# Structural, Mechanical, and Transport Properties of Scandia and Yttria Partially Stabilized Zirconia Crystals

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Abstract—Crystals of  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  (x = 0.003-0.045, y = 0.005-0.03) solid solutions have been grown by directional solidification in a cold crucible. All of the crystals consist of a mixture of two tetragonal phases of zirconia, *t* and *t*', differing in the degree of tetragonality ( $c/\sqrt{2}a$ ): 1.014–1.015 and 1.004–1.005 for the *t*- and *t*'-phases, respectively. All of the crystals have high microhardness (13.5–15.0 GPa) and high fracture toughness (on the order of 6–7 MPa m<sup>1/2</sup>). Their fracture toughness decreases with an increase in the total content of the stabilizing oxides, which is well consistent with the associated changes in phase composition, namely, with the increase in the percentage of the (transformable) *t*-phase. All of the crystals are similar in electrical conductivity: on the order of 0.04 S/cm at a temperature of 1173 K.

*Keywords:* solid electrolyte, zirconia, crystal growth, ionic conductivity, mechanical properties **DOI:** 10.1134/S0020168519070021

#### INTRODUCTION

Partially stabilized zirconia (PSZ) crystals and ceramics have great potential for engineering and medical applications [1-3]. One of the most important engineering applications of these materials is the use of them as solid electrolytes for solid oxide fuel cells (SOFCs) [4-7]. The key requirements that should be satisfied by SOFC solid electrolytes were described in detail by Basu [8]. In particular, their oxygen ion conductivity at their operating temperature should be at least 0.1 S/cm, and their bending strength should be above 400 MPa. Moreover, it is extremely desirable that they have high microhardness and fracture toughness. Meeting the last requirement would make it possible to reduce the thickness of electrolytic membranes to 70–100  $\mu$ m, thereby substantially improving the energy performance of SOFCs.

Cubic 8–9 mol %  $Y_2O_3$  stabilized zirconia-based solid solutions are widely used as electrolytes in hightemperature SOFCs because they have high oxygen ion conductivity at ~1000°C [9]. However, they are typical brittle materials and have a very low fracture toughness in spite of their high microhardness. An alternative material that can be used as solid electrolytes is ~3 mol %  $Y_2O_3$  partially stabilized ZrO<sub>2</sub> crystals, which offer excellent mechanical properties and have an acceptable high-temperature electrical conductivity [10, 11]. In addition, cubic solid solutions in the  $ZrO_2$ - $Sc_2O_3$  system are known to have the highest ionic conductivity among the zirconia-based materials [6, 12].

Traditionally, zirconia-based solid solutions are prepared by various ceramic processing techniques. An alternative approach to the synthesis of such materials is to prepare them by directional solidification in a cold crucible. This method allows one to prepare crystals with the maximum possible density. Unlike in the case of ceramics, the preparation of materials in the form of crystals allows their electrical transport properties to not be influenced by a number of factors, such as the grain size, the distribution of the components of solid solutions over their grains and grain boundaries, intergranular stress, and variations in these characteristics at high temperatures, approaching the operating temperatures of SOFCs. Thus, investigation of crystals allows one to assess the contribution of the bulk conductivity of a solid electrolyte, while excluding the grain-boundary contribution.

The objectives of this work were to grow  $(ZrO_2)_{1-x-y}$ -(Sc<sub>2</sub>O<sub>3</sub>)<sub>x</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>y</sub> (x = 0.003-0.045, y = 0.005-0.03) crystals and study their mechanical and transport properties with the aim of assessing the potential of these materials for use as electrolytic membranes in SOFCs.

