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# Melt growth, structure and properties of $(ZrO_2)_{1-x}(Sc_2O_3)_x$ solid solution crystals (x=0.035-0.11)



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#### ABSTRACT

Crystals of  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  solid solutions with x=0.035, 0.06, 0.09 and 0.11 have been grown for the first time using the directional crystallization technique. Analysis of the scandium distribution along the crystal showed that the composition of all specimens is homogeneous, and the  $Sc_2O_3$  concentration is almost identical to its content in the charge. All specimens exhibit a little decline in the scandium concentration along the crystal, this indicating that the effective distribution coefficient Sc is slightly greater than 1. The structure of as-grown crystals has been studied as a function of the  $Sc_2O_3$  stabilising oxide concentration by X-ray diffraction, transmission electron microscopy and Raman spectroscopy. Crystals containing 3.5 mol%  $Sc_2O_3$  are a mixture of the monoclinic and tetragonal phases, the crystals containing 6 mol%  $Sc_2O_3$  have a tetragonal structure, those with 9 mol%  $Sc_2O_3$  represent the rhombohedral one and the specimens with 11 mol%  $Sc_2O_3$  represent the rhombohedral phase with inclusions of the cubic phase. The electrical conductivity was measured as a function of temperature by electrochemical impedance spectroscopy. The conductivity of the scandia stabilized crystals, in spite of their inhomogeneity, presence of stresses and low fracture toughness, is comparable with that of the yttria stabilized zirconia crystals.

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### 1. Introduction

Scandia stabilized zirconia used as solid oxide fuel cell membranes rise great interest due to their highest ionic conductivity among  $ZrO_2$  based solid electrolytes. The use of these materials allows reducing the operating temperature of the fuel cells to 800 °C which is quite important for increasing the stability, service life and reliability of electrochemical devices [1–9]. In practice solid electrolytes are mainly used as gas-tight ceramic membranes synthesized by various ceramics technologies.

The structural, mechanical and electrical properties of these ceramic membranes largely depend on their microstructure (grain size, grain boundaries, intergranular stresses, porosity etc.) which are in turn controlled by the synthesis process conditions. An alternative method of obtaining zirconia-based materials is the synthesis of crystalline materials by directional crystallization from the melt by means of direct radio-frequency (RF) melting in a cold crucible (skull melting technique) [10–12]. Scandia stabilized zirconia crystals have never been grown. We can find the only work dealing with investigation of the domain structure of the  $ZrO_2-Sc_2O_3$  crystals (10 mol%) [13]. To assess the possibility of using materials obtained from directionally solidified melt as components of the SOFC it is necessary to investigate their characteristics.

The aim of this work is to grow and study the phase composition, structure and properties of  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  solid solution crystals (x=0.035-0.11 mol%).

### 2. Experimental procedure

Zirconia and scandia powders of not less than 99.99% purity grade were the initial materials. The charge composition varied between 3.5 and 11 mol% Sc<sub>2</sub>O<sub>3</sub>. The crystals of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  solid solutions were grown by directional crystallization of the melt in a water-cooled crucible 130 mm in diameter. The growth apparatus

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was Kristall-407 (frequency 5.28 MHz, maximum output power 60 kW). The charge weight was 6 kg. The directional crystallization of the melt was achieved by moving the crucible with the melt downward relative to the induction coil at a 10 mm/h rate. The weight of the ingots was 4.5-5.0 kg. After the installation was shut down the ingot cooled down spontaneously. The cooling of the ingots was monitored by measuring the temperature on the surface of the upper heat screen with a Gulton 900-1999 radiation pyrometer (above 1000 °C) and a Pt/Pt-Rh thermocouple (1000 °C down to 500 °C). The average ingot cooling rate from the melt temperature to 1000 °C was 150-200 K/min and then down to 500 °C. 30 K/min. The process vielded ingots consisting of column crystals that could be mechanically separated into individual crystals. Typical dimensions of the crystals were 8-15 mm in cross-section and 40-50 mm in length. For structural studies we cut wafers perpendicular to the < 100 > direction.

