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Phase composition and local structure of scandia and yttria stabilized zirconia solid solution

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ABSTRACT

The local crystalline structure of scandia stabilized zirconia has been studied and compared with the structure of yttria stabilized zirconia for the same stabilizing oxide concentration range (8–10 mol.%). The single crystal materials have been grown by directional melt crystallization. Changes in the local crystalline structure and phase transformations in the crystals have been studied after heat treatment at 1000 °C for 400 h in air. Optical spectroscopy has shown changes in the local neighborhood as a result of heat treatment induced phase

Optical spectroscopy has shown changes in the local neighborhood as a result of heat treatment induced phase transformations in the solid solutions.

1. Introduction

The combination of high oxygen ionic conductivity and chemical stability of the zirconia base materials promotes their general application as solid state electrolytes in electrolytic membranes of solid oxide fuel cells and in high temperature electrochemical oxygen sensors designed for operation in different environments, including aggressive ones.

There are indications that the dependence of ionic conductivity on stabilizing oxide concentration in the $\text{ZrO}_2-\text{Ln}_2\text{O}_3$ materials (Ln = Y, Gd, Yb, Sc) is nonmonotonic. The highest ionic conductivity depending on stabilizing oxide types and material fabrication methods is observed in a range of 7–11 mol.% [1–5]. The origins of the decrease in the ionic conductivity of the materials with a further increase in the stabilizing oxide concentration were studied earlier [3–17]. The results of these works suggest that the conductivity of the material depends not only on the phase composition of the solid solutions but also on the mutual arrangement of anion vacancies relative to cations and other anion vacancies in the solid solution.

Oxygen vacancies in zirconia base solid solutions form as a result of

heterovalent substitution of zirconium cations for stabilizing impurity cations [7,18]. It should be noted that the fabrication of high performance electrolytic membranes requires not only identifying the factors affecting their oxygen ionic conductivity but also detecting the causes of long-term performance degradation of solid electrolytes under operating conditions [19–21].

The effect of local crystalline structure of $ZrO_2-Ln_2O_3$ solid solutions on their ionic conductivity was studied earlier [12,15,16,22,23]. It was shown that a stabilizing impurity ion locating in the first coordination shell of an oxygen vacancy may act as a trap for the vacancy. An increase in the concentration of these ions will reduce the ionic conductivity of the material. Association of oxygen vacancies will give the same result.

The location of anion vacancies relative to Zr^{4+} and Ln^{3+} ions in $ZrO_2-Ln_2O_3$ solid solutions is studied by experimental methods (X-ray diffraction, neutron diffraction and optical spectroscopy) [9–12,17] and mathematical simulation [13–16].

Earlier [22,23] we used optical spectroscopy with Eu^{3+} ions as spectroscopic probes for studying the local neighborhood of cations in solid solutions for yttria and gadolinia stabilized crystals depending on the stabilizing oxide concentration in a wide concentration range

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(2.7–38 mol.% Y_2O_3 and 2.7–33 mol.% Gd_2O_3). We showed that an increase in the Y^{3+} and Gd^{3+} stabilizing oxide concentration to above 10 mol.% significantly increases the concentration of impurity cations $(Y^{3+} \mbox{ and } Gd^{3+})$ having vacancies in the nearest coordination shell and acting as traps for the anion vacancies. This fact contributes to the decrease in the ionic conductivity in the $ZrO_2–Y_2O_3$ and $ZrO_2–Gd_2O_3$ solid solutions.

Researchers pay great attention to the ZrO₂-Sc₂O₃ and ZrO₂-Sc₂O₃. Ln₂O₃ solid solutions (Ln = Y, Ce, Yb). The ionic conductivity of these materials is higher than that of the currently widely used ZrO₂-Y₂O₃ solid electrolytes [5,16,24–30], allowing their use as electrolytic membranes suitable for medium working temperatures [29,31–33]. In the opinion of other authors [26,27] a possible cause of the higher conductivity of ZrO₂-Sc₂O₃ is that, because of the small Sc³⁺ ion size, the interaction of Sc³⁺ ions with oxygen vacancies and other Sc³⁺ ions is predominantly electrostatic. However, when describing the interaction between stabilizing oxide cations and vacancies in ZrO₂-Y₂O₃ one should take into account not only electrostatic interactions but also elastic ones.