Chemical composition	Notation	Total mole percentage of the stabilizing oxides	Description of the crystals
$(ZrO_2)_{0.972}(Sc_2O_3)_{0.003}(Y_2O_3)_{0.025}$	0.3Sc2.5YSZ	2.8	Crack-free white opaque
$(ZrO_2)_{0.972}(Sc_2O_3)_{0.008}(Y_2O_3)_{0.02}$	0.8Sc2YSZ	2.8	crystals
$(ZrO_2)_{0.968}(Sc_2O_3)_{0.012}(Y_2O_3)_{0.02}$	1.2Sc2YSZ	3.2	
$(ZrO_2)_{0.963}(Sc_2O_3)_{0.012}(Y_2O_3)_{0.025}$	1.2Sc2.5YSZ	3.7	
$(ZrO_2)_{0.963}(Sc_2O_3)_{0.017}(Y_2O_3)_{0.02}$	1.7Sc2YSZ	3.7	
$(ZrO_2)_{0.96}(Sc_2O_3)_{0.017}(Y_2O_3)_{0.023}$	1.7Sc2.3YSZ	4.0	
$(ZrO_2)_{0.96}(Sc_2O_3)_{0.02}(Y_2O_3)_{0.02}$	2Sc2YSZ	4.0	
$(ZrO_2)_{0.95}(Sc_2O_3)_{0.02}(Y_2O_3)_{0.03}$	2Sc3YSZ	5.0	Severely cracked
$(ZrO_2)_{0.95}(Sc_2O_3)_{0.03}(Y_2O_3)_{0.02}$	3Sc2YSZ	5.0	semitransparent crystals
$(ZrO_2)_{0.95}(Sc_2O_3)_{0.045}(Y_2O_3)_{0.005}$	4.5Sc0.5YSZ	5.0	

 Table 1. Chemical composition, brief notation, and description of the crystals

#### EXPERIMENTAL

Crystal of  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  (x = 0.003-0.045, y = 0.005-0.03) solid solutions were grown by directional solidification in a cold crucible in a Kristall-407 induction-heated skull melter. The growth process was run in a water-cooled 120-mm-diameter copper crucible. Directional solidification was carried out by translating the crucible relative to an induction coil at a rate of 10 mm/h. The weight of the growth charge was 4–5 kg. The crystal growth process was described in greater detail elsewhere [13].

The phase composition of the crystals was determined by X-ray diffraction on a Bruker D8 diffractometer with  $CuK_{\alpha}$  radiation. The structure of the crystals was examined by transmission electron microscopy (TEM) on a JEOL JEM-2100 operated at an accelerating voltage of 200 kV and by scanning electron microscopy (SEM) on a JEOL JSM-840.

The transport properties of the crystals were studied at frequencies from 1 Hz to 5 MHz and tempera-



**Fig. 1.** Surface microstructure on the faces of the 1.2Sc2.5YSZ crystals.

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tures from 450 to 900°C at 50°C intervals using a Solartron SI 1260 analyzer. In our measurements, we used plates  $7 \times 7 \text{ mm}^2$  in lateral dimensions and 0.5 mm in thickness, cut from the crystals and fitted with symmetric platinum electrodes. To this end, platinum paste was applied to the plates and fired at a temperature of 950°C for 1 h in air. The ac voltage applied to the plates was 24 mV peak. Impedance spectra were analyzed in detail using ZView software.

### **RESULTS AND DISCUSSION**

The compositions and description of the grown  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  crystals are presented in Table 1.

The crystals were similar in shape and dimensions to yttria partially stabilized zirconia crystals. It is worth noting that increasing the total content of the stabilizing oxides ( $Sc_2O_3 + Y_2O_3$ ) from 2.8 to 5.0 mol % increases the amount of cracking in the bulk of the crystals. The high crack density made it difficult to prepare samples for characterization. Because of this, in further investigation we used samples with a total content of the stabilizing oxides no higher than 4.0 mol %.

Figure 1 shows a characteristic microstructure of the growth surface of the crystals, a so-called tweed structure composed of elements that intersect at angles near  $80^{\circ}$ — $90^{\circ}$ . Such surface morphology was observed previously on yttria partially stabilized zirconia crystals. It depends on the crystal structure of the material and reflects not only the crystal growth conditions but also the conditions under which the real structure of the crystal was formed [14].