Phase analysis was carried out using Raman scattering spectroscopy on a Renishawin Via Raman spectrometer and X-ray diffraction on a Bruker D8 diffractometer in CuK $\alpha$ -radiation with a position sensitive LYNXEYE detector, the DIFFRAC software package and PDF-2 data bank. The powder diffraction patterns were analyzed by Rietveld method with the Topaz program, where the structural parameters reported by Fujimori et al. [14], were used as the initial parameters for the tetragonal, cubic, monoclinic and rhombohedral phases.

The structure of the crystals was studied under a JEM 2100 microscope at an acceleration voltage of 200 keV. For electron microscopic studied the specimens were thinned to a thickness of 200 µm using ion beam etching under a PIPS apparatus (Precision Ion Polishing System, Gatan). The chemical composition of the crystals was determined by X-ray spectral analysis under a JEOL 5910 LV (Japan) electron scanning microscope equipped with INCA ENERGY (Oxford Instruments, England) energy-dispersive (EDS) system. Melted zirconia and scandia were used as standards. The accuracy in determining the concentration of scandia and zirconia was  $\pm 5\%$  of measured value. The density of the crystals was measured by hydrostatic weighing on a Sartorius balance (measuring error 0.05%). The microhardness tester with a 100–300 g load.

The conductivity of the crystals was studied in the 573–1173 K range with 50k steps using a Solartron SI 1260 analyzer in the 1–5 MHz range. The resistivity was measured in a measurement cell using the four-probe method in a Nabertherm high temperature furnace (Nabertherm GmbH, Germany). The measurements were carried out on crystal plates size of 7\*7 mm<sup>2</sup> and thickness of 0.5 mm with symmetrically connected platinum electrodes. Platinum electrodes were annealed in air at the temperature 950 °C for 1 h. The ac amplitude applied to the sample was 24 mV. The impedance frequency spectrum was analyzed in detail using the ZView (ver. 2.8) (Scribner Associates, Inc., USA) software. The resistivity of the crystals was calculated based on the resultant impedance spectra, and then the specific conductivities of the crystals were calculated. Equivalent circuits described earlier [15] were used for the calculation of the impedance spectra.

#### 3. Results and discussion

The crystals of the solid solution  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  where x=0.035, 0.06, 0.09 and 0.11, hereinafter referred to as 3.5ScZr, 6ScZr, 9ScZr and 11ScZr, respectively, were grown. The selected compositions are shown in the  $ZrO_2$ -Sc<sub>2</sub>O<sub>3</sub> phase diagram (Fig. 1) with arrows.

All the experimental crystals had the shapes and the sizes similar to those of the  $Y_2O_3$  stabilized zirconia crystals grown



**Fig. 1.** Metastable phase diagram of the  $ZrO_2-Sc_2O_3$  system [16]. (The arrows show the compositions of the grown crystals).

using directional crystallization in a cold crucible [17,18]. The appearance of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  was unique for each of the compositions (Fig. 2).

For example, the 3.5ScZr specimens are opaque white crystals (Fig. 2a), containing on the growth surface microcracks observed using optical microscopy, which formed as a result of a monoclinic-tetragonal phase transition during cooling. The 6ScZr specimens are uniformly translucent crystals without microcracks but with a large number of macrocracks in the bulk (Fig. 2b). The optical image shows a regular structure, which is similar to the "tweed" one (Fig. 2b, inset). The 9ScZr specimens are inhomogeneously translucent opalescent crystals without microcracks (Fig. 2c) with a complex bulk microstructure. The 11ScZr specimens are almost transparent crystals without cracks (Fig. 2d). The optical image shows a well-resolvable large-block microstructure.

Thus, it can be seen that none of the grown crystals are optically homogeneous and that the 3.5ScZr and 6ScZr composition specimens contain as-grown cracks in the bulk. The cracking of the crystals having these compositions is probably caused by phase transitions in the high- temperature region of the  $ZrO_2 - Sc_2O_3$  phase diagram and/or high thermomechanical stresses induced during crystal cooling.

