



# Phase compositions, structures and properties of scandia-stabilized zirconia solid solution crystals co-doped with yttria or ytterbia and grown by directional melt crystallization



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## ABSTRACT

The effect of co-doping an impurity on the transport parameters and cubic phase stabilization of  $ZrO_2$ - $Sc_2O_3$ -based solid solutions has been compared for  $Y_2O_3$  and  $Yb_2O_3$  dopants. Solid solution crystals of  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Yb_2O_3)_y$  and  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  ( $x = 0.08$ – $0.10$ ,  $y = 0.01, 0.02$ ) were grown by directional melt crystallization in a cold crucible. Co-doping of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  crystals ( $x = 0.08$ – $0.10$ ) with 2 mol%  $Y_2O_3$  or  $Yb_2O_3$  for all experimental compositions produced transparent homogeneous single crystals of the  $t'$  phase or the cubic phase. For co-doping of the scandia-stabilized zirconia crystals with 1 mol%  $Y_2O_3$  or  $Yb_2O_3$ , the stabilization of the high-temperature phases depended on the  $Sc_2O_3$  content in the solid solutions. For co-doping of the solid solutions with 1 mol%  $Y_2O_3$  or  $Yb_2O_3$ , the conductivity of the crystals increased with the  $Sc_2O_3$  concentration. For co-doping of the crystals with 2 mol%  $Y_2O_3$  or  $Yb_2O_3$ , the conductivity decreased with the  $Sc_2O_3$  concentration. At scandia concentrations of 9–10 mol%, the high-temperature conductivity of the crystals co-doped with ytterbia were higher compared to those with yttria co-doping. The  $(ZrO_2)_{0.9}(Sc_2O_3)_{0.09}(Yb_2O_3)_{0.01}$  crystals had the highest conductivity over the entire experimental temperature range.

## 1. Introduction

Materials based on  $ZrO_2$ - $Sc_2O_3$  solid solutions used in solid oxide fuel cells (SOFCs) are of great interest because they have the highest ionic conductivity among zirconia-based solid electrolytes [1–4]. However, there are problems with compounds having the highest conductivity, i.e.,  $ZrO_2$  – (9–11) mol%  $Sc_2O_3$ , when used as materials for electrolytic membranes; these problems are unstable transport characteristics at operating temperatures and a transformation of a rhombohedral phase to a cubic phase during heating. Stabilizing the highly conductive cubic phase is one of the possible ways to solve these problems by co-doping  $ZrO_2$  –  $Sc_2O_3$  solid solutions with yttria or rare-earth element oxides [5–10]. The choice of co-doped impurities is dictated by the necessity to obtain a single-phase cubic solid solution stable in the range from room temperature to operating temperatures

(700–1000 °C) and to maintain the high conductivity typical of the  $ZrO_2$ - $Sc_2O_3$  system. Efficient impurities that stabilize the high-temperature cubic phase are yttria and ytterbia [9,11–16]. In particular, a recently published article [17] conducted a detailed study on the effect of 1 mol%  $Yb_2O_3$  co-doping on the metastable tetragonal phases present in 8–9 mol%  $Sc_2O_3$ - $ZrO_2$ . X-ray diffraction (XRD), transmission electron microscopy (TEM) and Raman spectroscopy analysis confirmed the metastable  $t'$  phase in  $8Sc_2O_3$ - $9ZrO_2$  and  $t''$  phase in  $9Sc_2O_3$ - $9ZrO_2$ .

It is well known that the phase composition and properties of solid electrolytes depend significantly on the material synthesis technique that is used [18]. For example, the phase composition of molten materials may differ significantly from the phase composition of materials synthesized at low temperatures. In this work, we synthesized the materials by directional melt crystallization in a cold crucible. This method was used earlier for synthesizing crystals of a wide range of

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solid electrolytes [19–22].

The aim of this work is to synthesize  $ZrO_2$ - $Sc_2O_3$  solid solution crystals co-doped with yttria or ytterbia to study their transport properties and to compare the effect of the impurities ( $Y_2O_3$  or  $Yb_2O_3$ ) on the transport parameters and cubic phase stabilization of  $ZrO_2$ - $Sc_2O_3$ -based solid solutions.

## 2. Experimental

$(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Yb_2O_3)_y$  and  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  solid solution crystals ( $x = 0.08$ – $0.10$ ,  $y = 0.01$ ,  $0.02$ ) were grown using directional melt crystallization in a cold crucible [23]. The crystals were grown in a Kristall-407 unit (frequency 5.28 MHz, maximum output power 60 kW). The raw materials were zirconia, scandia and ytterbia powders of at least 88.88% purity. A mixture of the powders in the required weight ratio was placed in a crucible (120 mm in diameter) that contained a set of water-cooled copper tubes. To start the melting process, we added 5–10 g of Zr metal into the powder. Directional melt crystallization was achieved by moving the melt container down relative to the inductor at a 10 mm/h speed. The weight of the melt was 5–6 kg. After switching off the growth unit, the melt was cooled in the crucible to room temperature. The temperature of the ingot surface was recorded with a Gulton 900–1999 radiation pyrometer in a 2000–1000 °C range and a Pt/Pt-Rh thermocouple in the 1000–500 °C range; the ingot cooling rates in these temperature ranges were ~200 °C/min and ~30 °C/min, respectively. The melt crystallized to an ingot consisting of discrete crystals that could be mechanically separated from one another after ingot cooling.

