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Structure and transport characteristics of single crystals of zirconia stabilized by scandia and co-doped with terbium oxide

M.A. Borik^a, A.S. Chislov^{a,b}, G.M. Korableva^c, A.V. Kulebyakin^{a,*}, I.E. Kuritsyna^c, N. A. Larina^d, E.E. Lomonova^a, F.O. Milovich^{a,b}, V.A. Myzina^a, P.A. Ryabochkina^d, N. Yu. Tabachkova^{a,b}

^a Prokhorov General Physics Institute of the Russian Academy of Sciences, 38 Vavilov str., 119991 Moscow, Russia

range.

^b National University of Science and Technology (MISIS), 4 Leninskiy prospekt, 119049 Moscow, Russia

^c Institute of Solid State Physics of the Russian Academy of Sciences, 2 Academician Osip'yan str., 142432 Chernogolovka, Moscow District, Russia

^d Ogarev Mordovia State University, 68 Bolshevistskaya str., 430005 Saransk, Republic of Mordovia, Russia

ARTICLE INFO ABSTRACT Keywords: The effect of doping with $Tb_2O_{3.5}$ on the phase composition, structure and transport characteristics of ZrO_2 -Directional melt crystallization Sc_2O_3 solid solutions has been studied. Single crystals of $(ZrO_2)_{1.x.y}(Sc_2O_3)_x(Tb_2O_{3.5})_y$ solid solutions, where (x Skull melting = 0.08-0.10; y = 0.01-0.02), were grown by directional crystallization of the melt in a cold crucible. The phase Single crystal composition and structure of crystals were studied by X-ray diffraction, Raman spectroscopy, optical and Zirconia transmission electron microscopy. The electrical conductivity of single crystals was measured by impedance Solid electrolytes spectroscopy. It is shown that the stabilization of the pseudocubic t"-phase in crystals containing 8 mol% Sc₂O₃ Ionic conductors observed at the addition of 2 mol% $Tb_2O_{3.5}$. The introduction of 1 mol% $Tb_2O_{3.5}$ into crystals containing 9 and 10 mol% Sc_2O_3 also leads to the formation of the t" -phase. The conductivity of crystals with a pseudocubic t"

1. Introduction

Materials based on zirconia, stabilized with scandium oxide, show high values of ionic conductivity and are promising as solid electrolytes for various electrochemical devices, for example, solid oxide fuel cells [1–4], electrolyzers and sensors [5,6]. Membranes made from zirconia, stabilized by scandium oxide, can significantly lower the operating temperature of solid oxide fuel cells, which is important for increasing their service life.

The phase diagram for the ZrO_2 - Sc_2O_3 system is given in [7–11], but the boundaries of the existence of phases differ according to different data and are determined only approximately. This is due to the existence of metastable phases in this system and, accordingly, the dependence of the phase composition on the method and conditions of material synthesis. The study of the structure and transport characteristics of ZrO_2 -(9–11 mol%) Sc₂O₃ solid solutions was carried out in [12–14]. It is shown that prolonged high-temperature annealing of solid solutions based on ZrO₂ stabilized only by Sc₂O₃ can lead to a change in the phase composition and degradation of transport characteristics. Degradation is associated with three independent causes of aging of solid electrolytes based on ZrO2. This is the decomposition of a solid solution with the formation of new phases; ordering of oxygen vacancies in the crystal lattice of a solid solution; change in the specific electrical resistance of grain boundaries [13,15,16]. Degradation problems are attempted to be solved both by technological methods [17-19] in the synthesis of ceramic materials and by introducing additional dopants. Doping solid electrolytes based on ZrO2-Sc2O3 with rare-earth oxides makes it possible to obtain stable cubic solid solutions with high conductivity. CeO₂ [20–22], Y₂O₃ [23–25], Yb₂O₃ [22,26,27], Gd₂O₃ [22,28], Sm₂O₃ [22] and Eu₂O₃ [29] are used as co-doped oxides. The selection of codoped oxides is determined by obtaining a stable single-phase cubic solid solution in a wide temperature range and maintaining the high conductivity characteristic of the ZrO₂ - Sc₂O₃ system. The main factors influencing the electrical conductivity of solid solutions based on ZrO2

structure depends on both the total concentration of stabilizing oxides and the $Tb_2O_{3.5}$ content. The $(ZrO_2)_{0.9}(Sc_2O_3)_{0.09}(Tb_2O_{3.5})_{0.01}$ single crystals had the maximum conductivity over the entire temperature