As shown in many earlier works [8,19–22], the addition of ceria or yttria to the  $ZrO_2 - Sc_2O_3$  system increases the phase stability and electrical conductivity of these materials.

Data on the chemical composition, density and mechanical properties of the crystals are summarized in Table 1.

The crystals have high microhardness and low fracture toughness. The table above shows the limit indenter loads to specimen cracking. The microhardness summarized in Table 1 was measured at these loads.

The data shown in Table 1 suggest that the  $Sc_2O_3$  concentration is almost identical to its content in the charge. Scandia distribution along the crystal axes is shown in Fig. 3. All the specimens exhibit a little decline in the scandium concentration along the crystal, this indicating that the effective distribution coefficient of Sc is slightly greater than 1. This behavior of stabilizing cation distribution during directional crystallization of melt was also observed for the  $ZrO_2$ - $Y_2O_3$  system at low  $Y_2O_3$  concentrations [17]. This indicates the



**Fig. 2.** Appearance and structure (inset in the bottom right corner) of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$ : x=0.035 (a), x=0.06 (b), x=0.09 (c), and x=0.11 (d) solid solution crystals. The insets show optical images in transmitted light of the polished wafers 1 mm in thickness (Magnification  $25 \times$ ).

#### Table 1

Properties of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  solid solution crystals.

Sample	Sc <sub>2</sub> O <sub>3</sub> concentration (mol%) <sup>a</sup>	Chemical composition	Density (g/cm <sup>3</sup> )	Microhardness Hv, (kg/mm <sup>2</sup> )	Load (g)
3.5ScZr 6ScZr 9ScZr 11ScZr	$\begin{array}{c} 3.51 \pm 0.33 \\ 6.01 \pm 0.36 \\ 8.89 \pm 0.40 \\ 10.98 \pm 0.60 \end{array}$	$\begin{array}{l} Zr_{0.932}Sc_{0.068}O_{1.966}\\ Zr_{0.887}Sc_{0.113}O_{1.943}\\ Zr_{0.837}Sc_{0.163}O_{1.918}\\ Zr_{0.802}Sc_{0.198}O_{1.901} \end{array}$	$\begin{array}{c} 5.822 \pm 0.006 \\ 5.868 \pm 0.006 \\ 5.807 \pm 0.001 \\ 5.722 \pm 0.001 \end{array}$	$\begin{array}{c} 1240 \pm 40 \\ 1625 \pm 30 \\ 1590 \pm 40 \\ 1640 \pm 30 \end{array}$	300 300 200 100

<sup>a</sup> The Sc<sub>2</sub>O<sub>3</sub> concentration is calculated under the assumption that only  $Zr^{4+}$  and  $Sc^{3+}$  are present. Shown is the averaged  $Sc_2O_3$  concentration obtained by point-wise concentration measurements with a 1 mm step along the crystal.



identity of the high-temperature liquidus–solidus region in the phase diagrams of the  $ZrO_2-Sc_2O_3$  and  $ZrO_2-Y_2O_3$  systems in the studied range of stabilizing oxide concentrations. The  $Sc_2O_3$  concentration curves contain local and periodical composition inhomogeneities that are in excess of the measurement error and are probably determined by crystallization rate oscillations. The magnitude of these inhomogeneities increases with  $Sc_2O_3$ 

concentration and is exhibited the most clearly in the 9 and 11 mol%  $Sc_2O_3$  specimens. Probably, an additional factor is causing an inhomogeneous scandium distribution in these crystals is their block structure. The measurements of the scandium concentration along the cross-sections of the crystals suggested a homogeneous scandium distribution within the measurement error.

The phase composition and structure of the crystals were studied using X-ray diffraction of powder and bulk samples, and Raman scattering spectroscopy of the crystals.

