskiyprospekt 4, Moscow, Russia 119049

solid oxide fuel cells [1–3]. The ionic conductivity of zirconiabased solid solutions depends on the type and concentration of the stabilizing oxide and is determined by a wide range of factors. The most important factors are phase composition, phase transformations during heating from room temperature to the electrochemical cell operation temperature, and the concentration and mobility of oxygen vacancies contributing to the charge transport.

The dependence of the conductivity of these materials on the type and concentration of the stabilizing oxide was studied in detail earlier [4]. It was shown that an increase in the ionic radius of the stabilizing oxide leads to a decrease in the maximum value of the ionic conductivity. Furthermore, the stabilizing oxide concentration at which the conductivity is the highest decreases with an increase in the ionic radius of the stabilizing cation [4].

Detailed analysis of the effect of the interaction between oxygen vacancies with stabilizing oxide cations on the transport properties of fluorite structure oxides was reported elsewhere [5]. The presence of various type complexes in zirconia-based materials was also discussed [6–12]. The type of the forming complexes can be characterized by the position of the oxygen vacancies relative to the zirconium and doping impurity cations, i.e., by the local structure of the crystal lattice.

There are now a large number of works dealing with the computer simulation of local structural defects and their interaction in solid oxide electrolytes on the basis of different approaches [9–14]. One experimental technique for studying the local structure of crystals is optical spectroscopy. This technique, with Eu³⁺ ions as a probe, is widely used for studying the local structure of crystals, including zirconia-based solid solutions [8, 15-17]. It is desirable for correct interpretation of the data retrieved with the use of Eu³⁺ ions that the local neighborhood of these ions be the same as the local neighborhood of the stabilizing oxide cations. This requirement is satisfied if the ionic radii of the probing ion and the stabilizing oxide cation are close. Therefore, Gd₂O₃ was used as a stabilizing oxide in this work, since the ionic radii of Eu³⁺ and Gd³⁺ for the octahedral coordination shell are 1.066 and 1.053 A, respectively.

The structure and conductivity in ZrO_2 -Gd₂O₃ system solid solutions were studied earlier [18, 19]. The conductivity of the ceramic specimens containing 2 to 11 mol% Gd₂O₃ in the 200 to 425 °C range suggests that the intergrain and bulk conductivity components in the material may be high for single-phase (tetragonal or cubic) compositions but low for specimens consisting of mixtures of these phases. Unlike the ZrO₂-Y₂O₃ ceramic, the ZrO₂-Gd₂O₃ system does not form vacancy clusters [18]. The conductivity of the single crystal specimens containing 10–15 mol% Gd₂O₃ at 831 °C decreases with an increase in the Gd₂O₃ concentration, while the conductivity activation energy increases [19].

In this work, we report experimental data on the crystalline structure, transport properties, and local structure of the $(ZrO_2)_{1-x}(Gd_2O_3)_x$ solid solutions for a wide range of compositions, i.e., (x = 0.03-0.33). To simplify the treatise of the results and exclude the effect of grain boundaries on the electrophysical properties of the material, we studied ZrO_2 -Gd₂O₃ crystals grown by directional melt crystallization.

Experimental

 $(ZrO_2)_{1-x}(Gd_2O_3)_x$ (x = 0.03-0.33) solid solution crystals were grown by directional melt crystallization in cold crucible [20]. Some compositions were additionally doped with 0.1 mol% Eu_2O_3 . The Eu^{3+} ions were used as a spectroscopic probe for study of the local crystal structure by the optical spectroscopy method.

The phase composition of the crystals was analyzed using X-ray diffraction on a Bruker D8 instrument in $CuK\alpha$

radiation and using a Raman spectroscopy. The excitation source was a 633-nm laser. The Raman spectra were recorded at multiple points along the crystal for phase composition homogeneity assessment.

The structure studies were carried out by transmission electron microscopy—TEM JEOL 2100 with accelerating voltage 200 KeV. 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. The radiation detector was a Hamamatsu R928 photodetector amplifier. Luminescence was excited at the ⁵D₁ level by second harmonics of YVO₄:Nd (λ_{ex} = 532 nm) and LiYF₄:Nd (λ_{ex} = 527 nm) lasers.

