



## Features of the local structure and transport properties of $ZrO_2$ - $Y_2O_3$ - $Eu_2O_3$ solid solutions



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### ABSTRACT

The features of the local crystal structure for the series of the  $(ZrO_2)_{1-x-y}(Y_2O_3)_x(Eu_2O_3)_y$  ( $x = 0.027$ – $0.38$ ;  $y = 0.001$ ;  $0.005$ ) solid solutions with different concentrations were revealed by the optical spectroscopy method. Comparative analysis of the features of the local crystal structure and the characteristics of the dependence of the ionic conductivity on the content of the stabilizer oxide in the  $ZrO_2$ - $Y_2O_3$  solid solutions was performed. Based on the results of this analysis, it was concluded that an increase in the relative fraction of the  $Y^{3+}$  ions with oxygen vacancies in the first coordination sphere prevents the diffusion of oxygen ions, leading to decreased ionic conductivity values.

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## 1. Introduction

Solid solutions of zirconia stabilized with yttrium oxide or rare earth oxides (RE) are of considerable interest for their use as solid oxygen-ion conducting electrolytes. This application is due to the presence of oxygen vacancies in their anion sublattice. As was described in the studies by Kuz'minov and co-authors [1] and by Pyatenko [2], the formation of oxygen vacancies is due to the need for charge compensation upon introducing the stabilizing  $Y_2O_3$  or RE oxides that provide heterovalent substitution of  $Zr^{4+}$  ions by  $Y^{3+}$ .

According to the studies by Aleksandrov and co-authors [3–5], the use of materials based on zirconia dioxide as a solid electrolyte for solid oxide fuel cells (SOFC) requires the solution of a number of scientific and technological problems. The main problems are related to obtaining materials with higher conductivity for medium

temperature range (500–700 °C), as well as increasing the long-term stability of the electrophysical characteristics of the solid electrolyte at the operating temperature range. It is impossible to solve these problems without identifying the various factors that affect the structure and properties of the zirconium-dioxide-based solid solutions. It should be noted that the ionic conductivity value and its change with the change of the stabilizing oxide concentration depend strongly on the local crystal structure of these solid solutions for which oxygen vacancies must be taken into account. This has attracted a significant research interest in the elucidation of the origins of the relationships between the transport properties and the local structure of the zirconia-based materials. These origins have been considered in the studies by H. Yugami and co-authors [6], W. Araki and co-authors [7], H. Ding and co-authors [8], and C.R.A. Catlow [9]. For example, H. Ding and co-authors [8] performed a modelling study of the local crystal structure and analysed the effects of the local crystal structure on ionic conductivity. H. Yugami and co-authors [6] studied the effect of the concentration of the stabilizing  $Y_2O_3$  oxide on the features of the formation of the local structure in a  $ZrO_2$ - $Y_2O_3$ - $Eu_2O_3$  polycrystal with a cubic structure synthesized in an arc xenon furnace. Using selective laser spectroscopy, they identified the dominant optical

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centres as  $\text{Eu}^{3+}$  ions formed with the participation of the oxygen vacancies that depend on the stabilizing oxide concentration. It was suggested that oxygen vacancies interact with the cations of the matrix and form clusters at certain stabilizer oxide concentrations that affect the ionic conductivity and lead to an increase in the activation energy. However, it should be noted that these studies investigated polycrystalline samples, and the presence of grain boundaries in these samples can significantly affect the transport properties of the material. Such an influence is excluded when similar studies are conducted on single-crystal samples.

Therefore, the present work aimed to reveal the relationship between the local crystal structure and transport properties for single crystals of the  $(1-x-y)$  mol.%  $\text{ZrO}_2$ - $x$  mol.%  $\text{Y}_2\text{O}_3$ - $y$  mol.%  $\text{Eu}_2\text{O}_3$  (where  $x = 2.7, 3.6, 8, 12, 14, 16, 20, 30, 38$  mol.%,  $y = 0.1, 0.5$  mol.%) solid solutions grown by directional melt crystallization with high-frequency heating in a cold container.

## 2. Experimental

The compositions of the crystals of the  $(1-x-y)$  mol.%  $\text{ZrO}_2$ - $x$  mol.%  $\text{Y}_2\text{O}_3$ - $y$  mol.%  $\text{Eu}_2\text{O}_3$  (where  $x = 2.7, 3.6, 8, 12, 14, 16, 20, 30, 38$  mol.%,  $y = 0.1, 0.5$  mol.%) solid solutions chosen as the targets of our investigation and the appropriate designations used in the rest of the paper are presented in Table 1.