Noteworthy, ZrO₂-Sc₂O₃ compounds are more complex materials than ZrO₂-Y₂O₃ from the viewpoint of phase composition and phase transitions. Unlike ZrO₂-Y₂O₃ solid solutions which have a cubic structure over a relatively wide range of Y2O3 stabilizing oxide concentrations (9-33 mol.%), ZrO₂-Sc₂O₃ cubic solid solutions having a fluorite structure only exist in a narrow concentration range, i.e., from 8 to 12 mol.% Sc₂O₃. The ZrO₂-Sc₂O₃ phase diagram is quite complex, and there are still several variants of it, for which phase limits vary [34-36]. Along with the monoclinic, tetragonal and cubic phases, metastable enriched tetragonal t' and t" phases and an ordered rhombohedral β phase (Sc₂Zr₇O₁₇) exist in a narrow Sc₂O₃ concentration range (5-12 mol.%). This large number of phases is caused by the close ionic radii of Zr⁴⁺ and Sc³⁺ accounting for the absence of lattice stresses and favoring redistribution of stabilizing impurity ions and oxygen vacancies. This in turn makes the structure of ZrO₂-Sc₂O₃ quite sensitive to the synthesis conditions of the materials [34-36].

Even a small content of the rhombohedral phase in ZrO_2 - Sc_2O_3 precludes its use as a material for electrolytic membranes because a rhombohedral-to-cubic phase transition occurs in the 500–650 °C range [37] which is well resolved in the electrical conductivity *vs* temperature curve [20,21,38].

There are currently insufficient experimental data on the effect of local structure of ZrO_2 - Sc_2O_3 solid solutions on the ionic conductivity of scandia stabilized zirconia [17,29,39]. Experimental studies of this effect were only carried out for ceramics synthesized under different conditions. Grain boundaries in the material were shown to affect the microstructure and transport properties of the material. The possibility of obtaining materials of similar compositions in the form of single crystals significantly simplifies the treatise of experimental results on their structure and transport properties.

The aim of this work was to study the phase composition and local structure of $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Eu_2O_3)_y$ solid solutions where x = 0.08, 0.09, 0.10 and y = 0.001 and compare them with the phase composition and local structure of $(ZrO_2)_{1-x-y}(Y_2O_3)_x(Eu_2O_3)_y$ solid solutions where x = 0.08, 0.09, 0.10 and y = 0.001. To detect the cause of long-term performance degradation of solid electrolytes under operating conditions, we studied the phase compositions and local structures of $(ZrO_2)_{1-x-y}(Y_2O_3)_x(Eu_2O_3)_y$ after heat treatment.

2. Experimental materials and methods

The compositions of the $(ZrO_2)_{1,x,y}(R_2O_3)_x(Eu_2O_3)_y$ crystals where R = Y, Sc and x = 0.08, 0.09, 0.10 and y = 0.001 and the respective specimen notations are presented in Table 1.

The crystals were grown in a Kristall-407 unit by directional melt crystallization with direct RF heating [40] from a 130 mm diameter cold crucible at a crystallization rate of 10 mm/h. The growth atmosphere

Та	ble	1	

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Crystal composition	Crystal notation
$\begin{array}{l} (ZrO_{2})_{0.919}(Y_2O_3)_{0.08}(Eu_2O_3)_{0.001} \\ (ZrO_{2})_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001} \\ (ZrO_{2})_{0.899}(Y_2O_3)_{0.10}(Eu_2O_3)_{0.001} \\ (ZrO_{2})_{0.919}(Sc_2O_3)_{0.08}(Eu_2O_3)_{0.001} \\ (ZrO_{2})_{0.909}(Sc_2O_3)_{0.09}(Eu_2O_3)_{0.001} \end{array}$	$\begin{array}{c} 0.1 Eu_2O_3{\text{-}8} \; \text{YSZ} \\ 0.1 Eu_2O_3{\text{-}9} \; \text{YSZ} \\ 0.1 Eu_2O_3{\text{-}10} \; \text{YSZ} \\ 0.1 Eu_2O_3{\text{-}8ScSZ} \\ 0.1 Eu_2O_3{\text{-}8ScSZ} \\ 0.1 Eu_2O_3{\text{-}9ScSZ} \end{array}$
$(ZrO_2)_{0.899}(Sc_2O_3)_{0.10}(Eu_2O_3)_{0.001}$	0.1Eu2O3-10ScSZ

was air. The raw materials were high-purity zirconia, yttria (scandia) and europia.