The chemical composition of the as-grown crystals was studied using a JEOL 5910 LV scanning electron microscope with an INCA energy dispersion unit. Molten zirconia, scandia, yttria, and ytterbia were used as references for the crystal composition study. The structure of the crystals was studied using X-ray diffraction (Bruker D8, Germany) with a standard method used for single crystals. For the X-ray study, the crystals were cut into plates perpendicular to the  $\langle 100 \rangle$  direction. The phase composition of the crystals was also studied using Raman scattering spectroscopy (Renishaw inVia Raman spectrometer). The excitation source was a 532 nm laser. The instrument for Raman study of the crystals at room temperature and at operating temperatures of up to 1000 °C was described in detail earlier [24–26].

Transmission electron microscopy (TEM) was carried out using a JEM 2100 (Jeol, Japan) microscope at an acceleration voltage of 200 keV. An ultrasonic disc cutter was used to cut samples into discs 3 mm in diameter, which were then polished to a thickness of ~100 µm. The discs were further dimpled to a thickness of ~25 µm in a dimple grinder and then ion-milled in a precision ion polishing system (Gatan, PIPS II).

The conductivity of the zirconia base crystals was studied in a 400–900 °C range with a Solartron SI 1260 frequency analyser over a 1 Hz – 5 MHz frequency range with a 24 mV AC current amplitude. The test plates had an area of  $7 \times 7 \text{ mm}^2$  each and were 0.5 mm in thickness. The current contacts were produced on the reverse side of the crystals by burning in a platinum paste at 950 °C for 1 h in air. The impedance spectra were processed with ZView (ver. 2.8) (Scribner Associates, Inc., USA) software. The specific conductivity of the crystals was calculated from the impedance spectrum processing results, while taking into account the specimen dimensions.

## 3. Results and discussion

Table 1 shows the compositions of the solid solutions, their brief notations used hereafter, and the phase composition and lattice parameters of the crystals.

The as-grown crystals had columnar shapes that were typical of crystals grown by crystallization in a cold crucible. The transverse dimension of the crystals was 20 mm, with a length of 30–50 mm (Fig. 1).

Analysis of the appearance of the crystals provides initial information on their phase composition, i.e., whether a crystal is single-phase or contains multiple phases. The presence of multiple phases or structural defects may cause light scattering at defects or phase boundaries, making the crystal opalescent or semitransparent.

The 8Sc1YSZ crystals were almost completely inhomogeneous and semitransparent, and only the top parts that formed at the end of crystallization had some small transparent regions (Fig. 1a). At higher  $Sc_2O_3$  concentrations in the solid solutions (9 mol%), 9Sc1YSZ, the crystals had transparent regions in the bottom parts of the 9Sc1YSZ crystals forming at an early crystallization stage and semitransparent (opaque) regions in the top parts of the crystal (end of crystallization). Some 9Sc1YSZ crystals exhibited interchanging transparent and opaque regions in the middle parts of the as-crystallized melt ingots (Fig. 1b). Transparent single crystals without visible defects containing 1 mol%  $Y_2O_3$  were only obtained at a 10 mol%  $Sc_2O_3$  concentration (Fig. 1c). All the crystals doped with 2 mol%  $Y_2O_3$  (8Sc2YSZ, 9Sc2YSZ, and 10Sc2YSZ) were homogeneous and transparent single crystals.

The appearance of the crystals stabilized with 1 mol%  $Yb_2O_3$  differed from that of the crystals stabilized with 1 mol%  $Y_2O_3$ . The 8Sc1YbSZ crystals were homogeneous and opaque, without visible defects (Fig. 1d). The 9Sc1YbSZ crystals, unlike the 9Sc1YSZ crystals, were transparent and homogeneous single crystals (Fig. 1e). At higher  $Sc_2O_3$  concentrations in the solid solutions (10 mol%, 10Sc1YbSZ), the crystals were opalescent and contained microcracks in the bulk (Fig. 1f). Doping with 2 mol%  $Yb_2O_3$ , by analogy with 2 mol%  $Y_2O_3$  doping, produced transparent and homogeneous single crystals.

The phase composition of the crystals additionally doped with 1 mol%  $Y_2O_3$  changed with an increase in the  $Sc_2O_3$  concentration. The phase composition of the 8Sc1YSZ crystals was inhomogeneous along the ingot length. Most of the 8Sc1YSZ crystal volume contained the tetragonal  $ZrO_2$  modification ( $c/\sqrt{2a} \sim 1.005$ ), and only the top parts of the crystals contained a mixture of cubic and tetragonal phases. The 9Sc1YSZ crystals were two-phase and contained regions with tetragonal and cubic structures. The 10Sc1YSZ crystals were single-phase and had a cubic fluorite structure. The 8Sc2YbSZ, 9Sc2YbSZ, and 10Sc2YbSZ crystals were single-phase cubic single crystals. The lattice parameters of the crystals stabilized with 2 mol%  $Y_2O_3$  decreased monotonically with an increase in the  $Sc_2O_3$  concentration.