The crystals were grown by directional melt crystallization with high-frequency heating in a cold container using a Kristall-407 instrument in a 130 mm diameter cold crucible at a growth rate of 10 mm/h in the air. As initial materials, high purity zirconium, yttrium, and europium oxides were used.

Polished plates cut from the crystals listed in Table 1 were used as the samples for spectroscopic studies.

The luminescence spectra of the samples at  $T = 300$  K and  $T = 77$  K were recorded using a Horiba FHR 1000 spectrometer. A Hamamatsu R928 photomultiplier was used as the photodetector.

The  $^5\text{D}_1$  level of  $\text{Eu}^{3+}$  ions was excited using the second-harmonic radiation of  $\text{YVO}_4:\text{Nd}$  ( $\lambda_{\text{exc.}} = 532$  nm) and  $\text{LiYF}_4:\text{Nd}$  ( $\lambda_{\text{exc.}} = 527$  nm) lasers. The  $^5\text{L}_6$  level of the  $\text{Eu}^{3+}$  ions was excited by the third harmonic radiation of a  $\text{LiYF}_4:\text{Nd}$  laser with a wavelength of 351 nm.

The data for the experimental determination of lattice parameters for the crystals of the  $(1-x-y)$  mol.%  $\text{ZrO}_2$ - $x$  mol.%  $\text{Y}_2\text{O}_3$ - $y$  mol.%  $\text{Eu}_2\text{O}_3$  (where  $x = 2.7, 3.6, 8, 12, 14, 16, 20, 30, 38$  mol.%,  $y = 0.1, 0.5$  mol.%) concentration series were obtained from the X-ray diffraction patterns recorded with a Bruker D8 diffractometer using  $\text{CuK}_\alpha$  radiation. The processing of the experimental data was carried out using the JSPDS PDF-2 database. For structural studies we cut wafers perpendicular to the  $\langle 100 \rangle$  direction.

The measurements of the ionic conductivity values of the  $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$ - $\text{Eu}_2\text{O}_3$  crystals with different stabilizing  $\text{Y}_2\text{O}_3$  oxide concentrations were carried out using a Solartron SI 1260 frequency analyser at the 1 Hz–5 MHz range in the 623–1173 K temperature

range. The resistivity was measured in a measurement cell using the four-probe method.

## 3. Phase composition of $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$ - $\text{Eu}_2\text{O}_3$ crystals

Analysis of the diffractograms for the  $0.1\text{Eu}_2\text{O}_3$ -2.7YSZ and  $0.1\text{Eu}_2\text{O}_3$ -3.6YSZ crystals indicates that they are characteristic of a tetragonal structure. Analysis of the diffraction profile was hindered by the superimposition of the split reflections due to the presence of the tetragonal lattice and  $\text{CuK}_\alpha$ -doublet splitting; therefore, we conducted an additional experiment with  $\text{CuK}_\beta$  radiation which allowed us to definitely confirm that the splitting is due to the presence of the two tetragonal phases. As an example, Fig. 1 shows the diffractogram of the  $0.1\text{Eu}_2\text{O}_3$ -2.7YSZ crystal. In the upper right corner of Fig. 1, a fragment of the X-ray diffraction pattern corresponding to the large angles  $\theta$  is shown. The presence of the reflections from the (006) and (330) planes in the X-ray diffraction patterns provides evidence of the presence of twins in the  $0.1\text{Eu}_2\text{O}_3$ -2.7YSZ (and  $0.1\text{Eu}_2\text{O}_3$ -3.6YSZ) crystals. In the  $0.1\text{Eu}_2\text{O}_3$ -2.7YSZ,  $0.1\text{Eu}_2\text{O}_3$ -3.6YSZ crystals, two tetragonal phases of zirconium dioxide (transformable t and nontransformable t') are present that belong to the  $\text{P4}_2/\text{mnc}$  space symmetry group and differ in their degree of tetragonality ( $c/\sqrt{2}a$ ) values [10].

For the  $0.1\text{Eu}_2\text{O}_3$ -8.0YSZ,  $0.1\text{Eu}_2\text{O}_3$ -12.0YSZ,  $0.1\text{Eu}_2\text{O}_3$ -14.0YSZ,  $0.1\text{Eu}_2\text{O}_3$ -16.0YSZ,  $0.1\text{Eu}_2\text{O}_3$ -20.0YSZ,  $0.1\text{Eu}_2\text{O}_3$ -30.0YSZ, and  $0.5\text{Eu}_2\text{O}_3$ -38.0YSZ crystals, the X-ray diffraction patterns were obtained and it was found that the patterns are typical of a cubic structure. As an example, Fig. 2 shows the diffractogram corresponding to the  $0.1\text{Eu}_2\text{O}_3$ -8.0YSZ crystal.