The X-ray diffraction patterns of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  specimens are shown in Fig. 4. The phase composition and crystal structure parameters of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  solid solutions are shown in Table 2. X-ray diffractograms from the powder specimens shows that the 3.5ScZr specimen contains two phases, the tetragonal and the monoclinic one, the predominant one being the monoclinic phase. The X-ray diffraction patterns from the 6ScZr and 9ScZr specimens contain only the reflections of the tetragonal phase, and those from the 11ScZr specimen exhibit reflections of the rhombohedral phase. The X-ray diffraction patterns from the glame along which the crystal was cut. Fig. 6(b)–(h) shows only the



Fig. 4. X-ray diffraction patterns of the powdered (a, c, e, g) and bulk (b, d, f, h) (ZrO<sub>2</sub>)<sub>1-x</sub>(Sc<sub>2</sub>O<sub>3</sub>)<sub>x</sub> specimens: (a, b) 3.5ScZr; (c, d) 6ScZr; (e, f) 9ScZr; (g, h) 11ScZr.

regions of the X-ray diffraction patterns in the vicinity of the sixth order reflection from the (100) plane for the 3.5ScZr, 6ScZr and 9ScZr specimens and the third order reflection from the (012) plane for the 11ScZr specimen. The simultaneous presence of the (006) and (600) plane reflections for the (100) plane oriented crystals is attributable to twinning along the {110} planes. Comparison of the phase composition data for the bulk and the powder samples made from those crystals suggests that mechanical

crushing of the specimens does not change their phase composition. Unlike the  $ZrO_2-Y_2O_3$  solid solution single crystals, the tetragonal phase in the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  crystals does not undergo a stress induced tetragonal-monoclinic transformation regardless of the tetragonality. This agrees with earlier data [9] where it was noted that cutting and grinding of specimens containing 4 mol%  $Sc_2O_3$  does not lead to any significant tetragonal-monoclinic phase transition. The tetragonal phases in the 3.5ScZr, 6ScZr and 9ScZr

Table 2 Phase composition and crystal structure parameters of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  solid solutions.

Specimen	Phase	Space group	Weight frac- tion, %	Lattice parameters, Å
3.5ScZr	m-ZrO <sub>2</sub>	P21/c	74.3 (5)	a = 5.1552 (5), $b = 5.2000$ (7), $c = 5.3111$ (4), $\beta = 98.9$ (3)°
6ScZr 9ScZr 11ScZr	$\begin{array}{c} t\text{-}ZrO_2\\ t\text{-}ZrO_2\\ t\text{-}ZrO_2\\ r\text{-}ZrO_2\\ c\text{-}ZrO_2\end{array}$	$P4_2/nmc$ $P4_2/nmc$ $P4_2/nmc$ $R\overline{3}m$ $Fm\overline{3}m$	25.7 (5) 100.0 (3) 100.0 (2) 92.7 (6) 7.3 (7)	$\begin{array}{l} a = 3.5965 \ (3), \ c = 5.1651 \ (5) \\ a = 3.5961 \ (4), \ c = 5.1353 \ (5) \\ a = 3.5952 \ (3), \ c = 5.1221 \ (4) \\ a = 3.5636 \ (7), \ c = 9.0215 \ (6) \\ a = 5.098 \ (5) \end{array}$

crystals have low tetragonality (c/ $\sqrt{2a}$ ) [23], i.e. 1.016, 1.010 and 1.007 for the 3.5ScZr, 6ScZr and 9ScZr compositions, respectively. The tetragonality decreases with an increase in the Sc<sub>2</sub>O<sub>3</sub> concentration, and the structure of the crystals becomes closer to the cubic phase.