The phase compositions of the crystals additionally doped with 1 mol%  $Yb_2O_3$  also changed with an increase in the  $Sc_2O_3$  concentration. The 8Sc1YbSZ crystals were homogeneous and tetragonal ( $c/\sqrt{2a} \sim 1.005$ ). The 9Sc1YbSZ crystals were single-phase cubic crystals, while the 10Sc1YbSZ crystals contained two phases, i.e., the cubic and rhombohedral zirconia modifications. The 8Sc2YSZ, 9Sc2YSZ, and 10Sc2YSZ crystals were single-phase cubic single crystals. The lattice parameters of the crystals stabilized with 2 mol%  $Yb_2O_3$ , and by analogy the crystals stabilized by doping with 2 mol%  $Y_2O_3$ , decreased with an increase in the  $Sc_2O_3$  concentration in the crystals.

For example, Fig. 2 shows typical diffraction patterns of the 8Sc1YbSZ and 9Sc1YbSZ crystals for the surfaces of plates cut perpendicular to the  $\langle 100 \rangle$  direction.

Thus, co-doping of the  $(ZrO_2)_{1-x}(Sc_2O_3)_x$  crystals ( $x = 0.08$ – $0.10$ ) with 2 mol%  $Y_2O_3$  or  $Yb_2O_3$  produced homogeneous transparent crystals with a fluorite structure. At a co-doping impurity ( $Y_2O_3$  or  $Yb_2O_3$ ) concentration of 1 mol%, the phase compositions of the crystals depended on the  $Sc_2O_3$  concentration. The high-temperature cubic phase of the Sc1YSZ crystals stabilized at a total stabilizing oxide concentration of 11 mol%, whereas for the Sc1YbSZ crystals, the stabilization occurred at a total stabilizing oxide concentration of 10 mol%. Despite the smaller ionic radius of  $Yb^{3+}$  compared with that of  $Y^{3+}$ , the cubic phase stabilized in crystals co-doped with  $Yb_2O_3$  at lower  $Sc_2O_3$  concentrations in the solid solution than for crystals co-doped with  $Y_2O_3$ .

In binary  $ZrO_2$ - $R_2O_3$  systems, a decrease in the ionic radius reduces the temperature of the transition from the high-temperature cubic phase to the low-temperature tetragonal phase, leading to the

**Table 1**Composition, notation, phase composition and lattice parameters of the  $(\text{ZrO}_2)_{1-x-y}(\text{Sc}_2\text{O}_3)_x(\text{Yb}_2\text{O}_3)_y$  and  $(\text{ZrO}_2)_{1-x-y}(\text{Sc}_2\text{O}_3)_x(\text{Y}_2\text{O}_3)_y$  crystals.

Composition	Specimen	Phase composition	Lattice parameter	
			a, nm	c, nm
$(\text{ZrO}_2)_{1-x-y}(\text{Sc}_2\text{O}_3)_x(\text{Y}_2\text{O}_3)_y$				
$(\text{ZrO}_2)_{0.91}(\text{Sc}_2\text{O}_3)_{0.08}(\text{Y}_2\text{O}_3)_{0.01}$	8Sc1YSZ	t'	0.3600(1)	0.5119(2)
		c	0.5103(1)	
$(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.08}(\text{Y}_2\text{O}_3)_{0.02}$	8Sc2YSZ	c	0.5101(1)	
$(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.09}(\text{Y}_2\text{O}_3)_{0.01}$	9Sc1YSZ	t'	0.3601(1)	0.5109(2)
		c	0.5095(1)	
$(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.09}(\text{Y}_2\text{O}_3)_{0.02}$	9Sc2YSZ	c	0.5098(1)	
$(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.10}(\text{Y}_2\text{O}_3)_{0.01}$	10Sc1YSZ	c	0.5093(1)	
$(\text{ZrO}_2)_{0.88}(\text{Sc}_2\text{O}_3)_{0.10}(\text{Y}_2\text{O}_3)_{0.02}$	10Sc2YSZ	c	0.5096(1)	
$(\text{ZrO}_2)_{1-x-y}(\text{Sc}_2\text{O}_3)_x(\text{Yb}_2\text{O}_3)_y$				
$(\text{ZrO}_2)_{0.91}(\text{Sc}_2\text{O}_3)_{0.08}(\text{Yb}_2\text{O}_3)_{0.01}$	8Sc1YbSZ	t'	0.3598(1)	0.5113(2)
$(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.08}(\text{Yb}_2\text{O}_3)_{0.02}$	8Sc2YbSZ	c	0.5099(1)	
$(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.09}(\text{Yb}_2\text{O}_3)_{0.01}$	9Sc1YbSZ	c	0.5094(1)	
$(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.09}(\text{Yb}_2\text{O}_3)_{0.02}$	9Sc2YbSZ	c	0.5096(1)	
$(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.10}(\text{Yb}_2\text{O}_3)_{0.01}$	10Sc1YbSZ	c	0.5095(1)	
		r	0.3563(2)	0.9003(2)
$(\text{ZrO}_2)_{0.88}(\text{Sc}_2\text{O}_3)_{0.10}(\text{Yb}_2\text{O}_3)_{0.02}$	10Sc2YbSZ	c	0.5095(1)	