The conductivity of the crystals was studied in the 400– 900 °C range 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.

Results and discussion

The compositions, notations, phase compositions, and densities of the test crystals are summarized in Table 1. The crystals stabilized gadolinium had generally the same shape, color, and dimensions as the yttrium-stabilized crystals. All the crystals had columnar shapes which are typical of the growth technique used. The 3GdSZ and 4GdSZ crystals were white and non-transparent. The 8GdSZ crystals were homogeneous and semitransparent and had no visible bulk defects. For Gd₂O₃

Table 1 Compositions, notations, and densities of test crystals

Crystal composition	Notation	Phase composition	Density ρ , g/cm ³
(ZrO ₂) _{0.97} (Gd ₂ O ₃) _{0.03}	3GdSZ	Tetragonal ZrO ₂	6.259 ± 0.002
(ZrO ₂) _{0.96} (Gd ₂ O ₃) _{0.04}	4GdSZ	Tetragonal ZrO ₂	6.251 ± 0.002
(ZrO ₂) _{0.92} (Gd ₂ O ₃) _{0.08}	8GdSZ	Tetragonal ZrO ₂	6.394 ± 0.002
(ZrO ₂) _{0.90} (Gd ₂ O ₃) _{0.10}	10GdSZ	Cubic ZrO ₂	6.481 ± 0.002
(ZrO ₂) _{0.88} (Gd ₂ O ₃) _{0.12}	12GdSZ	Cubic ZrO ₂	6.533 ± 0.002
(ZrO ₂) _{0.86} (Gd ₂ O ₃) _{0.14}	14GdSZ	Cubic ZrO ₂	6.586 ± 0.002
(ZrO ₂) _{0.84} (Gd ₂ O ₃) _{0.16}	16GdSZ	Cubic ZrO ₂	6.634 ± 0.002
(ZrO ₂) _{0.80} (Gd ₂ O ₃) _{0.20}	20GdSZ	Cubic ZrO ₂	6.702 ± 0.002
(ZrO ₂) _{0.67} (Gd ₂ O ₃) _{0.33}	33GdSZ	Cubic ZrO ₂	6.863 ± 0.002

concentrations in the ZrO_2 -based solid solutions of above 10 mol%, the crystals were homogeneous and transparent.

X-ray diffraction study of the phase composition of the crystals showed that the crystals containing 3 to 8 mol% Gd_2O_3 -stabilizing oxides are the tetragonal modification of zirconia. The crystals with Gd_2O_3 concentrations of 10 to 33 mol% had a cubic fluorite structure.

As can be seen from Table 1, the density of the ZrO_2 -Gd₂O₃ system crystals increases with Gd₂O₃ concentration.

Transmission electron microscopy study of the crystals showed that the structure of all the $(ZrO_2)_{1-x}(Gd_2O_3)_x$ tetragonal crystals (x = 3, 4, and 8) consisted of twins (Fig. 1). We did not find twin-free regions in these crystals. The shape and sizes of the twins changed depending on the Gd₂O₃ concentration in the crystals. The 3GdSZ crystals contained large twins. Primary twin plates in the crystals also underwent twinning. Secondary twinning plane traces in the crystals were at an approximately 60 angle degrees relative to the traces of their respective primary twinning plane. The twinning plane is a {110} type one. The sizes of the twins in the crystals decreased with an increase in the Gd₂O₃ concentration. The structure of the 4GdSZ is a mixture of large and fine twins. The 8GdSZ only contained small twins with a relatively homogeneous size distribution.

The typical structural image for crystals with a Gd_2O_3 concentration of 10 mol% or higher corresponded to the defectfree structure of single-phase cubic single crystals. However, the electron diffraction patterns of the solid solutions containing (10–12) mol% Gd_2O_3 had reflections of the tetragonal phase. The electron diffraction patterns of the crystals containing (14–20) mol% Gd_2O_3 indicated a cubic fluorite structure. The electron diffraction pattern of the crystal containing 33 mol% Gd_2O_3 had reflections in regions not corresponding to fluorite structure reflections. Figure 2 shows electron diffraction patterns for the 10GdSZ, 14GdSZ, and 33GdSZ crystals.