* Corresponding author. *E-mail address:* kulebyakin@lst.gpi.ru (A.V. Kulebyakin).

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Received 5 July 2021; Received in revised form 9 December 2021; Accepted 9 December 2021 Available online 15 December 2021 0167-2738/© 2021 Elsevier B.V. All rights reserved. are the concentration of the stabilizing oxide and the radius of the rareearth element cation. In this regard, it is of interest to use oxides of rareearth elements with variable valence as co-doping additives. The ratio of cations with different valences in stabilized solid solutions based on ZrO₂ depends on the temperature and partial pressure of ambient oxygen. As well as, changes in the valence state of rare-earth oxides can also be facilitated by stresses in the crystal lattice of a solid solution, which arise when the Zr⁴⁺ cation is replaced by a rare-earth cation with a large ionic radius. The ratio of cations with different valences will affect the concentration of oxygen vacancies that arise in ZrO₂-based solid solutions upon heterovalent doping. In this work, terbium was chosen as the cation of the co-doped oxide with variable valence. Terbium ions have valences Tb³⁺ and Tb⁴⁺, while the sizes of ionic radii for coordination number 8 with respect to oxygen are 1.03 Å to 0.88 Å, respectively.

The aim of this work is to study the effect of doping with $Tb_2O_{3.5}$ on the phase composition, structure and transport characteristics of ZrO_2 - Sc_2O_3 solid solutions.

2. Materials and methods

The growth of crystals was carried out by the method of directed crystallization of the melt at a rate of 10 mm/h in a water-cooled copper container 130 mm in diameter using direct high-frequency heating [30]. Zirconium (ZrO₂), scandium (Sc₂O₃) and terbium (Tb₄O₇) oxides with a basic oxide content of at least 99.95% were used to prepare the initial charge. The initial oxide powders were mechanically mixed and placed in a water-cooled cold container. Metallic zirconium (99.8%) was used for the initial heating of the charge, which was placed in the central part of the powdery charge of the container. The amount of metal and the formula content of terbium oxide were taken into account when calculating the specified composition. The crystallized ingot was removed from the cold container and disassembled into individual single crystals after the finishing of the crystallization process and cooling to room temperature.

The phase composition of the crystals was studied using X-ray diffraction with a Bruker D8 instrument with $CuK\alpha$ incident radiation at room temperature. The as-grown crystals had no predominant crystallographic orientation. Therefore, each crystal was preliminarily oriented along specific crystallographic directions in the diffractometer. Then, the crystals were cut into plates on a diamond disc cutting machine. Phase analysis was carried out by X-ray diffraction using a standard method used for single crystals. The diffractograms were processed by means Eva software using the PDF 2 database.

The phase analysis was carried out using Raman spectroscopy on asgrown crystals in the wavenumber range of 150–1000 cm⁻¹ on a Renishaw inVia Raman confocal microscope. A laser with a radiation wavelength of 532 nm was used as an excitation source. The laser focus point was chosen using a built-in optical microscope (×20). The focused beam diameter on the sample was ~1 µm. To record the Raman spectra, the laser radiation power was set equal to 100 mW, and the signal accumulation time was 5 s.

Absorption spectra were recorded on a Perkin Elmer Lambda 950 spectrophotometer.

The crystal structure was investigated by optical and transmission electron microscopy (TEM). Optical images of the crystals were obtained in polarized transmitted light using a Carl Zeiss AxioImager Z2 microscope. TEM studies were carried out on a JEM-2100 microscope at an accelerating voltage of 200 kV.