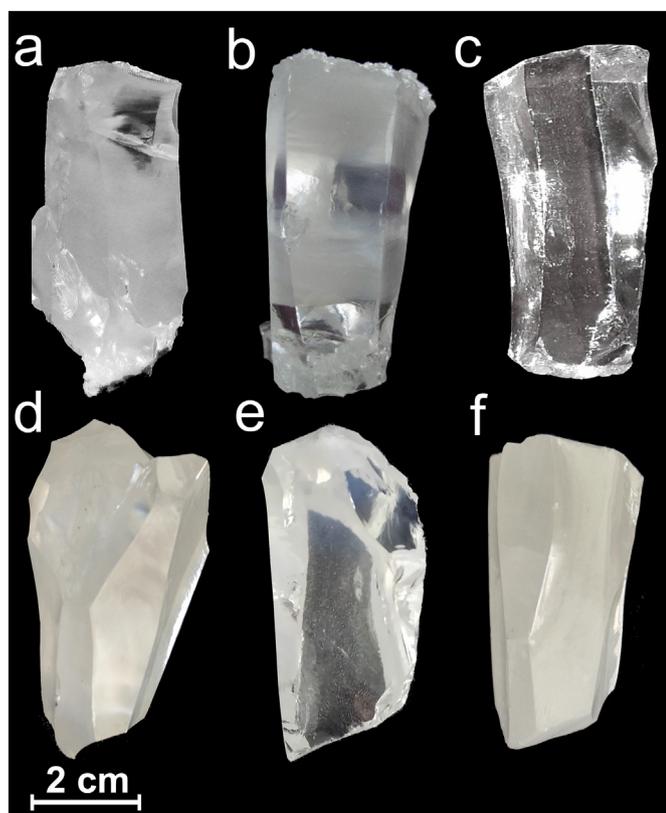


Fig. 1. Appearance of the (a) 8Sc1YSZ, (b) 9Sc1YSZ, (c) 10Sc1YSZ, (d) 8Sc1YbSZ, (e) 9Sc1YbSZ and (f) 10Sc1YbSZ crystals.

preservation of a high-temperature cubic phase at room temperature for low stabilizing oxide concentrations. This regularity may also hold for the studied ternary systems.

The phase compositions of the crystals were also studied using Raman spectroscopy. Fig. 3 shows the Raman spectra of the test crystals. The Raman spectra of the 8Sc1YSZ and 8Sc1YbSZ crystals contained peaks typical of the tetragonal phase [27,28]. In the Raman spectra of the 9Sc1YSZ crystals, the peaks were broadened due to the presence of the cubic and tetragonal phases in the crystals. The Raman spectra of the 10Sc1YbSZ crystals contained peaks that were also broadened and corresponded to the rhombohedral phase [28], which

was possibly due to the presence of the cubic phase in these crystals.

The Raman spectra of the 10Sc1YSZ, 8Sc2YSZ, 9Sc2YSZ, 9Sc1YbSZ and 8Sc2YbSZ crystals were similar and contained, along with the cubic phase peaks, a  $480\text{ cm}^{-1}$  peak that had been reported to correspond to the tetragonal t' phase [29–31]. This phase had a tetragonality degree of  $c/\sqrt{2}a = 1$  but belonged to the  $P4_2/nmc$  space symmetry group due to the shift of the oxygen ions in the anion sublattice [30]. Raman spectra typical of the t-ZrO<sub>2</sub>, t'-ZrO<sub>2</sub> and c-ZrO<sub>2</sub> phases were reported earlier [32]. Thus, the structure of these crystals identified as cubic using X-ray diffraction were the tetragonal t' phase, as indicated by Raman spectroscopy. Only the spectra of the 10Sc2YSZ, 9Sc2YbSZ, and 10Sc2YbSZ crystals corresponded to the cubic phase.

Fig. 4 shows the TEM images and the corresponding selected area electron diffraction (SAED) patterns for the 8Sc1YbSZ and 9Sc1YbSZ crystals. The TEM images of the 8Sc1YbSZ crystal (Fig. 4a) showed a twinning structure that was typical of the t' phase [1]. Similar TEM images were also obtained for other crystals that contained the tetragonal phase. The twins formed during single crystal cooling as a result of the cubic-to-tetragonal transition in accordance with the ZrO<sub>2</sub>-Sc<sub>2</sub>O<sub>3</sub> phase diagram. The presence of these defects changed the optical transparency of the crystals due to light scattering at twin boundaries. The 9Sc1YbSZ crystals (Fig. 4b) did not contain twins. The bright-field image was typical of single-phase cubic crystals. However, the SAED patterns of the 9Sc1YbSZ crystals contained reflections that were impossible for the perfect fluorite type structure but were allowed for a tetragonal structure. The presence of the 110- and 112-type reflections suggested ordered shifting of the oxygen atoms and hence a distortion of the  $Fm\bar{3}m$  space group symmetry. Thus, the data suggested that the crystalline structure of the 9Sc1YbSZ crystals corresponded to the structure of the tetragonal t' phase.

Similar TEM images and the corresponding SAED patterns were also observed for the 10Sc1YSZ, 8Sc2YSZ, 9Sc2YSZ, and 8Sc2YbSZ crystals. These data also agreed with the Raman data for the crystals.