Thus, transmission electron microscopy shows that the 14GdSZ, 16GdSZ, and 20GdSZ crystals have a cubic fluorite structure. The 10GdSZ and 12GdSZ crystals contain the t`` phase which has a tetragonality degree of 1 but its space group is $P4_2/nmc$ due to the shift of the oxygen ions in the anion

sublattice [21]. The 33GdSZ crystals exhibit initial ordering of the oxygen vacancies; yet, without the formation of the $Zr_2Gd_2O_7$ phase as indicated by the presence of reflections in the electron diffraction pattern regions corresponding to the $Zr_2Gd_2O_7$ phase, this suggests the lack of a long-range order in the structure.

Figure 3 shows the temperature functions of the specific conductivity of the test crystals in Arrhenius coordinates. It can be seen that the temperature functions have a linear pattern in the entire experimental temperature range.

Figure 4 shows the 900 °C specific conductivity and the activation energy of the test crystals as functions of Gd_2O_3 concentration. It can be seen that the conductivity of the crystals changes in a nonmonotonic manner with an increasing Gd_2O_3 concentration. The ionic conductivity peak corresponds to the ZrO_2 - Gd_2O_3 solid solutions with a Gd_2O_3 -stabilizing oxide concentration of 10–12 mol%. Increasing the Gd_2O_3 concentration to above 12 mol% caused a dramatic decline of the conductivity. The activation energy increases with the Gd_2O_3 concentration reaching the maximum value (1.34 eV) for the 33 mol% Gd_2O_3 composition.

Thus, the conductivity of the crystals increases monotonically with Gd_2O_3 concentration in the tetragonal phase composition region. As the Gd_2O_3 concentration increases from 8 to 10 mol%, the phase composition changes and the conductivity of the solid solutions increases rapidly. The highest conductivity was obtained for the crystals with a Gd_2O_3 -stabilizing oxide concentration of 10 mol%. This composition is close to the cubic/tetragonal phase boundary. Compositions corresponding to the single-phase cubic region show a decrease in their ionic conductivities with an increase in the Gd_2O_3 concentration.

Introduction of Gd³⁺ ions which are larger than Zr⁴⁺ ones into the zirconia-based solid solutions corresponding to the cubic phase region causes several phenomena that affect the ionic conductivity of the solid solutions. On the one hand, the introduction of larger Gd³⁺ ions increases the lattice parameter; on the other hand, it causes lattice deformation which was shown earlier [4, 9] to reduce the mobility of oxygen ions. There is another possible cause of the decline in the ionic conductivity of cubic zirconia. First-principle calculations

Fig. 1 Images of twins in a 3GdSZ, b 4GdSZ, and c 8GdSZ crystals



Fig. 2 Electron diffraction patterns for **a** 10GdSZ, **b** 14GdSZ, and **c** 33GdSZ crystals. Insets show bright field image of crystal structure



[10] showed that to induce ionic conductivity in stabilized zirconia, one should introduce active oxygen vacancies to be localized in the vicinity of the zirconium ion. Increasing the fraction of stabilizing oxide cations and having an anion vacancy in the first coordination shell reduces the fraction of active vacancies, and hence reduces the ionic conductivity. Another factor in the decrease of the ionic conductivity at high-stabilizing oxide concentrations is the formation of anionic vacancy associations [8].

A detailed study of the local structure of ZrO_2 -Gd₂O₃ for different stabilizing oxide concentrations [22] provided the fundamental experimental results that are required for the analysis of the dependence of the ionic conductivity on a Gd₂O₃-stabilizing oxide concentration in the ZrO_2 -Gd₂O₃ solid solutions.