The study of the electrical transport properties of crystals was carried out by the four-probe method on alternating current. The frequency dependences of the complex impedance were measured with a Solartron SI 1260 analyzer in the frequency range 0.1 Hz-5 MHz. The amplitude of the applied ac signal to the sample was 24 mV Measurements were carried out in the heating mode with the step of 50 °C and holding at a given temperature for 30–40 min. The measurements were carried out on plates $7 \times 7 \text{ mm}^2$ and 0.5 mm thick with symmetric platinum



Fig. 1. Appearance of a fragment of a crystal ingot after growing.

electrodes. For this, platinum paste was applied to the plates, after which annealing was carried out at a temperature of 950 °C for one hour in air. The impedance frequency spectrum was analyzed in detail using the ZView (ver.2.8) software. The resistivity of the crystals was calculated based on the resultant impedance spectra. The ohmic resistance of crystals (R_b) was calculated using the equivalent electrical circuit model: (R_b–CPE_b)(R_{electrode}–CPE_{electrode}) (in 623–773 K temperature range) and LR_b(R_{electrode}–CPE_{electrode}) (in 773–1173 K temperature range), where R_{electrode} is the resistance of the electrode/electrolyte boundary, CPE_{electrode} is a constant phase element that characterizes processes at the electrode interface *L*- inductance of current leads. The conductivity (σ) was determined as $\sigma = 1/\text{Rb}$ (l/S), where l is the sample thickness and S is the contact area. The impedance spectra were processed with ZView (ver. 2.8) (Scribner Associates, Inc., USA) software.

3. Results and discussion

A series of $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Tb_2O_{3.5})_y$ crystals, where x = 0.08-0.10, y = 0.01-0.02 were grown. Hereinafter, the crystals are designated as xScyTbSZ, where x and y are the concentration in mol% of stabilizing scandium and terbium oxide, respectively.

The appearance of a broken crystal ingot is shown in Fig. 1, obtained by directional crystallization of the melt in a cold crucible. The ingot consists of a row of columnar crystals enclosed on three sides in a shell of sintered initial charge. Crystals were mechanically separated from each other and then used to prepare samples for research.

Crystals of the 8Sc1TbSZ composition were homogeneous, without visible defects, with noticeable light scattering. Crystals of other compositions were transparent. All crystals after growth had a red-orange color. The color intensity of the crystals increased with an increase in the concentration of terbium oxide. This color of the crystals indicates the presence of tetravalent cations of terbium in solid solutions, which have absorption bands in the visible region. The absorption spectra of terbium ions in the range 200–3300 nm (Fig. 2) were recorded to study the presence of ions Tb³⁺/Tb⁴⁺ in crystals.

The spectrums of crystals after growth has a broad absorption band in the range of 340–580 nm, caused by charge transfer $O^{2-} \rightarrow Tb^{4+}$ [31,32]. As well as by a number of lines in the IR region, corresponding to intraconfigurational 4f–4f optical transitions from the ground state of ⁷F₆ to excited multiplets ⁷F_{0,1,2}, ⁷F₆ \rightarrow ⁷F₃, ⁷F₆ \rightarrow ⁷F₄ of Tb³⁺ ions [32]. Annealing the crystals in air at 1000 °C did not lead to significant changes in the absorption spectra of the crystals. Thus, the crystals under study contain both Tb³⁺ and Tb⁴⁺ ions, and annealing in air does not significantly change the ratio of Tb³⁺ and Tb⁴⁺ cations.

The study of crystals by optical microscopy methods allows obtaining preliminary information about the internal structure of crystals. Images of a plane-parallel plates made of an 8Sc1TbSZ crystal in transmitted light and a plate made of a transparent 9Sc1TbSZ crystal in polarized light are shown in Fig. 3. The plates were cut along the crystal growth axis; their thickness was 1 mm.



Fig. 2. Absorption spectrum of $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Tb_2O_{3.5})_y$ crystals.



