



Structure and transport properties of melt grown Sc_2O_3 and CeO_2 doped ZrO_2 crystals



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ARTICLE INFO

Classification codes:

A60

A70

B00

B80Keywords:

Single crystals

Solid oxide fuel cell

Solid solutions

Ionic conducting materials

ZrO₂-Sc₂O₃-CeO₂

ABSTRACT

In this work we report a study of $(\text{ZrO}_2)_{1-x-y}(\text{Sc}_2\text{O}_3)_x(\text{CeO}_2)_y$ solid solution crystals ($x = 0.08\text{--}0.10$; $y = 0.005\text{--}0.015$) grown by skull melting technique. The crystal structure of the material was studied using X-ray diffraction, Raman spectroscopy and impedance spectroscopy. The study showed that optically homogeneous and transparent crystals cannot be grown from the melt in the experimental composition range. For overall stabilizing oxide concentrations of above 10 mol% the crystals contained a cubic phase and a rhombohedral one, whereas at concentrations of lower than 10 mol% a cubic and a tetragonal phases coexisted. Ceria introduction into the $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x$ system increases its high-temperature ionic conductivity. The highest ionic conductivity was observed in 0.5 mol% ceria containing crystals.

1. Introduction

Zirconia based materials find general application as solid electrolytes for solid oxide fuel cells [1,2]. An important practical task is the development of new materials having highest ionic conductivity aimed at reducing the working temperature of solid electrolytes thus increasing their service life, simplifying the design and reducing the cost of the materials used for the fabrication of solid oxide fuel cells.

Scandia (ScSZ) stabilized zirconia base ceramics have the highest conductivity at moderate temperatures [3]. However, a major disadvantage of these materials is the degradation of their conductivity during long-term operation due to an unstable phase composition. The materials with the highest conductivity in the ZrO_2 –(10–12) mol% Sc_2O_3 composition range exhibit a transition from the cubic to the rhombohedral phase accompanied by a significant decrease in the conductivity [3,4]. Partial replacement of scandia for other oxides in the ZrO_2 – Sc_2O_3 system aimed at increasing the stability of the high-conductivity cubic phase proves to be one of the most efficient solutions to these problems [5]. Many researchers modify the electrolyte structure by introducing, along with scandia rare-earth or other metal oxides [6–13]. Of these materials, scandia and ceria co-stabilized zirconia based ones currently attract increasing attention [9–13]. From this

viewpoint, one of the most attractive systems which have a high ionic conductivity at 700–900 °C is the Sc_2O_3 – CeO_2 – ZrO_2 one. For example, the 10 Sc_2O_3 –90 ZrO_2 ceramics co-doped with 1 mol% CeO_2 have an ionic conductivity of 16.7 mS/cm at 600 °C [7]. A number of studies have been devoted to the investigation of the physicochemical and transport properties of materials of this system [8–13]. Noteworthy, the ionic conductivity of ceramics having the same chemical composition depends largely on their phase composition, microstructure, density and other parameters which in turn depend on the material synthesis technology [14–17]. For example, the total ionic conductivity of the ceramics depends largely on the grain boundary conductivity.

The aim of this work is to synthesize Sc_2O_3 – CeO_2 – ZrO_2 crystals and to study their structure and physicochemical properties, including the transport ones. As shown earlier, the total conductivity of these crystalline materials only depends on their bulk conductivity even if a twin structure is present [17]. Thus, the study of the transport properties of the crystals will provide information on the contribution of the bulk conductivity component of the solid electrolyte excluding the contribution of the grain boundary conductivity, in order to simplify the analysis of ionic conductivity mechanisms.

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2. Experimental

$(\text{ZrO}_2)_{1-x-y}(\text{Sc}_2\text{O}_3)_x(\text{CeO}_2)_y$ solid solution crystals ($x = 0.08\text{--}0.10$; $y = 0.005\text{--}0.015$) were grown by the directional melt crystallization in a cold crucible technique [14]. $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x$ crystals ($x = 0.08\text{--}0.10$) were synthesized for reference.

The scandia and ceria distributions along the crystals were studied under a JEOL 5910 LV scanning electron microscope with an INCA Energy dispersive attachment. The reference specimens used for the crystal composition analysis were molten zirconia, scandia and ceria. The phase analysis was conducted using X-ray diffraction on a Bruker D8 diffractometer in $\text{CuK}\alpha$ radiation and Raman spectroscopy. The excitation source was a 532 nm laser. The structure of the crystals was studied under a JEM 2100 microscope at a 200 keV acceleration voltage.

The density was measured by hydrostatic weighing on a Sartorius hydrostatic weighing instrument. The microhardness of the crystals was measured on a DM 8 B AUTO microhardness tester with a 50 g load.

The conductivity of the zirconia based crystals was measured in the 400–900 °C temperature range with a Solartron SI 1260 frequency characterizing device in the 1 Hz to 5 MHz range with a 24 mV AC voltage signal. The test wafers were $7 \times 7 \text{ mm}^2$ in size and 0.5 mm thick. The electric contacts were formed by applying platinum paste on the opposite sides of the crystals by burning-in at 950 °C for 1 h in air. The impedance spectra were processed using the ZViewv. 2.8 software. The conductivity of the crystals was calculated based on the data derived from the impedance spectra taking into account the size of the specimens.