The phase compositions of the crystals determined by X-ray diffraction show that all of the crystals under study consist of a mixture of two tetragonal phases of zirconia, *t* and *t'*, both having space group  $P4_2/mnc$ . The 0.8Sc2YSZ crystals were found to contain a small



Fig. 2. TEM images of twins in the (a) 1.2Sc2YSZ, (b) 1.2Sc2.5YSZ, (c) 1.7Sc2YSZ, and (d) 1.7Sc2.3YSZ crystals.

amount of the monoclinic (*m*) phase. The degree of tetragonality varied only slightly with the chemical composition of the crystals:  $c/\sqrt{2}a = 1.014-1.015$  for the *t*-phase and  $c/\sqrt{2}a = 1.004-1.005$  for the *t*'-phase. The *t*-phase is transformable, that is, mechanical stress may cause it to undergo a martensitic transformation to the monoclinic phase, whereas the *t*'-phase is "nontransformable," without a mechanical stress-induced tetragonal-to-monoclinic phase transition. Increasing the total content of the stabilizing oxides increases the percentage of the *t*'-phase and reduces that of the *t*-phase. Similar phase analysis results were obtained previously for  $(ZrO_2)_{1-x}(Y_2O_3)_x$  (x = 0.028-0.04) crystals [11, 15].

TEM examination showed that all of the partially stabilized crystals had a twinned structure, without

twin-free regions. Figure 2 shows TEM images of twins in the 1.2Sc2YSZ, 1.2Sc2.5YSZ, 1.7Sc2YSZ, and 1.7Sc2.3YSZ crystals.

It follows from Fig. 2 that increasing the total content of the stabilizing oxides slightly reduces the twin size. The crystals are twinned on the {110} planes, inclined to the fourfold axis (*C* axis). Twinning is possible on the (101) and (011) planes, but not on the (110) plane, which is parallel to the *C* axis and is a mirror plane. Twin regions in a crystal can be slightly misoriented relative to each other. The misorientation angles evaluated using electron diffraction patterns were no greater than  $2^\circ$ , which corresponds to lowangle boundaries in the crystal. A twinned structure is formed during cooling of a parent cubic single crystal as a result of the cubic-to-tetragonal phase transition and is accompanied by thermoelastic stress relaxation

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Sample	Total mole percentage of the stabilizing oxides	Density, g/cm <sup>3</sup>	Microhardness, GPa	Fracture toughness $K_{\rm Ic}$ , MPa m <sup>1/2</sup>
0.3Sc2.5YSZ	2.8	6.090(3)	$13.55\pm0.25$	$7.2 \pm 0.3$
0.8Sc2YSZ	2.8	6.059(3)	$13.84\pm0.25$	$9.5 \pm 0.3$
1.2Sc2YSZ	3.2	6.020(2)	$14.14\pm0.20$	$6.2 \pm 0.3$
1.2Sc2.5YSZ	3.7	6,055(2)	$13.78\pm0.45$	$7.0 \pm 0.3$
1.7Sc2YSZ	3.7	6.040(3)	$13.90\pm0.15$	$6.5 \pm 0.3$
1.7Sc2.3YSZ	4.0	6.034(3)	$14.66\pm0.26$	$7.0 \pm 0.3$
2Sc2YSZ	4.0	6.032(1)	$14.96\pm0.20$	$5.7 \pm 0.3$
2Sc3YSZ	5.0	6.009(3)	$15.10\pm0.25$	$4.8\pm0.3$

**Table 2.** Density, microhardness, and fracture toughness of the  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  crystals

in the crystal. In this process, the crystal retains the orientation relationship of a cubic single crystal [3].

Table 2 presents the measured density, microhardness, and fracture toughness of the  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  crystals with various compositions.

All of the samples under study had high microhardness: in the range from 13.5 to 15.0 GPa. Moreover, we observed a weak tendency for the microhardness to rise with an increase in the total content of the stabilizing oxides. A more pronounced opposite tendency is observed for the fracture toughness of the samples: it decreases with an increase in the total content of the stabilizing oxides. Characteristically, most of the crystals under study have a high fracture toughness (on the order of 6–7 MPa m<sup>1/2</sup>), which is due to the transformation toughening mechanism: mechanical stress causes a martensitic transformation of the (thermodynamically metastable) *t*-phase into the (stable) *m*-phase [13].