The specimens for spectroscopy were in the form of polished rectangular plates cut from the crystals the compositions of which are summarized in Table 1.

The crystals were annealed in a Supertherm HT04/16 high-temperature resistance furnace at 1000 $^{\circ}$ C for 400 h in an air atmosphere.

The phase compositions of the crystals were studied using X-ray diffraction directly for crystal specimens cut parallel to the $\{100\}$ crystallographic plane of the fluorite structure. The diffractometer was Bruker D8, the radiation being CuK α .

To characterize the phase compositions of the crystals we also used the Raman spectroscopy method. The spectra were recorded on an Integra Spectra instrument ($\lambda_{ex} = 633$ nm).

The local structures of the crystals were studied using optical spectroscopy by analyzing the luminescent spectra of the $ZrO_2-Y_2O_3-Eu_2O_3$ and $ZrO_2-Sc_2O_3-Eu_2O_3$ crystals. The Eu^{3+} ions were used as a spectroscopic probe. The concentration of the Eu^{3+} ions was 0.1 mol.%. The luminescence spectra were recorded at T = 300 K with a Horiba FHR 1000 spectrometer. The radiation detector was a Hamamatsu R928 photoelectron amplifier. The luminescence was excited in FHR 1000 to the 5D_1 level of Eu^{3+} ions with the second harmonics of a YVO4:Nd laser ($\lambda_{ex} = 532$ nm).

3. Results and discussion

Table 2 shows the phase compositions of the crystals as determined by X-ray diffraction. In the experimental range of compositions the Y_2O_3 stabilized crystals contained only the cubic ZrO_2 modification. The lattice parameters a of these crystals increased almost linearly with the Y_2O_3 concentration. In the Sc_2O_3 stabilized crystals the phase compositions of the solid solutions varied depending on the Sc_2O_3 concentration. The $0.1Eu_2O_3$ -8ScSZ and $0.1Eu_2O_3$ -9ScSZ crystals were tetragonal, and the $0.1Eu_2O_3$ -10ScSZ crystal was a mixture of cubic and rhombohedral phases.

The Raman spectra of the 0.1Eu2O3-8 YSZ, 0.1Eu2O3-9 YSZ,

Table 2	2			
Phase c	compositions	and lattice	e parameters	of crystals.

Specimen	Phase composition	Space	Lattice pa	Lattice parameter	
		symmetry group	a, nm	c, nm	а
0.1Eu ₂ O ₃ -	t	P4 ₂ /nmc	0.3596	0.5123	1.007
0.1Eu ₂ O ₃ - 9ScSZ	t	P4 ₂ /nmc	0.3595	0.5122	1.007
0.1Eu ₂ O ₃ -	с	Fm3m	0.5091	0.9010	
10ScSZ	r	R3m	(1) 0.3562 (1)	(2)	
0.1Eu ₂ O ₃ -8 YSZ	c	Fm3m	0.5138 (1)		
0.1Eu ₂ O ₃ -9 YSZ	c	Fm3m	0.5141 (1)		
0.1Eu ₂ O ₃ - 10 YSZ	с	Fm3m	0.5144 (1)		

 $0.1Eu_2O_3\text{-}10\,$ YSZ, $0.1Eu_2O_3\text{-}8ScSZ$, $0.1Eu_2O_3\text{-}9ScSZ\,$ and $0.1Eu_2O_3\text{-}10ScSZ\,$ crystals are shown in Fig. 1.

The Raman spectra of the $0.1Eu_2O_3$ -(8-10)YSZ crystals contain, along with the peaks typical of the $0.1Eu_2O_3$ -(8-10)YSZ cubic phase, a peak at 480 cm⁻¹ which is typical of the tetragonal phase of $0.1Eu_2O_3$ -(8-10)YSZ [41–44]. The relative intensity of this peak decreases with an increase in the yttria concentration.