Figure 5 shows Eu³⁺ ion luminescence spectra for ZrO₂-Gd₂O₃ crystals with 4, 8, 10, 14, 20, and 33 mol% Gd₂O₃ concentrations and 0.1 mol% Eu₂O₃ concentration formed by the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ optical transitions in these ions recorded under excitation to the ${}^{5}D_{1}$ level with $\lambda = 532$ nm of radiation.

Roman digit I in the luminescence spectra marks the peaks corresponding to the optical spectra of Eu³⁺ ions having an oxygen vacancy in the first coordination shell [22]. The peaks



Fig. 3 Temperature functions of specific conductivity of $(ZrO_2)_{1-x}(Gd_2O_3)_x$ crystals

corresponding to optical centers and having no oxygen vacancy in the first coordination shell but having one oxygen vacancy in the second coordination shell are marked as II [22]. It can be seen from Fig. 6 that as the Gd₂O₃ concentration increases, the relative intensity of the peaks corresponding to optical centers I and II of Eu³⁺ ions changes. At Gd₂O₃ concentrations < 8 mol%, the intensities of the peaks corresponding to optical centers II is higher than the intensities of the peaks corresponding to optical centers I. At Gd₂O₃ concentrations ≥ 8 , the intensities of the peaks corresponding to optical centers I become higher than the intensities of the peaks corresponding to optical centers II. At Gd₂O₃ concentrations of 20 and 33 mol%, the luminescence spectra have additional peaks (III) which were attributed to Eu³⁺ ions having two oxygen vacancies at diagonal positions of the cubic cell [22]. The positions of the III type Eu^{3+} ion optical centers are similar to the positions of the Y^{3+} ions with the C_2 -point symmetry in the Y_2O_3 structure.

Assuming that the Eu^{3+} ions in the experimental crystals are located at the same positions as the Gd^{3+} ions, one can conclude from the above results that for Gd_2O_3 concentrations of above 8–10 mol%, the relative fraction of oxygen vacancies located in the first coordination shell of the Gd^{3+} ions increases. An increase in the fraction of vacancies that do not



Fig. 4 Conductivity of $(ZrO_2)_{1-x}(Gd_2O_3)_x$ crystals at 900 °C and conductivity activation energy as functions of Gd_2O_3 concentration. Approximate phase limits are shown for reference



Fig. 5 Luminescence spectra for ZrO₂-Gd₂O₃-Eu₂O₃ crystals with 4, 8, 10, 14, 20, and 33 Gd₂O₃-stabilizing oxide concentrations formed by ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions in Eu³⁺ ions under excitation to the ${}^{5}D_{1}$ level ($\lambda = 532$ nm) at T = 300 K

contribute to the diffusion of oxygen ions is a factor reducing the ionic conductivity of the material. The formation of oxygen vacancy associations at Gd_2O_3 concentrations of above 20 mol% makes an additional contribution to the further decrease in the ionic conductivity.

The distribution of the structural elements in ZrO₂-based solid solutions stabilized with rare-earth metal oxides was reported earlier [23]. An increase in the concentration of the stabilizing oxide leads to an increase in the number of oxygen vacancies, and hence in the number of cation positions with seven and six-coordination oxygen neighborhood. Two oxygen six-vertex types can be separated depending on vacancy locations. One is characterized by the presence of two oxygen vacancies located along a diagonal on a face of the cubic crystalline cell. The other oxygen six-vertex type is characterized by two anion vacancies located along a spatial diagonal of the cube. Figure 6 shows models of the fluorite structures without and with the introduction of anion vacancies. It should be noted that earlier spectral luminescence studies [8, 15] and those conducted in this work for zirconia-based solid solutions with high-stabilizing oxide concentrations revealed sixcoordination cation positions with two oxygen vacancies located along a diagonal on a face of the cubic crystalline cell.

Using the method described earlier [23], we calculated the elative concentrations of cations located in eight- (α_8), seven-(α_7), and six-coordination (α_6) oxygen neighborhood as a function of Gd₂O₃ concentration. We will consider equiprobable and inequiprobable oxygen vacancy distribution cases.