Typical impedance spectra for crystals with different phase compositions are shown in Fig. 5. The 8Sc1YSZ and 9Sc1YSZ were two-phase crystals (t + c); the 10Sc1YbSZ crystal was also a two-phase crystal (c + r); 8Sc1YbSZ was single-phase (t); and 9Sc1YbSZ and 10Sc1YSZ were single-phase (c). Despite the different phase compositions of the crystals, their impedance spectra had no fundamental differences. These spectra exhibited arcs in their high-frequency portions, which corresponded to bulk conductivity, as well as low-frequency arcs, which characterized the polarization resistance of the electrodes. There were no intermediate arcs corresponding to grain boundary conductivity. One could therefore assume that the twin and phase

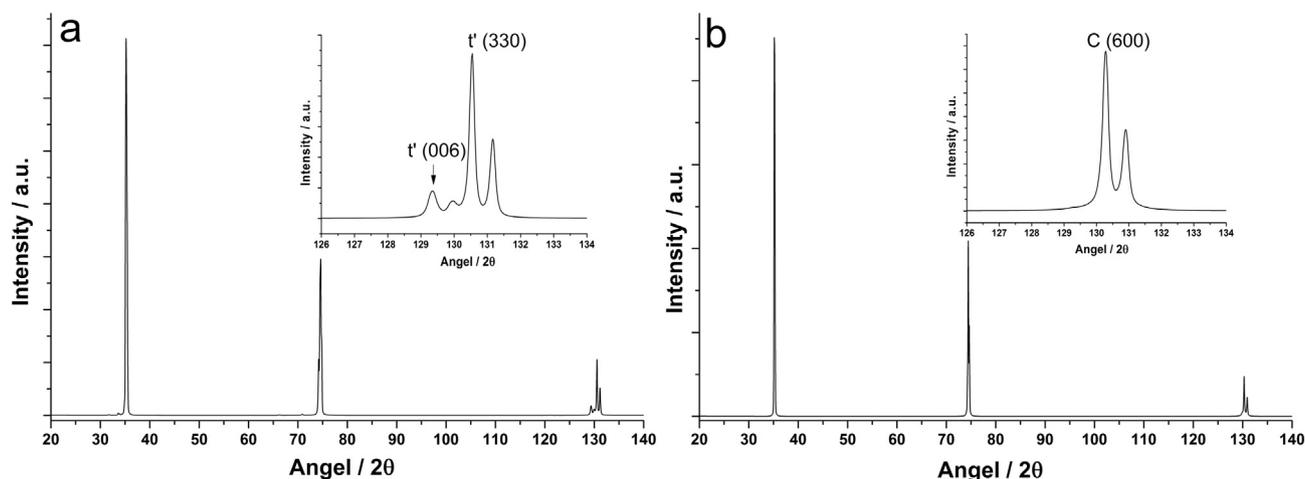


Fig. 2. Diffraction patterns of the (a) 8Sc1YbSZ and (b) 9Sc1YbSZ crystals for the surfaces of plates cut perpendicular to the  $\langle 100 \rangle$  direction.

boundaries did not contribute to the total conductivity of the crystals.

Fig. 6 shows the specific conductivity of the crystals as a function of temperature in Arrhenius coordinates. It could be seen from the specific conductivity vs. temperature curves that only the curve of the 10Sc1YbSZ crystal had a bend in the 450–550 °C range caused by the rhombohedral-to-cubic phase transition. The 10Sc1YbSZ crystals had the highest conductivity among all the  $(\text{ZrO}_2)_{1-x-y}(\text{Sc}_2\text{O}_3)_x(\text{Y}_2\text{O}_3)_y$  crystals in the entire experimental temperature range, and the 9Sc1YbSZ crystals had the highest conductivity for the  $(\text{ZrO}_2)_{1-x-y}(\text{Sc}_2\text{O}_3)_x(\text{Yb}_2\text{O}_3)_y$  crystal series.

Fig. 7 shows the conductivity of the ScYbSZ and ScYSZ crystals as a function of the  $\text{Sc}_2\text{O}_3$  content.

Fig. 7 suggested that the conductivity of the crystals increased with the  $\text{Sc}_2\text{O}_3$  content in the crystals co-doped with 1 mol%  $\text{Y}_2\text{O}_3$  or  $\text{Yb}_2\text{O}_3$ . The conductivity of the crystals co-doped with 2 mol%  $\text{Y}_2\text{O}_3$  or  $\text{Yb}_2\text{O}_3$  decreased with an increase in the  $\text{Sc}_2\text{O}_3$  concentration. For comparable  $\text{Sc}_2\text{O}_3$  and stabilizing oxide concentrations, the conductivity of the crystals co-doped with  $\text{Yb}_2\text{O}_3$  was always higher than that of the crystals co-doped with  $\text{Y}_2\text{O}_3$ . The patterns of the experimental conductivity vs. concentration curves could be accounted for by taking into account the specimen phase composition data. The conductivities of the single-phase tetragonal 8Sc1YbSZ and 8Sc1YSZ crystals and those of the