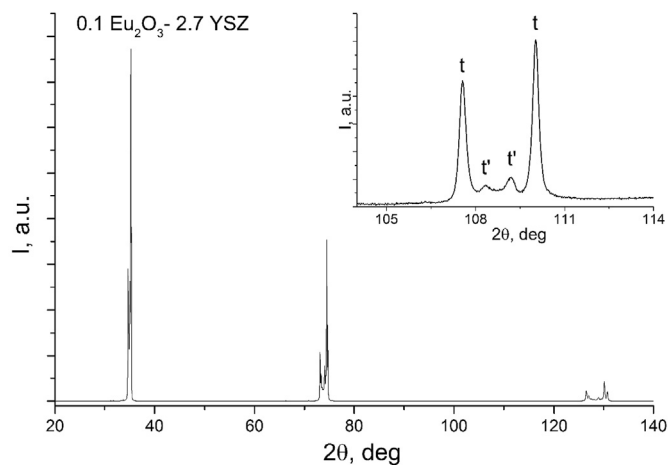
Based on the experimental data obtained by X-ray diffraction, the crystal lattice parameters were determined for the  $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$ - $\text{Eu}_2\text{O}_3$  crystals and are presented in Table 2.

## 4. Features of the local structure and ionic conductivity of $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$ - $\text{Eu}_2\text{O}_3$ crystals

Optical spectroscopy is a widely used and well-tested method for studying the local structure of crystalline materials. For the zirconia-based materials, the  $\text{Eu}^{3+}$  ion is often chosen as a spectroscopic probe. This is due to a relatively simple arrangement of its energy levels compared to the other RE ions. This greatly simplifies and allows a more unambiguous interpretation of the optical

**Table 1**  
Compositions of the studied crystals and appropriate designations.

No	Crystal composition	Designation
1	97.2 mol.% $\text{ZrO}_2$ -2.7 mol.% $\text{Y}_2\text{O}_3$ -0.1 mol.% $\text{Eu}_2\text{O}_3$	0.1 $\text{Eu}_2\text{O}_3$ -2.7YSZ
2	96.3 mol.% $\text{ZrO}_2$ -3.6 mol.% $\text{Y}_2\text{O}_3$ -0.1 mol.% $\text{Eu}_2\text{O}_3$	0.1 $\text{Eu}_2\text{O}_3$ -3.6YSZ
3	91.9 mol.% $\text{ZrO}_2$ -8 mol.% $\text{Y}_2\text{O}_3$ -0.1 mol.% $\text{Eu}_2\text{O}_3$	0.1 $\text{Eu}_2\text{O}_3$ -8.0YSZ
4	87.9 mol.% $\text{ZrO}_2$ -12 mol.% $\text{Y}_2\text{O}_3$ -0.1 mol.% $\text{Eu}_2\text{O}_3$	0.1 $\text{Eu}_2\text{O}_3$ -12.0YSZ
5	85.9 mol.% $\text{ZrO}_2$ -14 mol.% $\text{Y}_2\text{O}_3$ -0.1 mol.% $\text{Eu}_2\text{O}_3$	0.1 $\text{Eu}_2\text{O}_3$ -14.0YSZ
6	83.9 mol.% $\text{ZrO}_2$ -16 mol.% $\text{Y}_2\text{O}_3$ -0.1 mol.% $\text{Eu}_2\text{O}_3$	0.1 $\text{Eu}_2\text{O}_3$ -16.0YSZ
7	79.9 mol.% $\text{ZrO}_2$ -20 mol.% $\text{Y}_2\text{O}_3$ -0.1 mol.% $\text{Eu}_2\text{O}_3$	0.1 $\text{Eu}_2\text{O}_3$ -20.0YSZ
8	69.9 mol.% $\text{ZrO}_2$ -30 mol.% $\text{Y}_2\text{O}_3$ -0.1 mol.% $\text{Eu}_2\text{O}_3$	0.1 $\text{Eu}_2\text{O}_3$ -30.0YSZ
9	61.5 mol.% $\text{ZrO}_2$ -38 mol.% $\text{Y}_2\text{O}_3$ -0.5 mol.% $\text{Eu}_2\text{O}_3$	0.5 $\text{Eu}_2\text{O}_3$ -38.0YSZ



**Fig. 1.** X-ray diffraction pattern obtained using  $\text{CuK}_\alpha$  radiation for the  $0.1\text{Eu}_2\text{O}_3$ -2.7YSZ crystal. In the upper right corner, the fragment of the X-ray diffraction pattern for the reflections from the (006) and (330) planes of this crystal obtained using  $\text{CuK}_\beta$  radiation is shown.

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