Thus, X-ray diffraction suggests that the $0.1Eu_2O_3$ -(8–10)YSZ crystals have a cubic structure while the Raman data indicate that the structure of the crystals is t' phase (Fig. 1a).

The Raman spectra of the $0.1Eu_2O_3$ -8ScSZ and $0.1Eu_2O_3$ -9ScSZ crystals (Fig. 1b) are typical of the tetragonal phase but quite broadened, possibly due to the presence of additional cubic or t'' phase. It is almost impossible to distinguish different tetragonal phases from the Raman spectra. The Raman spectra of the $0.1Eu_2O_3$ -10ScSZ crystals contain peaks that are typical of the rhombohedral phase and also significantly broadened. The possibility that the cubic or t'' phase is present in the $0.1Eu_2O_3$ -10ScSZ crystals along with the rhombohedral phase can hardly be judged about from the Raman spectra because the peaks of these phases overlap with those of the rhombohedral phase. According to X-ray diffraction data, the $0.1Eu_2O_3$ -10ScSZ crystals contain both the rhombohedral and cubic phases.

Fig. 2 shows the T = 300 K luminescence spectra of the 0.1Eu₂O₃-8 YSZ, 0.1Eu₂O₃-9 YSZ and 0.1Eu₂O₃-10 YSZ crystals which relate to the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions of Eu³⁺ ions as a result of excitation to the ${}^{5}D_{1}$ level.

Earlier [45], based on analysis of the luminescence spectra for the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions of Eu³⁺ ions in ZrO₂-Y₂O₃-Eu₂O₃ crystals with different Y₂O₃ concentrations and taking into account results [46], we identified the main types of optical centers of Eu³⁺ ions in those crystals. For example [45], the 585.5 nm peak refers to the Type I optical center. This type of optical centers is a Eu^{3+} ion which has one oxygen vacancy surrounded by an oxygen seven-vertex. The point symmetry of this Eu^{3+} ion optical center should be trigonal (C_{3v}). The ${}^{7}F_{1}$ level of Eu³⁺ ions should in this case be split in two Stark components. Additional lattice distortions lower the symmetry, and the ${}^{7}F_{1}$ level of Eu^{3+} ions will then be split in three Stark components [46]. The luminescence spectra shown in Fig. 2 for the 0.1Eu₂O₃-8 YSZ, 0.1Eu₂O₃-9 YSZ and 0.1Eu₂O₃-10 YSZ crystals are superimposition of the spectra for different optical centers of Eu³⁺ ions with unevenly broadened peaks. It therefore seems to be impossible to definitely estimate the number of Stark components corresponding to the ⁵D₁ level for the Type I optical centers of Eu^{3+} ions.



Fig. 2. Luminescence spectra of $0.1Eu_2O_3\text{-}8$ YSZ, $0.1Eu_2O_3\text{-}9$ YSZ and $0.1Eu_2O_3\text{-}10$ YSZ crystals, $\lambda_{ex}=532$ nm, T=300 K.

The peaks at 586.6 and 587.3 nm in the luminescence spectra of the 0.1Eu₂O₃-8 YSZ, 0.1Eu₂O₃-9 YSZ and 0.1Eu₂O₃-10 YSZ crystals correspond to the Type II optical centers of Eu³⁺ ions. Optical spectra of this type do not contain oxygen vacancies in the first coordination shell but have oxygen vacancies in the second coordination shell. The local symmetry of these centers is C₁. According to earlier results [46], these Eu³⁺ centers have lower ⁷F₁ level splitting by the crystalline field as compared with that for Type I centers.

The band in the 600–615 nm range caused by the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ optical transition of Eu³⁺ ions is asymmetrical and has an expressed hump at 603 nm. Taking into account earlier experimental results [46] we considered the asymmetrical 600–615 nm band to be a superimposition of peaks at 603 and 606 nm, respectively. The 603 nm peak pertains to Type I optical centers and the 606 nm peak refers to Type II optical centers. It can be well seen from Fig. 2 that the 603 nm hump is the most expressed in the 0.1Eu₂O₃-10 YSZ crystals.