A transmission electron microscopy study showed that the all investigated crystals contain twins. The pattern and size of the twins differ in crystals with different  $Sc_2O_3$  concentrations (Fig. 5). The morphology of the twin structure changes nonmonotonically with the Sc<sub>2</sub>O<sub>3</sub> concentration in the crystals. The 3.5ScZr specimen contains large needle shaped twins that are typical of the monoclinic phase (Fig. 5a). The twin structure of the 6ScZr specimen is relatively homogeneous and fine grained (Fig. 5b). Twinning in this specimen was also confirmed by X-ray diffraction data, and similar twin structure morphology was observed in ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> solid solution specimens [24]. The size of the twins increases with an increase in the Sc<sub>2</sub>O<sub>3</sub> concentration, as in the 9ScZr specimen. It can be seen from Fig. 5c that the primary twin plates of the crystals also undergo twinning. The traces of secondary twinning planes are at an angle of approx. 45° to the trace of the primary twinning plane. The largest twins are observed in the rhombohederal 11ScZr specimen (Fig. 5d). The TEM images shown in Fig. 5 suggest that the phase composition of the specimens agrees with the data of phase analysis obtained using X-ray diffraction. Only the 9ScZr specimen contains a local rhombohederal phase inclusion.

Raman spectroscopy data on the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  crystals are shown in Fig. 6.

The Raman spectrum of the 3.5ScZr contains peaks that are typical of the monoclinic and tetragonal phases [26,14]. The spectrum of the 6ScZr crystals contains 6 peaks corresponding to the tetragonal phase. With an increase in the Sc<sub>2</sub>O<sub>3</sub> concentration to 9 mol% (the 9ScZr specimen) the crystal retains its tetragonal structure. However, the peaks are significantly broadened, and additional peaks appear. The Raman spectrum of the 11ScZr crystals notably differs from those of the other experimental spectra and agrees well with earlier data [27] which showed that arc melting grown ZrO<sub>2</sub>-22 mol% ScO<sub>1.5</sub> specimens have a rhombohedral structure. This agrees with our X-ray phase analysis data on the 11ScZr specimens which also show the presence of a rhombohedral structure. The star-marked peak in the spectra of the 9ScZr and 11ScZr specimens was attributed by the authors of [26] to a defect structure of the material showing itself in structure disordering caused by the static redistribution of the scandium cations and the accompanying oxygen vacancies.

Comparison of the spectra of the 9ScZr and 11ScZr specimens suggests that the broadening of existing and the appearance of new peaks in the 9ScZr specimen spectrum can be attributed to the presence of the rhombohedral phase in the crystal along with the tetragonal one. For the  $ZrO_2$ –9.0 mol% Sc<sub>2</sub>O<sub>3</sub> specimen we recorded the spectra in several points and from different specimens of the crystal of this composition by a micro Raman spectrometer. The local analysis data show that the Raman spectra differ in different points of the as-grown specimens. In some points the Raman spectrum contains the peaks of the rhombohedral phase along with those of the tetragonal phase. This can be accounted for by oscillations of the scandia concentration along the crystal (Fig. 3).

Experimental results on the phase composition of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  specimens obtained using different methods are summarized in Table 3.

Using a set of complementary phase composition investigation methods including transmission electron microscopy allows obtaining more precise and reliable data. The data summarized in Table 3 suggest that the phase compositions of the powders and the crystals are identical according to the X-ray phase analysis data. This testifies to the absence of phase transformations in 6ScZr and 9ScZr crystals that could be initiated during powder preparation. For the 3.5ScZr specimen the proportions of the tetragonal and monoclinic phases did not show measurable phase change after mechanical crushing of the specimen, which also points to the absence of stresses induced phase transformation. We were not able to determine quantitatively content of cubic phase in 11ScZr crystal due to block structure of the sample, therefore assessment of cubic phase stability is not possible in this case.

Importantly, the specimen 9ScZr do not contain the cubic phase. This does not agree with the results of other works that dealt with specimens of similar compositions synthesized using the ceramics technology at sintering temperatures not exceeding 1600 °C [28,29] in which the presence of the cubic phase was identified. A probable origin of this discrepancy is that our experimental crystals were grown from the melt, and therefore their thermal history differs significantly from that of the ceramic specimens. Phase composition of 11ScZr specimen is in agreement with data for quenched arc melted polycrystalline specimens containing 18–20 mol% ScO<sub>1.5</sub> (10–11 mol% Sc<sub>2</sub>O<sub>3</sub>) in which traces of the cubic phase were observed [25].