Fig. 3. Images of 8Sc1TbSZ (a) and 9Sc1TbSZ (b) crystal plates.

The image of the 8Sc1TbSZ crystal (Fig. 3a) shows regions with weak and strong light scattering, which have a pronounced banded structure. Moreover, the distribution of these regions in crystals grown in different parts of the crystallized ingot was arbitrary. No characteristic structural features were observed in transparent homogeneous 9Sc1TbSZ crystals. The interference pattern clearly shows itself on the plates in transmitted polarized light, indicating the presence of residual thermal stresses. The thermal stresses arise upon rapid spontaneous cooling of crystals after growth. The images in the light microscope, obtained with the remaining investigated transparent crystals, were similar to those of the 9Sc1TbSZ crystals.

The phase composition of the crystals was analyzed by X-ray diffractometry on plates cut from the crystals perpendicular to the $\langle 100 \rangle$ axis. Diffraction patterns from 8Sc1TbSZ and 8Sc2TbSZ samples are shown in Fig. 4 as an example. Identification of crystal modifications of Sc-stabilized ZrO₂ was carried out using standard powder diffraction cards with the reference code of 00–051-1603 (for t phase) and 01–089-5485 (for c phase).

The 8Sc1TbSZ crystals contained only the tetragonal modification ZrO₂ with a degree of tetragonality $c/\sqrt{2a} = 1.004$. Diffraction maxima corresponding to the cubic phase were observed only in crystals with the same content of Sc₂O₃ (8Sc2TbSZ) but with an increase in the concentration of terbium oxide to 2 mol%. All other crystals under study were also single-phase with a cubic fluorite structure. The phase composition and lattice parameters of the crystals under study are given in Table 1.



Fig. 4. Diffraction patterns from samples 8Sc1TbSZ (a) and 8Sc2TbSZ (b).

Table 1

Phase composition and lattice parameters of crystals according to X-ray diffraction.

Sample	Phase composition*	Space group symmetry	Lattice parameters, nm
8Sc1TbSZ	ť'	P4 ₂ /nmc	a = 0.3600(1) c = 0.5113(1)
8Sc2TbSZ	c	Fm3m	a = 0.5102(1)
9Sc1TbSZ	c	Fm3m	a = 0.5097(1)
9Sc2TbSZ	с	Fm3m	a = 0.5100(1)
10Sc1TbSZ	с	Fm3m	a = 0.5095(1)

t', c – tetragonal and cubic modifications of ZrO₂.



Fig. 5. Raman spectra of (ZrO₂)_{1-x-y} (Sc₂O₃)_x(Tb₂O_{3.5})_y crystals.

An increase in the lattice parameter of solid solutions with an increase in the concentration of $Tb_2O_{3.5}$ and a constant concentration of Sc_2O_3 is observed in the region of cubic solid solutions. The lattice parameter of cubic crystals decreases with an increase in the Sc_2O_3 concentration and a constant $Tb_2O_{3.5}$ concentration.

An analysis of the Raman spectra makes it possible to detect the tetragonal t" -phase in the samples, which is not identified by the X-ray diffraction method. This phase differs from the highly symmetric cubic phase only by a slight displacement of oxygen ions in the anionic sublattice and has a degree of tetragonality equal to 1. The Raman spectra of

the crystals under study shows in Fig. 5.

The bands at 632 cm⁻¹, 480 cm⁻¹, 156 cm⁻¹, and 240 cm⁻¹ are present in the Raman spectrum of the 8Sc1TbSZ crystal, which are characteristic of tetragonal solid solutions based on ZrO₂. The band in the region of 480 cm⁻¹, which is more characteristic of the tetragonal phase, is also observed in the spectra of the remaining crystals, together with the bands characteristic of the cubic phase (~ 620 cm⁻¹). This type of spectrum is characteristic of the presence of the t"-phase in crystals [33]. The presence in all spectra of weakly pronounced bands in the region of ~370 cm⁻¹ and ~ 700 cm⁻¹ is associated with the formation of oxygen vacancies in the crystal lattice upon heterovalent substitution of zirconium cations by terbium or scandium cations.