 Equiprobable oxygen vacancy distribution case: the cation coordination number may vary from 8 to 0 and corresponds to the Bernoulli distribution, and the relative concentrations of the eight, seven, and six vertices are determined by the following formula:

$$\alpha_{8-i} = C_8^i \gamma^i (1-\gamma)^{8-i},\tag{1}$$

where *i* is the number of oxygen vacancies in the cation neighborhood (0, 1, or 2) and γ is the relative concentration of oxygen vacancies.

2) Inequiprobable oxygen vacancy distribution case: this case is considered in accordance with the thermodynamically model proposed elsewhere [24]. This model considers the association/dissociation equilibrium of cations and a variable number of oxygen vacancies in the first coordination shell. This equilibrium state is represented as a multilevel energy pattern the bottom level of which corresponds to the case of one oxygen vacancy in the cation neighborhood. The higher energy levels correspond to cations having lower coordination numbers. Under this model the α_{n-1}/α_n concentration ratio is expressed as the level population ratio as follows:

$$\alpha_{\mathbf{n}-1}/\alpha_{\mathbf{n}} = k_{\mathbf{n}-1}/k_{\mathbf{n}} exp(-\Delta E_{\mathbf{n}}/kT), \qquad (2)$$

where $\Delta E_{\mathbf{n}}$ is the difference of formation energies of cation neighborhoods with the **n** and **n**-1 coordination numbers, $k_{\mathbf{n}}$ and $k_{\mathbf{n}-1}$ are the statistical weights of the respective levels, k is



Fig. 6 Models of the fluorite structures without and with the introduction of anion vacancies: \mathbf{a} eight vertex, \mathbf{b} seven vertex, \mathbf{c} six vertex (1), and \mathbf{d} six vertex (2)

the Boltzmann constant, and *T* is the thermodynamic equilibrium temperature.

From crystal chemistry standpoints, $\Delta E_n \gg kT$ for n < 6, which corresponds to the formation of eight, seven, and six vertices. This case is described by the following set of equations:

$$\begin{aligned} &\alpha_{8} + \alpha_{7} + \alpha_{6}' + \alpha''_{6} = 1, \\ &\alpha_{7} + 2\alpha_{6}' + 2\alpha''_{6} = 8\gamma, \\ &\alpha_{6}'/\alpha_{7} = k_{6}'/k_{7} \exp\left(-\Delta E_{6}'/kT\right), \\ &\alpha''_{6}/\alpha_{7} = k''_{6}/k_{7} \exp(-\Delta E''_{6}/kT). \end{aligned}$$

$$(3)$$

The ` and `` indices refer to the two six-vertex types.

Given ΔE , $\Delta E_6 \gg kT$, the formation of six vertexes is impossible, and the above set of equation reduces to the following relationships:

$$\alpha_8 = 1 - 8\gamma, \alpha_7 = 8\gamma. \tag{4}$$

For ΔE , ΔE_{6} , $\Delta E_{6} = 0$, the above set of equations describes a case that is close to equiprobable vacancy distribution over the lattice sites, while coordination numbers less than 6 are not excluded.

If the above set of equations obey the condition $0 > \Delta E^{3}$ $a_{6}^{*} = \Delta E^{5}_{6} \gg kT$, they reduce to the following form:

$$\alpha_8 = 1 - 4\gamma, \alpha_6 = 4\gamma, \tag{5}$$

which corresponds to the absence of seven vertexes. $\Delta E'_{6}$, $\Delta E'_{6} = 0$.

In this work, we calculated the lattice parameters of the ZrO_2 -Gd₂O₃ solid solutions with different stabilizing oxide concentrations using the α_8 , α_7 , and α_6 parameters for equiprobable oxygen vacancy distribution (case 1) and nonequiprobable oxygen vacancy distribution satisfying the condition (ΔE ``₆, ΔE `₆ = 0) when the structure contains cation vacancies with eight-, seven-, and six-coordination oxygen neighborhood (case 2).