The intensity ratios of the peaks corresponding to Type I and II optical centers in the luminescence spectra of the $0.1Eu_2O_3$ -(8–10)YSZ crystals are almost the same and change but slightly in the experimental concentration range.

Fig. 3 shows the luminescence spectra of the $0.1Eu_2O_3$ -8 YSZ, $0.1Eu_2O_3$ -9 YSZ and $0.1Eu_2O_3$ -10 YSZ crystals as well as those of the



Fig. 1. Raman spectra of (a) $0.1Eu_2O_3$ -(8–10)YSZ and (b) $0.1Eu_2O_3$ -(8–10)ScSZ crystals, $\lambda_{ex} = 633$ nm, T = 300 K.

0.1Eu₂O₃-8ScSZ, 0.1Eu₂O₃-9ScSZ and 0.1Eu₂O₃-10ScSZ crystals.

Comparison of the luminescence spectra for the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition of Eu³⁺ ions in the 0.1Eu₂O₃-8 YSZ and 0.1Eu₂O₃-9 YSZ crystals with those of the 0.1Eu₂O₃-8ScSZ and 0.1Eu₂O₃-9ScSZ crystals suggests that the luminescence spectra of the 0.1Eu₂O₃-8ScSZ and 0.1Eu₂O₃-9ScSZ crystals have lower relative intensities of the peaks corresponding to Type I optical centers, as compared with the luminescence spectra of the 0.1Eu₂O₃-9 YSZ crystals.

Furthermore, for the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ ions, the typical hump at 603 nm corresponding to Type I optical centers is less pronounced for the 0.1Eu₂O₃-8 YSZ and 0.1Eu₂O₃-9 YSZ crystals. This indicates that the relative fraction of the Eu³⁺ ion optical centers having vacancies in the first coordination shell is lower in the 0.1Eu₂O₃-8ScSZ and 0.1Eu₂O₃-9 YSZ crystals than in the 0.1Eu₂O₃-8 YSZ and 0.1Eu₂O₃-9 YSZ crystals.

The decrease in the relative fraction of the Eu³⁺ ion optical centers having vacancies in the first coordination shell as detected by optical spectroscopy in the 0.1Eu₂O₃-8ScSZ and 0.1Eu₂O₃-9ScSZ crystals as compared with the 0.1Eu₂O₂-8 YSZ and 0.1Eu₂O₂-9 YSZ crystals is in agreement with earlier experimental results [17,26–28]. Study of the structure of ZrO₂–Y₂O₃ and ZrO₂-Sc₂O₃ solid solutions by EXAFS [17] and computer simulation of their structure showed that oxygen vacancies in ZrO₂-Y₂O₃ crystals predominantly occupy the first coordination shells of Zr^{4+} ions and the second coordination shells of Y^{3+} ions. In ZrO₂-Sc₂O₃ solid solutions, oxygen vacancies have similar probabilities to occupy the first and the second coordination shells of Zr⁴⁺ and Sc^{3+} ions. The conclusions made in the works referred to above required, in the authors' opinion, further experimental study because the effect of the type and concentration of stabilizing oxide on the local structures of solid solutions is one of the factors determining the ionic conductivity of zirconia base solid electrolytes.

The luminescence spectrum of the $0.1Eu_2O_3$ -10ScSZ crystals differs from that of the $0.1Eu_2O_3$ -8ScSZ and $0.1Eu_2O_3$ -9ScSZ crystals (Fig. 3). X-ray diffraction study of the phase composition showed that the structure of the $0.1Eu_2O_3$ -10ScSZ crystals was a mixture of rhombohedral and cubic phases (Table 1). We hypothesized that the pattern of the luminescence spectrum of Eu^{3+} ions in this crystal is determined by the specific features of optical center formation for these ions taking into account the variety of oxygen vertices typical of these phases [39]. Presumably the luminescence spectrum of the $0.1Eu_2O_3$ -10ScSZ crystal should be a superimposition of luminescence spectra of Eu^{3+} ion optical centers located in the centers of oxygen eight-, seven- and six-vertices.