The crystal structure was studied by the TEM method. Twins, which are formed when the single crystal is cooled during the cubic - tetragonal transition in accordance with the phase diagram, are visible in TEM images from 8Sc1TbSZ crystals. Tetragonal 8Sc1TbSZ crystals were opaque precisely because of the presence of twin boundaries scattering light. An image of twins in 8Sc1TbSZ crystals and an electron diffraction pattern corresponding to this region are shown in Fig. 6a. The TEM image and electron diffraction pattern obtained from the 8Sc2TbSZ crystal are shown in Fig. 6b. No visible defects (dislocations, dislocation loops, twins, etc.) were found in the TEM image of the 8Sc2TbSZ crystal. The obtained TEM images corresponded to the structure typical of cubic low-defect single crystals. Nevertheless, reflections forbidden for a cubic lattice and allowed for a tetragonal structure were observed in the diffraction patterns of this crystal. The presence of reflections of the (110) and (112) type indicates an ordered displacement of oxygen atoms and, accordingly, a violation of the symmetry characteristic of the Fm3m space group. The structure and shape of the electron diffraction patterns for the 9Sc1TbSZ, 9Sc2TbSZ, and 10Sc1TbSZ crystals were similar to the structure of the 8Sc2TbSZ crystal.

Thus, a comprehensive analysis of the data obtained by X-ray diffractometry, Raman scattering and TEM shows that homogeneous transparent 8Sc2YbSZ, 9Sc1TbSZ, 9Sc2TbSZ, and 10Sc1TbSZ single crystals have a t["]-phase structure. In this case, to stabilize the pseudocubic (t["]) phase in crystals containing 8 mol% Sc₂O₃, it is necessary to introduce at least 2 mol% Tb₂O_{3.5} and in crystals containing 9 and 10 mol% Sc₂O₃, it is sufficient to introduce 1 mol% Tb₂O_{3.5}.

Fig. 7 displays impedance spectra of the 8Sc1TbSZ (a), 9Sc1TbSZ (b), and 10Sc1TbSZ (c) crystals at 1173 K.

These impedance spectra exhibit an arc in the high-frequency spectrum region, which reflects bulk conductivity.

The temperature dependences of the specific conductivity of $(ZrO_2)_1$. x-y(Sc₂O₃)_x(Tb₂O_{3.5})_y crystals in Arrhenius coordinates are shown in Fig. 8.



Fig. 6. TEM image of the structure of 8Sc1TbSZ (a) and 8Sc2TbSZ (b) crystals. The insets show electron diffraction patterns from the corresponding regions.



Fig. 7. Impedance spectra of the 8Sc1TbSZ (a), 9Sc1TbSZ (b), and 10Sc1TbSZ (c) crystals at 1173 K and equivalent circuit.

The temperature dependences of the conductivity of all samples do not have any clearly pronounced bends, which probably indicates the absence of phase transitions in the investigated temperature range. In addition, these dependences are characterized by a noticeable curvature, indicating a different conduction mechanism in the high- and lowtemperature region.

The calculation of the activation energy (E_a) of the conductivity of crystals in two different temperature ranges was carried out using the Arrhenius equation:

$$\sigma = AT^{-1}exp\left(-\frac{E_a}{kT}\right),$$

where σ is the conductivity, A is the pre-exponential factor, T is the temperature in K, E_a is the activation energy, k is Boltzmann constant.

The activation energy of crystals for low- and high-temperature regions and the conductivity at different temperature are listed in Table 2.

The conductivity values of samples of all compositions increase monotonically with increasing temperature and the conductivity of the



Fig. 8. Temperature dependences of the electrical conductivity of $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Tb_2O_{3.5})_y$ crystals.

Table 2	
The activation energy (E _a) and the condu	activity of $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Tb_2O_{3.5})_y$
crystals.	