The lattice parameter for the series of ZrO_2 -Gd₂O₃ crystals studied was calculated as follows [25]:

$$d = \alpha_8 \cdot d_8 + \alpha_7 \cdot d_7 + \alpha_6 \cdot d_6, \tag{6}$$

where d_8 , d_7 , and d_6 are the lattice parameters for the cases when the cations occupy only eight-, seven-, and sixcoordination positions, respectively:

$$d_{8} = 2.31 \left[R_{Zr8} + R_{o} + \frac{2m_{Gd2O3}\Delta R_{Gd} + 2m_{Eu2O3}\Delta R_{Eu}}{100 + m_{Gd2O3} + m_{Eu2O3}} \right], (7)$$

$$d_{7} = 2.31 \left[R_{Zr7} + R_{o} + \frac{2m_{Gd2O3}\Delta R_{Gd} + 2m_{Eu2O3}\Delta R_{Eu}}{100 + m_{Gd2O3} + m_{Eu2O3}} \right], (8)$$

$$d_{6} = 2.31 \left[R_{Zr6} + R_{o} + \frac{2m_{Gd2O3}\Delta R_{Gd} + 2m_{Eu2O3}\Delta R_{Eu}}{100 + m_{Gd2O3} + m_{Eu2O3}} \right], (9)$$

where R_{Zr8} , R_{Zr7} , and R_{Zr6} are the ionic radii for the coordination numbers 8, 7, and 6, respectively, R_0 is the ionic radius of oxygen, m_{Gd2O3} and m_{Eu2O3} are the concentrations of the stabilizing oxides Gd₂O₃ and Eu₂O₃, respectively, in mol%, and $\Delta R_{Gd,Eu}$ is the difference between the ionic radii of Gd³⁺ (Eu³⁺) and Zr⁴⁺ with the coordination numbers 8, 7, or 6.

The lattice parameters of the ZrO_2 -Gd $_2O_3$ -Eu $_2O_3$ crystals calculated using Eq. (6) and experimental ones are shown in Fig. 7 as a function of Gd $_2O_3$ concentration.

The results illustrated in Fig. 7 suggest that the best fit of the experimental and calculated crystal lattice parameter is achieved for the inequiprobable distribution of oxygen vacancies, which is in agreement with the presence of oxygen vacancy pairs in the ZrO_2 -Gd₂O₃ structure that were revealed by spectroscopic analysis.

Figure 8 shows relative fractions of cations having eight-(α_8), seven- (α_7), and six-(α_6) vertex of oxygen in the neighborhood for inequiprobable distribution of oxygen vacancies and ionic conductivity as functions of Gd₂O₃ concentration in the ZrO₂-Gd₂O₃ solid solutions.

It can be seen from Fig. 8 that with an increase in the Gd_2O_3 concentration the fraction of the cations having the 7 (α_7) and 6 (α_6) oxygen coordination numbers increases while the fraction of the cations having the 8 (α_8) oxygen coordination number decreases. The interaction between a stabilizing oxide cation and an oxygen vacancy in the first coordination shell and the interaction between vacancies during the formation of vacancy associations are factors reducing the ionic conductivity of the solid solutions. However, the concentration dependence of the relative fractions of cations having different oxygen coordination numbers does not explain the presence of a maximum in the concentration dependence of the ionic conductivity. It seems that at Gd_2O_3 concentrations of below 14 mol%, the predominant factor is the phase composition of the crystals.



Fig. 7 Calculated and experimental lattice parameters of ZrO_2 -Gd₂O₃ crystals as a function of Gd₂O₃ concentration for (1) equiprobable and (2) inequiprobable oxygen vacancy distributions



Fig. 8 Relative fractions of cations having eight- (α_8) , seven- (α_7) , and six- (α_6) vertices in the neighborhood and ionic conductivity as functions of Gd₂O₃ concentration in ZrO₂-Gd₂O₃ solid solutions

Thus, our experimental results for the local structure of the ZrO_2 -Gd₂O₃ system solid solutions revealed specific features of the formation of optical centers which characterize the localization of the oxygen vacancies in the lattice depending on the concentration of the stabilizing oxide which significantly affects the ionic conductivity of the solid solutions.