two-phase 9Sc1YSZ crystal, which were a mixture of the tetragonal and cubic phases, were close at approximately 0.1 S/cm. The 9Sc1YbSZ crystals, which were single-phase pseudocubic crystals (the  $t''$  phase), had the highest conductivity. At a  $\text{Sc}_2\text{O}_3$  concentration of 10 mol% (the 10Sc1YbSZ specimen), the crystals had rhombohedral phase regions, and their conductivity decreased. The 10Sc1YSZ crystals were also single-phase pseudocubic crystals (the  $t''$  phase), but their conductivity was lower than that of the 9Sc1YbSZ crystals that had a similar crystalline structure. This difference in the conductivity could be attributed to the larger ionic radius of  $\text{Y}^{3+}$  compared with that of  $\text{Yb}^{3+}$ . The introduction of a larger ion in the case of a heterovalent substitution increases lattice stress and thus reduces the conductivity. Furthermore, the 10Sc1YSZ and 9Sc1YbSZ crystals had different stabilizing oxide concentrations (11 and 10 mol%, respectively). An increase in the total stabilizing oxide concentration to above a threshold level, which depends on the type of stabilizing impurity, reduces the conductivity of the crystals due to the formation of oxygen+ion clusters [33]. The conductivity of the single-phase cubic crystals stabilized with 2 mol%  $\text{Y}_2\text{O}_3$  or  $\text{Yb}_2\text{O}_3$  decreased with an increase in the total stabilizing oxide concentration. At a stabilizing oxide concentration of 2 mol%, the crystals with a total concentration of 10 mol%, i.e., 8Sc2YSZ and 8Sc2YbSZ, had the highest conductivity.

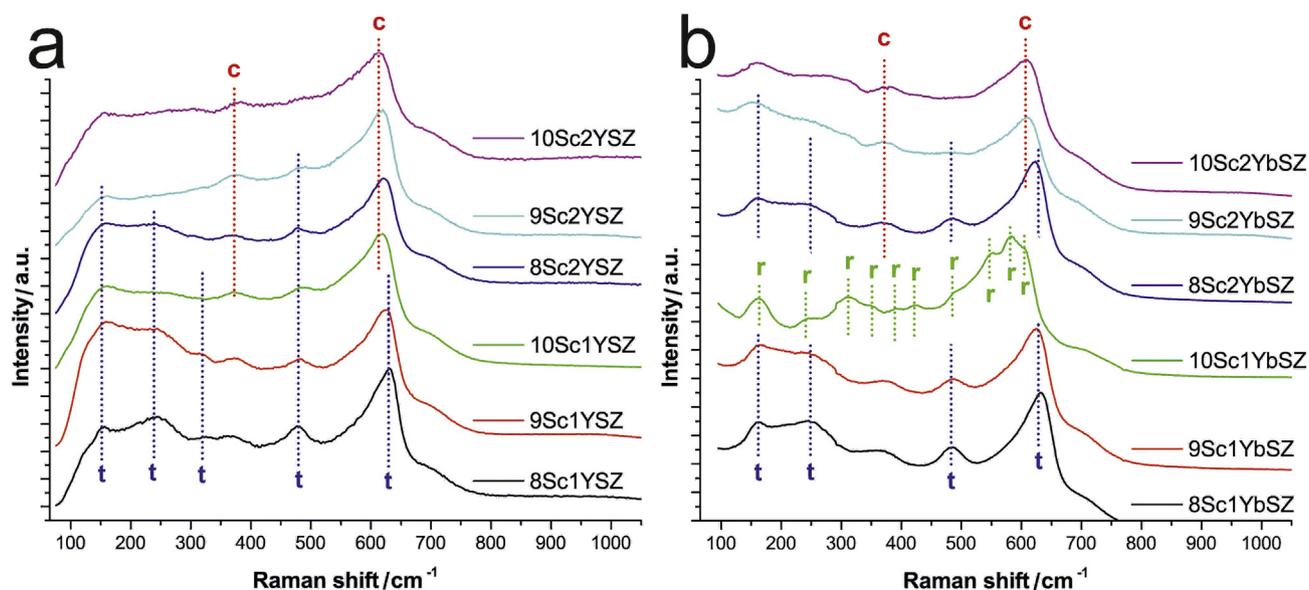


Fig. 3. Raman spectra of the (a)  $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x(\text{Y}_2\text{O}_3)_y$  and (b)  $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x(\text{Yb}_2\text{O}_3)_y$  crystals.

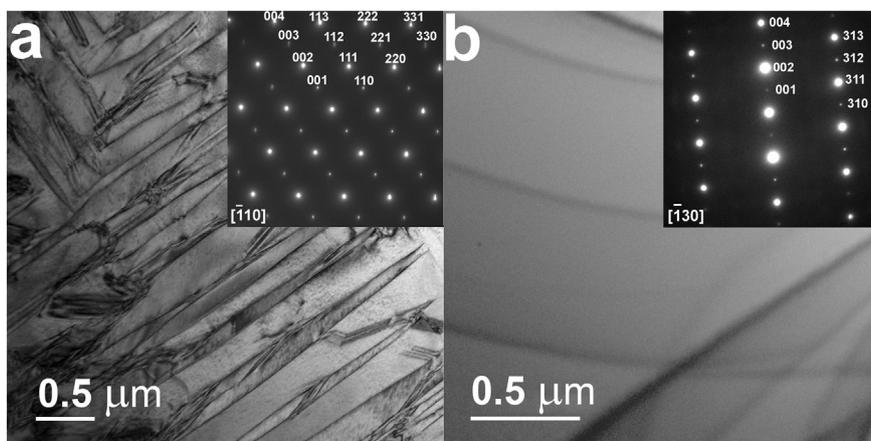


Fig. 4. TEM images of the (a) 8Sc1YbSZ and (b) 9Sc1YbSZ crystals. Insets show selected area electron diffraction patterns.