A very important parameter of solid electrolytes that determines the possibility of their practical application is their ionic conductivity. Zirconium dioxide based materials are known to be typical anionic conductors and to exhibit a minimum electronic contribution to the total electrical conductivity in the oxygen partial pressure range most important for practical applications [3].

The specific ionic conductivity ( $\sigma$ ) of the 6ScZr and 9ScZr specimens was calculated based on the analysis of the impedance spectra recorded at a constant temperature taking into account the sizes of the specimens using the following formula:

 $\sigma = (1/R)(l/S)(1)$ 

where R is the sample resistance, l is the specimen thickness and S is the contact area.

Fig. 7 shows characteristic impedance spectra obtained at 673 K. (We did not measure the electrical conductivity of the 3.5ScZr and 11ScZr due to the impossibility of producing specimens of required sizes).

Two regions can be found in the spectra: there is a semicircle with its center on the real axis in the high-frequency spectrum region that can be attributed to the electrical resistance of the crystal itself in this frequency range; and there is an arc characterizing polarization resistance of electrodes in the low-frequency region. The dependences of conductivity on the inverse temperature in the Arrhenius coordinates are shown in Fig. 8. For comparison Fig. 8 also contains data for the ZrO<sub>2</sub>– 8 mol% Y<sub>2</sub>O<sub>3</sub> cubic single crystal (8YSZ) studied earlier [30]. A similar temperature dependence of conductivity for high-density ceramics with 10.5–11 mol% scandia was observed elsewhere [22]. One can separate two temperature ranges in which the  $\ln(\sigma T)=f(1/T)$  functions are linear. These are the low-temperature range



**Fig. 5.** TEM images of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  crystals: (a) 3.5ScZr; (b) 6ScZr; (c) 9ScZr; (d) 11ScZr. The insets show diffraction patterns of the respective crystal specimen regions.

(623-823) K and the high temperature range (823-1173) K. We also did not observe of abrupt kinks in the dependences of conductivity on the inverse temperature for these specimens that may be indicative of the absence of phase transitions in this temperature range. We used the resultant dependences for calculating the activation energies of the crystals ( $E_a$ ). We used the Arrhenius–Frenkel equation:

$$\sigma = AT^{-1} \exp(E_a/kT) \tag{2}$$

where  $\sigma$  is the ionic conductivity, A is the constant, T is the absolute temperature,  $E_a$  is the activation energy and k is the Boltzmann constant.

Table 4 shows conductivity activation energies  $(E_a)$  for these intervals.

It is well-known that in the case of ion conductivity two temperature regions with different activation energies are observed that are attributed to different ion transport mechanisms [31]. There are also data that oxygen vacancies generated by doping zirconia with heterovalent cations form defect associations with the formation of ordered clusters [32]. In zirconium dioxide based materials, the activation energy  $E_a$  in the low-temperature region is the sum of the association energy ( $E_{as}$ ) which is required for the dissociation of the vacancy-cation clusters and the migration energy  $(E_m)$  of mobile ions:

$$E_a = E_{as} + E_m \tag{3}$$

According to this model, at high temperatures isolated vacancies migrate freely, and the activation energy is solely the migration energy  $E_m$  of the oxygen vacancies. At low temperatures vacancy association makes a significant contribution to the activation energy.

Thus, one can easily calculate that  $E_{as}$  for  $ZrO_2-Sc_2O_3$  anion conductors is approx. 0.34–0.49 eV which is close to  $E_{as}$  for the  $ZrO_2-Sc_2O_3$  and  $ZrO_2-Y_2O_3$  compounds calculated earlier [8].