Conclusion

 $(ZrO_2)_{1-x}(Gd_2O_3)_x$ solid solution crystals with a wide range of compositions (x = 0.03-0.33) were grown by a directional melt crystallization in cold crucible.

X-ray diffraction analysis showed the crystals with x = (0.03-0.08) to have a tetragonal structure. The crystals with x = 0.10-0.33 had a cubic fluorite structure. TEM studies confirmed the presence of a cubic fluorite structure in the 14GdSZ, 16GdSZ, and 20GdSZ crystals, and the 10GdSZ and 12GdSZ crystals had reflections corresponding to the tetragonal phase. This suggests that the structure of the 10GdSZ and 12GdSZ crystals is the t`` phase.

We showed that the conductivity of the crystals increases monotonically with Gd_2O_3 concentration in the tetragonal phase composition region. At Gd_2O_3 concentrations of 10 to 12 mol%, the conductivity has a clear maximum corresponding to the t`` phase region. Further increase in the Gd_2O_3 concentration (cubic solid solution region) reduces the ionic conductivity. The activation energy increases with Gd_2O_3 concentration for the entire range of compositions, the highest activation energy (1.34 eV) occurring in the solid solution containing 33 mol% Gd_2O_3 .

Studies of the local structure of the $(ZrO_2)_{1-x}(Gd_2O_3)_x$ crystals showed that with an increase in the Gd_2O_3 concentration to above 8 mol%, the relative fraction of oxygen vacancies located in the first coordination shell of Gd^{3+} ions increases.

At Gd_2O_3 concentrations of above 20 mol%, the Eu³⁺ luminescence spectra exhibit changes that can be attributed to the formation of oxygen vacancy pairs.

Comparison of the experimental values of the lattice parameter with those calculated using various models showed that the best fit between these data is provided by the model of inequiprobable distribution of oxygen vacancies. This model was used for calculating the fraction of cations having variable oxygen coordination numbers depending on Gd₂O₃ concentration. We showed that an increase in the Gd₂O₃ concentration leads to an increase in the fraction of cations having the 7 (α_7) and 6 (α_6) oxygen coordination numbers and a decrease in the fraction of cations having the 8 (α_8) oxygen coordination number.

Thus, the results of the study of the crystalline and local structure of the ZrO_2 - Gd_2O_3 system solid solutions allow us to identify the Gd_2O_3 concentration ranges in which the ionic conductivity of the crystals is mainly determined either by the phase composition or by the regularity of oxygen vacancy localization in the crystal lattice.

Funding information The work was carried out with financial support in part from the Russian Science Foundation (RSF grant no. 18-79-00323).

References

- Badwal SPS, Bannister MJ, Hannink RHJ (1993) Science and technology of zirconia V. Technomic. Lancaster, Basel
- Basu RN (2006) In: Basu S (ed) Materials for Solid Oxide Fuel Cells, chapter. Springer, New Delhi, p 12
- Yamamoto O, Arachi Y, Sakai H, Takeda Y, Imanishi N, Mizutani Y, Kawai M, Nakamura Y (1998) Zirconia based oxide ion conductors for solid oxide fuel cells. Ionics 4:403–408
- Arachi Y, Sakai H, Yamamoto O, Takeda Y, Imanishai N (1999) Electrical conductivity of the ZrO₂ –Ln₂O₃ (Ln - lanthanides) system. Solid State Ionics 121:133–139
- Kilner JA, Brook RJ (1982) A study of oxygen ion conductivity in doped non-stoichiometric oxides. Solid State Ionics 6:237–252
- Kilner JA, Waters CD (1982) The effects of dopant cation-oxygen vacancy complexes on the anion transport properties of nonstoichiometric fluorite oxides. Solid State Ionics 6:253–259
- Goff JP, Hayes W, Hull S, Hutchings MT, Clausen KN (1999) Defect structure of yttria-stabilized zirconia and its influence on the ionic conductivity at elevated temperatures. Phys Rev B 59(22)
- Yugami H, Koike A, Ishigame M, Suemoto T (1991) Relationship between local structures and ionic conductivity in ZrO₂-Y₂O₃ studied by site-selective spectroscopy. Phys Rev B 44:9214–9222
- Catlow CRA (1984) Transport in doped fluorite oxides. Solid State Ionics 12:67–73
- Zavodinsky VG (2004) The mechanism of ionic conductivity in stabilized cubic zirconia. Phys Solid State 46:441–445
- Tokiy NV, Perekrestov BI, Savina DL, Danilenko IA (2011) Concentration and temperature dependences of the oxygen migration energy in yttrium-stabilized zirconia. Phys Solid State 53: 1732–1736
- Ding H, Virkar AV, Liu F (2012) Defect configuration and phase stability of cubic versus tetragonal yttria-stabilized zirconia. Solid State Ionics 215:16–23