Fig. 4 shows Eu³⁺ ion luminescence spectra caused by the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions due to excitation to the ${}^{5}D_{1}$ level for the



Fig. 3. Luminescence spectra of $0.1Eu_2O_3$ -8 YSZ, $0.1Eu_2O_3$ -9 YSZ, $0.1Eu_2O_3$ -10 YSZ, $0.1Eu_2O_3$ -8ScSZ, $0.1Eu_2O_3$ -9ScSZ and $0.1Eu_2O_3$ -10ScSZ crystals, λ_{ex} = 532 nm, T = 300 K.

 $0.1Eu_2O_3-8$ YSZ, $0.1Eu_2O_3-9$ YSZ, $0.1Eu_2O_3-10$ YSZ, $0.1Eu_2O_3-8ScSZ$, $0.1Eu_2O_3-9ScSZ$ and $0.1Eu_2O_3-10ScSZ$ crystals after annealing at 1000 $^\circ C$ for 400 h in air.

It can be seen from Fig. 4 that the luminescence spectra of the 0.1Eu₂O₃-(8-10)YSZ crystals did not undergo any substantial changes after annealing. Comparison of the Raman spectra for the as-annealed crystals suggests that the most significant changes occur after annealing in the 0.1Eu₂O₃-8 YSZ and 0.1Eu₂O₃-9 YSZ crystals (Fig. 5a). The Raman spectra for the t'' phase have a pattern that is most typical of the tetragonal phase (Fig. 5a) although no changes occurred in the phase composition of the crystals according to X-ray diffraction. The absence of differences in the luminescence spectra before and after annealing is caused by the retention of the coordination numbers of the cations and oxygen in the tetragonal phase which is a derivative of a cubic fluorite structure. Therefore, the oxygen coordination number of the cations in the tetragonal phase is still 8, with the ratio of the quantities of 7- and 8coordination centers varying depending on oxygen vacancy concentration. In this narrow yttria stabilizing oxide concentration range (8-10 mol.%) these changes are negligible, and therefore the luminescence spectra before and after annealing are almost similar.

Also, annealing does not change the pattern of the spectrum for the $0.1Eu_2O_3$ -10ScSZ crystal. However, the pattern of the luminescence spectra for the $0.1Eu_2O_3$ -(8–9)ScSZ crystals after annealing changes compared with the pattern of the luminescence spectra for the as-grown spectra. The pattern of the luminescence spectrum for the as-annealed $0.1Eu_2O_3$ -9ScSZ crystal becomes similar to that of the $0.1Eu_2O_3$ -10ScSZ crystal before annealing. The luminescence spectrum of the as-annealed $0.1Eu_2O_3$ -8ScSZ crystal is a superimposition of the luminescence spectra of the $0.1Eu_2O_3$ -8ScSZ and $0.1Eu_2O_3$ -10ScSZ crystals before annealing.

The typical changes revealed in the luminescence spectra of the $0.1Eu_2O_3$ -8ScSZ and $0.1Eu_2O_3$ -9ScSZ crystals after annealing at 1000 °C for 400 h in air seem to be associated with the formation of cations with a coordination number of 6 which is typical of rhombohedral phase.

The Raman spectroscopy data (Fig. 5b) clearly show the presence of the rhombohedral phase in the $0.1Eu_2O_3$ -9ScSZ and $0.1Eu_2O_3$ -1OScSZ crystals after annealing. Along with the peaks typical of rhombohedral structures, the Raman spectra of the $0.1Eu_2O_3$ -9ScSZ crystals also exhibit intense peaks corresponding to a tetragonal structure. In the Raman spectra of the $0.1Eu_2O_3$ -8ScSZ crystals the rhombohedral phase peaks are superimposed, due to their low intensity, with the peaks corresponding to the tetragonal lattice of the crystals, and it is therefore impossible to state definitively from the Raman data that the rhombohedral phase is present in the crystal. One can only note that the peaks in



Fig. 4. Luminescence spectra of $0.1Eu_2O_3$ -8 YSZ, $0.1Eu_2O_3$ -9 YSZ, $0.1Eu_2O_3$ -10 YSZ, $0.1Eu_2O_3$ -8ScSZ, $0.1Eu_2O_3$ -9ScSZ and $0.1Eu_2O_3$ -10ScSZ crystals (T = 1000 °C, 400 h), λ_{ex} = 532 nm, T = 300 K.