4. Conclusions

We compared the phase composition and transport properties of the  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Yb_2O_3)_y$  and  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  solid solution crystals ( $x = 0.08-0.10, y = 0.01, 0.02$ ) grown by directional melt

crystallization in a cold crucible.

We show that the stabilization of the pseudocubic  $t''$  phase as a result of co-doping with scandia-stabilized zirconia with 1 mol%  $Y_2O_3$  occurs at a total stabilizing oxide concentration of 11 mol%, whereas the cubic fluorite structure stabilizes at 12 mol%. The stabilization of

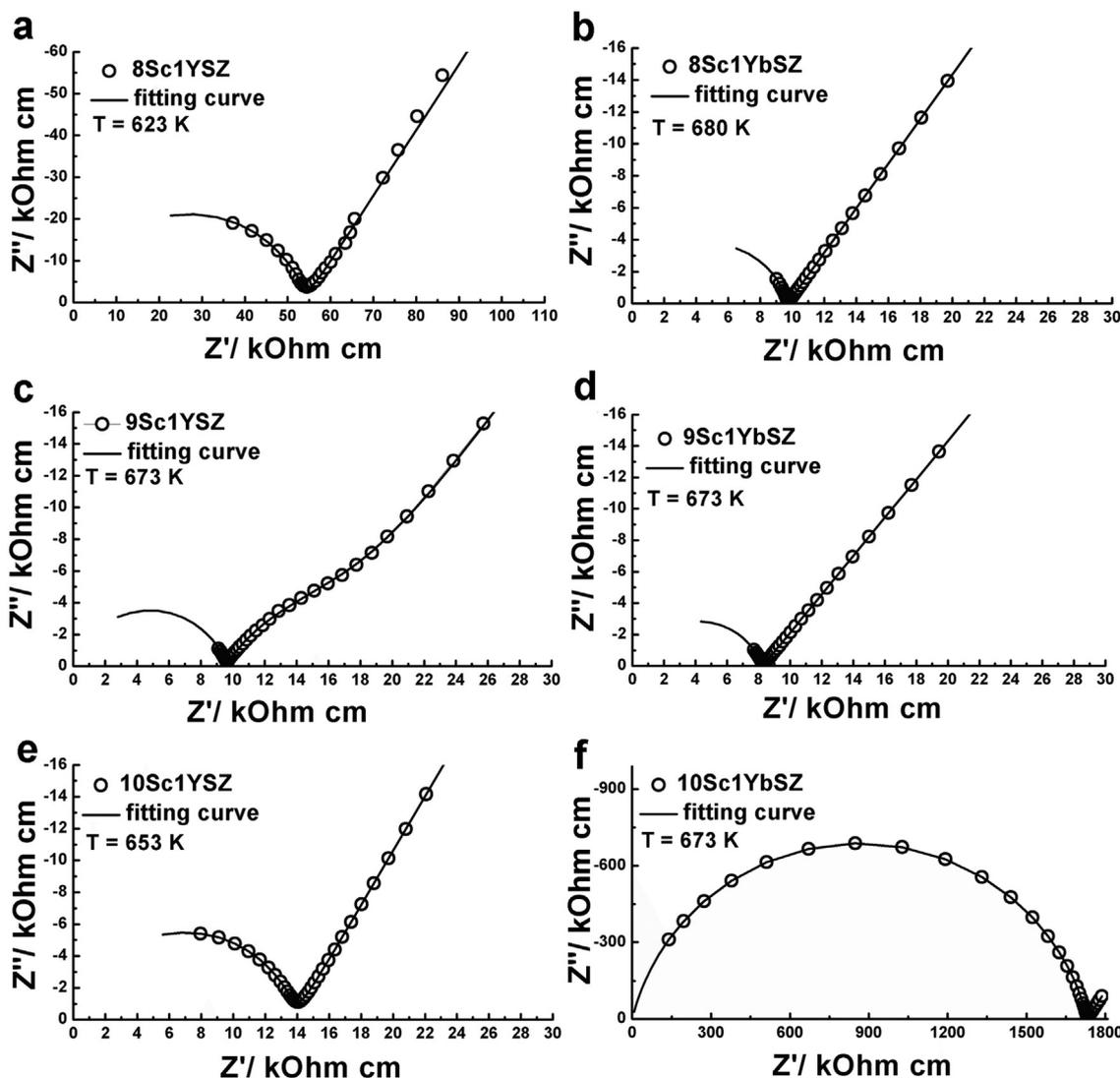


Fig. 5. Impedance spectra of the (a) 8Sc1YSZ, (b) 9Sc1YSZ, (c) 10Sc1YSZ, (d) 8Sc1YbSZ, (e) 9Sc1YbSZ and (f) 10Sc1YbSZ crystals.