Sample	E _{a,} eV		Conductivity, S/cm			
	623 K–873 K	873 K–173 K	873 K	973 K	1073 K	1173 K
8Sc1TbSZ	1.28	0.86	0.009	0.034	0.073	0.137
8Sc2TbSZ	1.29	0.89	0.010	0.038	0.090	0.168
9Sc1TbSZ	1.36	0.83	0.016	0.054	0.115	0.200
9Sc2TbSZ	1.39	0.91	0.009	0.033	0.078	0.153
10Sc1TbSZ	1.37	0.85	0.013	0.048	0.103	0.190

samples increases in the following sequence 8Sc1TbSZ, 9Sc2TbSZ, 8Sc2TbSZ, 10Sc1TbSZ, 9Sc1TbSZ at any fixed temperature. Thus, this behavior of the conductivity is in agreement with the above results on the phase analysis of crystals. The 8Sc1TbSZ crystals with a tetragonal structure have the minimum specific conductivity. The conductivity of crystals with a pseudocubic t" structure depends on both the total concentration of stabilizing oxides ($Sc_2O_3 + Tb_2O_{3,5}$) and the $Tb_2O_{3,5}$ content. Thus, the value of the specific electrical conductivity of 9Sc1TbSZ and 10Sc1TbSZ crystals is higher than for 8Sc2TbSZ and 9Sc2TbSZ crystals, respectively. It should be noted that the activation energy in the high-temperature region correlates with the conductivity of crystals with a pseudocubic t " structure, namely, the lower the activation energy, the higher the conductivity. In addition, crystals containing 2 mol% Tb₂O_{3.5} have a higher activation energy in the hightemperature region as compared to crystals containing 1 mol% Tb₂O_{3.5}. Comparison of the results obtained in this work with the results of the study of $(ZrO_2)_{1-x}(Sc_2O_3)_x$ crystals (x = 0.08–0.10) [34] shows that the introduction of Tb₂O_{3.5} into crystals $(ZrO_2)_{1-x}(Sc_2O_3)_x$ (x = 0.08 or 0.09) leads to a noticeable increase in the conductivity, while the conductivity of 10Sc1TbSZ crystals is insignificantly lower than the conductivity of 10ScSZ. The 9Sc1TbSZ crystals had the maximum specific conductivity, which was 0.20 S/cm at a temperature of 1173 K, which is comparable to the specific conductivity of the 10ScSZ ceramic and crystal samples [14,34].

4. Conclusions

 $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Tb_2O_{3.5})_y$ single crystals, where x = 0.08-0.10, y = 0.01-0.02, were grown from the melt by skull melting technique. Asgrown crystals had a red-orange color, which did not change after annealing in air. The color intensity increased with an increase in the

content of terbium oxide in the crystals. The absorption spectra of the crystals indicate the presence of both Tb^{3+} and Tb^{4+} ions in the crystals. A comprehensive study of the phase composition and structure of crystals by X-ray diffractometry, Raman scattering, TEM and optical microscopy were carried out. The 8Sc1TbSZ crystals had a tetragonal structure. It is shown that homogeneous transparent 8Sc2TbSZ, 9Sc1TbSZ, 9Sc2TbSZ, and 10Sc1TbSZ crystals are single-phase and have a pseudocubic structure (t"-phase). It was found that the introduction of 2 mol% Tb₂O_{3.5} into crystals containing 8 mol% Sc₂O₃ leads to the stabilization of the t'' -phase; the introduction of 1 mol% $Tb_2O_{3.5}$ into crystals containing 9 and 10 mol% Sc₂O₃ also leads to the formation of the t" -phase. The study of the conductivity of crystals by the method of impedance spectroscopy revealed that stabilization of the hightemperature the t" -phase by introducing Tb₂O_{3.5} into crystals leads to a noticeable increase in the conductivity. The 9Sc1TbSZ crystals had the maximum specific conductivity (0.20 S/cm at 1173 K), which is comparable to the specific conductivity of the 10ScSZ ceramic and crystal samples.

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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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