Fig. 5. Raman spectra of (a) $0.1Eu_2O_3$ -8 YSZ, $0.1Eu_2O_3$ -9 YSZ, $0.1Eu_2O_3$ -10 YSZ and (b) $0.1Eu_2O_3$ -8ScSZ, $0.1Eu_2O_3$ -9ScSZ, $0.1Eu_2O_3$ -10ScSZ crystals after annealing at 1000 °C for 400 h in air, $\lambda_{ex} = 633$ nm, T = 300 K.

the Raman spectra of these crystals are broadened suggesting the presence of the rhombohedral phase. Phase composition information obtained by X-ray diffraction for the $0.1Eu_2O_3$ -8ScSZ crystals do not either allows judging about the presence of the rhombohedral phase in these crystals.

Obviously, annealing redistributes the scandium stabilizing oxide between the phases that are present in the as-grown crystals. Enrichment of one of the phases with scandia leads to the formation of the rhombohedral phase while depletion of another phase leads to the formation of the tetragonal phase with the greater tetragonality degree. At a scandia concentration of 8 mol.% this can lead, instead of new phase precipitation, to the formation of cations with a coordination number of 6 in the solid solution, as indicated by the luminescence spectra of these crystals.

4. Summary

 $(ZrO_2)_{1,x-y}(R_2O_3)_x(Eu_2O_3)_y$ single crystals were grown by directional melt crystallization where R = Y, Sc and x = 0.08, 0.09, 0.10 and y = 0.001.

X-ray diffraction and Raman spectroscopy study of the phase composition of the crystals showed that the yttria stabilized zirconia single crystals with a yttria concentration of 8–10 mol.% have a t' phase structure. The phase composition of the scandia stabilized zirconia single crystals depended on the scandia concentration in the same concentration range. According to X-ray diffraction, the $0.1Eu_2O_3$ -8ScSZ and $0.1Eu_2O_3$ -9ScSZ crystals had a tetragonal structure while the $0.1Eu_2O_3$ -10ScSZ crystals contained the rhombohedral and cubic phases. The presence of the second phase in the $0.1Eu_2O_3$ -8ScSZ and $0.1Eu_2O_3$ -9ScSZ crystals as determined by Raman spectroscopy was suggested by the broadening of the tetragonal phase peaks.

Optical spectroscopy with Eu^{3+} ion probe identified the presence of Type I optical centers in the $0.1Eu_2O_3$ -(8-10)YSZ crystals, i.e., oxygen vacancies in the nearest neighborhood of cations (cation coordination number 7) and Type II optical centers for which an oxygen vacancy is absent in the first coordination shell (coordination number 8) but is present in the second coordination shell. Similar types of optical centers for the experimentally studied yttria concentration range were also observed after annealing at 1000 °C for 400 h in air.

Heat treatment changes the pattern of the Raman spectra of the $0.1Eu_2O_3$ -8 YSZ and $0.1Eu_2O_3$ -9 YSZ crystals making them more similar to those typical of a tetragonal structure.

The as-grown $0.1Eu_2O_3\text{-}8ScSZ$ and $0.1Eu_2O_3\text{-}9ScSZ$ crystals were also shown to contain Type I and II Eu^{3+} ion optical centers.

The luminescence spectrum of the $0.1Eu_2O_3$ -10ScSZ crystals differs from those for the $0.1Eu_2O_3$ -8ScSZ and $0.1Eu_2O_3$ -9ScSZ crystals which seem to be caused by the presence of optical centers consisting of cations located in the centers of oxygen six-vertices.

Among all the as-annealed scandia stabilized zirconia crystals, the local structure remained the same as in the as-grown state only in the $0.1Eu_2O_3$ -10ScSZ crystals. For the $0.1Eu_2O_3$ -9ScSZ crystals the local structure became similar to that of the $0.1Eu_2O_3$ -10ScSZ crystals which was confirmed by Raman spectroscopy: the rhombohedral phase formed in the crystals after heat treatment. The changes in the local structure of the as-annealed $0.1Eu_2O_3$ -8ScSZ crystals seem to be caused to the formation of Eu^{3+} ion centers with a coordination number of 6. However, Raman spectroscopy did not indicate clearly that the rhombohedral phase formed in these crystals.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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