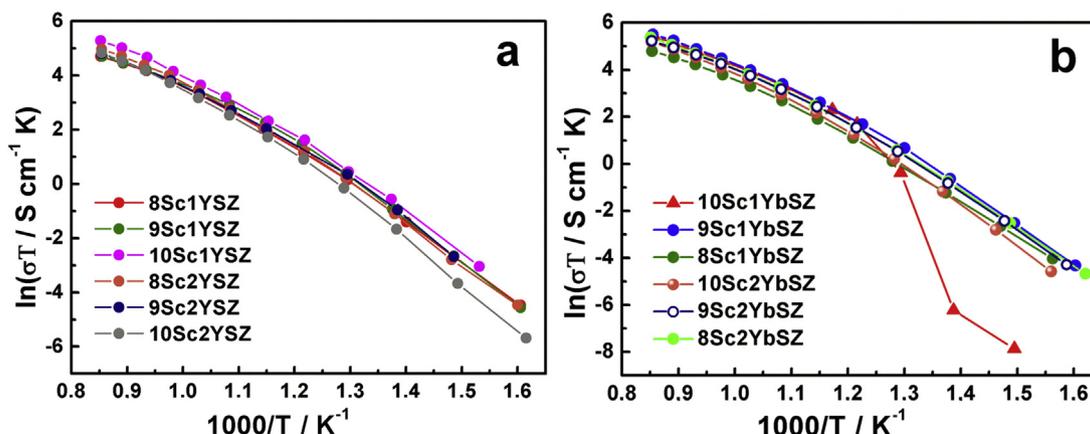


Fig. 6. Specific conductivity of the (a)  $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x(\text{Y}_2\text{O}_3)_y$  and (b)  $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x(\text{Yb}_2\text{O}_3)_y$  crystals as a function of temperature.

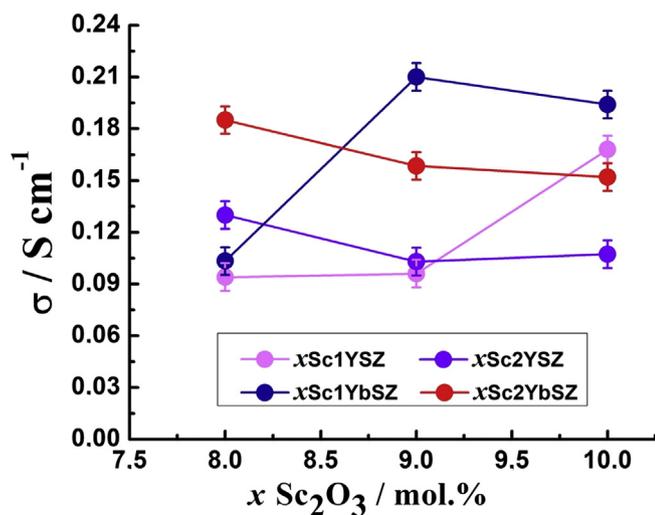


Fig. 7. Ionic conductivity at 900 °C of the  $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x(\text{Y}_2\text{O}_3)_y$  and  $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x(\text{Yb}_2\text{O}_3)_y$  crystals as a function of  $\text{Sc}_2\text{O}_3$  content.

the high-temperature phases as a result of co-doping with 2 mol%  $\text{Yb}_2\text{O}_3$  occurs at lower  $\text{Sc}_2\text{O}_3$  concentrations in the solid solutions than when co-doping with 1 mol%  $\text{Y}_2\text{O}_3$ . The pseudocubic  $t''$  phase in  $(\text{ZrO}_2)_{0.99-x}(\text{Sc}_2\text{O}_3)_x(\text{Yb}_2\text{O}_3)_{0.01}$  stabilizes at a total stabilizing oxide concentration of 10 mol%, whereas the cubic fluorite structure stabilizes at 11 mol%. Co-doping of the  $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x$  ( $x = 0.08\text{--}0.10$ ) crystals with 2 mol%  $\text{Y}_2\text{O}_3$  or  $\text{Yb}_2\text{O}_3$  for all the experimental compositions produce transparent and homogeneous  $t''$  phase or cubic phase single crystals.

We show that for co-doping of the solid solutions with 1 mol%  $\text{Y}_2\text{O}_3$  or  $\text{Yb}_2\text{O}_3$ , the conductivity of the crystals increases with  $\text{Sc}_2\text{O}_3$  concentration. For co-doping with 2 mol%  $\text{Y}_2\text{O}_3$  or  $\text{Yb}_2\text{O}_3$ , the conductivity decreases with  $\text{Sc}_2\text{O}_3$  concentration. The highest conductivities of the crystals co-doped with  $\text{Y}_2\text{O}_3$  or  $\text{Yb}_2\text{O}_3$  are observed at different  $\text{Sc}_2\text{O}_3$  contents (10 and 9 mol%, respectively). At  $\text{Sc}_2\text{O}_3$  contents of 9–10 mol %, the high-temperature conductivity of the crystals co-doped with  $\text{Yb}_2\text{O}_3$  is higher than that of the crystals co-doped with  $\text{Y}_2\text{O}_3$ . The 9Sc1YbSZ crystals have the highest conductivity over the entire experimental temperature range.

#### CRedit authorship contribution statement

**D.A. Agarkov:** Data curation, Investigation, Writing - review & editing. **M.A. Borik:** Methodology, Writing - original draft. **S.I. Bredikhin:** Supervision, Methodology. **I.N. Burmistrov:** Data curation, Investigation. **G.M. Eliseeva:** Data curation, Investigation. **A.V.**

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#### Declaration of competing interest

This statement is to certify that

- o All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.
- o This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.
- o The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.
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