Thus, the highest ionic conductivity of the test specimens in the 550–900 °C is observed in the 9ScZr crystals. The value of the ionic conductivity for the 9ScZr crystals at 800 °C is 0.053 S cm<sup>-1</sup>, which is greater than that for the cubic 8YSZ crystals (0.032 S cm<sup>-1</sup>) having the maximum conductivity in the  $ZrO_{2}$ –  $Y_2O_3$  system.

#### 4. Summary

Crystals of  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  solid solutions with x=0.035, 0.06, 0.09 and 0.11 have been grown for the first time using the



**Fig. 6.** Raman spectra of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  crystals. Notations: ( $\bullet$ ) monoclinic phase [25]; ( $\bullet$ ) tetragonal phase; ( $\bullet$ ) rhombohedral phase; ( $\star$ ) unidentified peaks.

Table 3

Phase composition of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  solid solution crystals.

Specimen	Phase composition						
	X-Ray phase analysis		Raman	Transmission electron			
	Powder	Crystals	scattering	meroscopy			
3.5ScZr	$\mathbf{m} + \mathbf{t}$	$\mathbf{m} + \mathbf{t}$	m+t	m+t			
6ScZr	t	t	t	t			
9ScZr	t	t	$t + r^{a}$	$t + r^{a}$			
11ScZr	$\mathbf{r} + \mathbf{c}$	$\mathbf{r}$ +c	r	r			

The predominant phase is marked by bold.

<sup>a</sup> present in local areas and in small quantities.



Fig. 7. Impedance spectra of the crystals 9ScZr and 6ScZr at 673 K. Equivalent circuits described earlier [15] were used to fit data.

directional crystallization technique. The as-grown crystals with 3.5 and 6 mol%  $Sc_2O_3$  are distinguished by the presence of cracks in the crystal bulk. Analysis of the scandium distribution along the



Fig. 8. Arrhenius plot of electrical conductivities for the samples: 9ScZr, 8YSZ, 6ScZr.

Table 4							
Conductivity activation	energies (	$E_a$ ) of the	8YSZ,	6ScZr	and	9ScZr	crystals

Materials	$E_a$ (eV)			
	623–823 K	823–1173 K		
8YSZ	$1.08\pm0.01$	$0.87 \pm 0.02$		
6ScZr	$1.13\pm0.01$	$0.79\pm0.02$		
9ScZr	$1.36\pm0.01$	$\textbf{0.87} \pm \textbf{0.02}$		

crystal has shown that the composition of all the experimental specimens is homogeneous and the Sc<sub>2</sub>O<sub>3</sub> concentration is almost identical to its concentration in the charge. All specimens exhibit a little decline in the scandium concentration along the crystal, this indicating that the effective distribution coefficient Sc is slightly greater than 1. Phase composition studies of the crystals using a set of complementary methods including X-ray phase analysis, Raman spectroscopy and transmission electron microscopy have shown that the crystals containing 3.5 mol% Sc<sub>2</sub>O<sub>3</sub> are a mixture of the monoclinic and tetragonal phases, the crystals containing 6 mol%  $Sc_2O_3$  have a tetragonal structure, those with 9 mol%  $Sc_2O_3$ have the tetragonal phase with inclusions of the rhombohedral one and the specimens with 11 mol% Sc<sub>2</sub>O<sub>3</sub> represent the rhombohedral phase with inclusions of the cubic phase. The tetragonal phases in the 3.5ScZr, 6ScZr and 9ScZr crystals have low tetragonality, i.e.  $c/\sqrt{2a}=1.016$ ; 1.010 and 1.007, respectively. With an increase in the Sc<sub>2</sub>O<sub>3</sub> concentration the tetragonality decreases, and the structure of the crystals becomes closer to the cubic phase.

The 3.5ScZr, 6ScZr and 9ScZr crystals do not either undergoes any stress induced phase transitions caused by mechanical treatment and crushing. We show that the crystals of all the experimental compositions have a twin structure the type of which depends on the crystal composition.

The highest ionic conductivity of the test specimens in the 550-900 °C range is observed in the 9ScZr crystals.

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