The observed variation of fracture toughness with the total content of the stabilizing oxides correlates well with the phase compositions of the crystals. As pointed out above, raising the total content of the stabilizing oxides leads to a reduction in the percentage of the *t*-phase, whereas the contribution of the transformation toughening mechanism to fracture toughness is proportional to the volume fraction of the *t*-phase [16]. Therefore, the observed tendency toward a reduction in fracture toughness with an increase in the total content of the stabilizing oxides is due to the reduction in the percentage of the (transformable) *t*-phase. These results are consistent with previously reported data on the mechanical properties of yttria partially stabilized zirconia crystals. In particular, an increase in Y2O3 content from 2.8 to 4.0 mol % was observed to be accompanied by a reduction in fracture toughness from 12.0 to 8.0 MPa  $m^{1/2}$  [11]. It is worth noting that partial  $Sc_2O_3$  substitution for  $Y_2O_3$  leads to a substantial drop in fracture toughness. Nevertheless, the fracture toughness of the  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$ crystals remains markedly higher than that of fully stabilized (cubic) zirconia  $(1-2 \text{ MPa m}^{1/2})$  [17]. It is also worth noting that the data on the fracture toughness of the 0.8Sc2YSZ crystals in Table 2 are inconsistent with the general relationships described above, which is possibly due to the presence of the monoclinic phase in these samples.

Figure 3 shows typical impedance spectra of the 0.3Sc2.5YSZ crystal at temperatures of 446 and 896°C. The spectrum at a temperature of 356°C has a high-frequency arc, which corresponds to bulk conductivity, and a low-frequency arc, which is due to the polarization resistance of the electrodes, without an intermediate arc attributable to grain-boundary conductivity. Similar spectra were obtained for the ScYSZ crystals with the other compositions. These data give grounds to believe that the phase and twin boundaries in the ScYSZ crystals make no contribution to their total conductivity.

Figure 4 shows Arrhenius plots of electrical conductivity for the  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  crystals. All of the crystals, except 0.8Sc2YSZ, are similar in conductivity: on the order of 0.04 S/cm at a temperature of 1173 K. The conductivity of the 0.8Sc2YSZ crystal at this temperature is markedly lower, which is probably due to the presence of the monoclinic phase. At comparable concentrations of the stabilizing oxides, the conductivity of the  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$ crystals is about a factor of 1.5 higher than that of  $(ZrO_2)_{1-x}(Y_2O_3)_x$  crystals [10]. All of the crystals were found to have similar activation energies for conduction: 0.93–0.95 and 0.85–0.87 eV in the temperature ranges 673–823 and 973–1173 K, respectively.

#### CONCLUSIONS

Crystals of  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  (x = 0.003-0.045, y = 0.005-0.03) solid solutions have been grown by directional solidification in a cold crucible. According to X-ray diffraction characterization results, the crystals consist of a mixture of two tetragonal phases of zirconia, t and t', differing in the degree of tetragonality ( $c/\sqrt{2}a$ ): 1.014-1.015 and 1.004-1.005 for the t- and t'-phases, respectively. All of the crystals



Fig. 3. Impedance spectra of the 0.3Sc2.5YSZ crystal at temperatures of (a) 719 and (b) 1169 K.

have a well-defined twinned structure. Increasing the total content of the stabilizing oxides slightly reduces the twin size. All of the samples studied have high



**Fig. 4.** Arrhenius plots of ionic conductivity for the  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  crystals.

microhardness (13.5–15.0 GPa) and high fracture toughness (on the order of 6–7 MPa m<sup>1/2</sup>). The observed tendency for the fracture toughness to decrease with an increase in the total content of the stabilizing oxides is well consistent with the associated changes in phase composition, namely, with the increase in the percentage of the (transformable) *t*-phase.

All of the crystals are similar in electrical conductivity: on the order of 0.04 S/cm at a temperature of 1173 K.

Thus, the comparatively high high-temperature electrical conductivity of the  $(ZrO_2)_{1-x-y}(Sc_2O_3)_x(Y_2O_3)_y$  crystals, in combination with their excellent mechanical properties, makes these materials potentially attractive for use as planar electrolytic membranes for SOFCs. The optimal compositions for this purpose are those with a total content of scandia and yttria in the range 3.7–4.0 mol %.

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