- Li X, Hafskjold B (1995) Molecular dynamics simulations of yttrium-stabilized zirconia. J Phys Condens Matter 7:1255–1271
- Eichler A (2001) Tetragonal Y-doped zirconia: structure and ion conductivity. Phys Rev B 64:174103–1-174103-8
- Dexpert-Ghys J, Faucher M, Caro P (1984) Site selective spectroscopy and structural analysis of yttria-doped zirconias. J Solid State Chem 54:179–192
- Voronko YK, Zufarov MA, Sobol AA, Ushakov SN, Tsymbal LI (1997) Spectroscopy and the structure of Eu³⁺ activator centers in partially stabilized zirconium and hafnium dioxide. Inorg Mater 33: 452–464
- Borik MA, Volkova TV, Kuritsyna IE, Lomonova EE, Myzina VA, Ryabochkina PA, Tabachkova NY (2019) Features of the local structure and transport properties of ZrO₂-Y₂O₃-Eu₂O₃ solid solutions. J Alloys Compd 770:320–326
- Dutta S, Bhattacharya S, Agrawal DC (2003) Electrical properties of ZrO2–Gd2O3ceramics. Mater Sci Eng B 100:191–198
- Kang TK, Nagasaki T, Igawa N, II-Hiunn K, Ohno H (1992) Electrical properties of cubic, stabalized, single ZrO2-Gd2O3 crystals. J Am Ceram Soc 75:2297–2299
- Borik MA, Lomonova EE, Osiko VV, Panov VA, Porodinkov OE, Vishnyakova MA, Voron'ko YK, Voronov VV (2005) Partially stabilized zirconia single crystals: growth from the melt and investigation of the properties. J Cryst Growth 275:2173–2179

- Yashima M, Sasaki S, Kakihana M, Yamaguchi Y, Arashi H, Yoshimura M (1994) Oxygen-induced structural-change of the tetragonal phase around the tetragonal-cubic phase-boundary in ZrO₂-YO_{1.5} solid-solutions. Acta Crystallogr B 50:663–672
- Borik MA, Volkova TV, Lomonova EE, Myzina VA, Ryabochkina PA, Tabachkova NY, Chabushkin AN, Kyashkin VM, Khrushchalina SA (2018) Spectroscopy of optical centers of Eu³⁺ ions in ZrO₂-Gd₂O₃-Eu₂O₃ crystals. J Lumin 200:66–73
- Voronko YK, Gorbachev AV, Sobol AA (1995) Raman scattering and the structure of cubic solid solutions based on zirconium and hafnium dioxide. Fiz Tverd Tela 37: 1939–1952. Sov Phys Solid State 37:1055–1069
- Osiko VV (1965) Thermodynamics of optical centers in CaF₂-TR³⁺ crystals. Fiz. Tverd. Tela 7: 1294–1302. Sov Phys Solid State 7: 1047–1055
- Aleksandrov VI, Valyano GE, Lukin BV, Osiko VV, Rautbort AE, Tatarintsev VM, Filatova VN (1976) The structure of single crystals of stabilized zirconium dioxide. Neorg Mater 12:273–277

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.