3. Results and discussion

Table 1 shows the notations, composition, density and microhardness of the synthesized crystals.

Fig. 1 shows the appearance of the 8Sc1CeSZ, 9Sc1CeSZ and 10Sc1CeSZ crystals. The crystals were semitransparent and opalescent, without cracks, and their shape and sizes were similar to those of the scandia and/or yttria stabilized zirconia crystals [18,19]. The optical inhomogeneities of the crystal microstructure that can be seen in the images are caused by the differences in the phase composition of the crystals which will be discussed below.

The color of the ceria stabilized crystals was inhomogeneous, varying from colorless to dark-orange. The inhomogeneous color can be attributed to the variation of the valence state of the cerium ion during the post-growth cooling of the crystal and to the fluctuation of the ceria concentration during crystallization. The former factor shows itself in a reduction of the color intensity up to the appearance of colorless regions on the crystal surface, this being primarily typical of crystals growing close to the peripheral regions of the crystallizing ingot. This a change in color indicates a decrease in the concentration of Ce^{3+} cations the absorption bands of which are located in the visible range and impart orange color to the growing crystals [20]. The $\text{Ce}^{3+} \rightarrow$

Ce^{4+} transition occurs during ingot cooling due to oxygen diffusion from the periphery to the center of the ingot. Air annealing of the crystals at 400–1200 °C eliminates the color inhomogeneity and produces colorless crystals. Vacuum annealing at 1200–1400 °C leads to the $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ transition and hence produces the homogeneous color of the crystals, ranging from orange to dark-red depending on the ceria content in the crystal [20]. The inhomogeneous crystal color showing itself in the formation of regions or strips with different color intensities is caused by ceria segregation toward the top part of the ingot due to the less than unity effective cerium distribution coefficient [20]. This local increase in the ceria concentration disturbs the normal crystallization process and accelerates the crystallization of the region enriched with the displaced impurity due to the constitutional supercooling at the crystallization front. Energy dispersive X-ray study of the scandia and ceria distributions along the crystals showed that the intense colored strips which are typically located in the top part of the crystals may contain 1.5–2 higher ceria compared with the homogeneously colored crystal regions.

Therefore the specimens used for studying the crystal structure and transport properties were cut from the crystal regions which did not contain strips with elevated cerium concentrations or growth defects typical of constitutional supercooling (cellular structure, inclusions, bubbles etc.) [20]. We could not synthesize optically homogeneous and transparent $(\text{ZrO}_2)_{1-x-y}(\text{Sc}_2\text{O}_3)_x(\text{CeO}_2)_y$ crystals in the experimental composition range, unlike scandia and yttria stabilized crystals grown using the same method [21].

The phase composition of the crystals was studied with X-ray diffraction and Raman spectroscopy. Table 2 summarizes X-ray data on the phase composition and lattice parameters of the crystals and data on the lattice parameters of the crystals annealed in air at 1200 °C for 2 h.

According to the phase analysis data, the 8Sc1CeSZ, 8ScSZ and 9ScSZ crystals are single-phase and tetragonal. Analysis of the lattice parameters of the tetragonal 8Sc1CeSZ and 8ScSZ crystals shows that ceria addition increases the lattice parameter a and reduces the lattice parameter c . The change of the lattice parameter c is greater than that of the lattice parameter a , this leading to a decrease in the tetragonality ($c/\sqrt{2}a$) of the 8Sc1CeSZ crystals. As a result the structure of the 8Sc1CeSZ crystals becomes closer to cubic than that of 8ScSZ. The data shown in Table 2 suggest that a decrease in the concentration of the Ce^{3+} cations after air annealing changes the structural parameters of the 8Sc1CeSZ crystal. Air annealing of the 8Sc1CeSZ crystals increases the tetragonality of their lattice. The as-annealed 8Sc1CeSZ crystal lattice parameters are almost the same as those of the 8ScSZ crystal. This behavior can be attributed to a decrease in the atomic radius of cerium due to Ce^{3+} ion oxidation to Ce^{4+} , their atomic radii being 1.143 and 0.97 Å, respectively [22]. Furthermore, this transition is accompanied by a decrease in the number of vacancies because Zr^{4+} ion substitution for Ce^{4+} in the lattice does not require charge compensation.

Along with the tetragonal phase the 8.5Sc0.5CeSZ crystal contains a

Table 1
Composition, density and microhardness of the synthesized crystals.

Notation	Composition	Density, g/cm ³	HV Microhardness, kgf/mm ²
8ScSZ	$(\text{ZrO}_2)_{0.92}(\text{Sc}_2\text{O}_3)_{0.08}$	5.862 ± 0.004	1610 ± 20
9ScSZ	$(\text{ZrO}_2)_{0.91}(\text{Sc}_2\text{O}_3)_{0.09}$	5.807 ± 0.001	1640 ± 20
8Sc1CeSZ	$(\text{ZrO}_2)_{0.91}(\text{Sc}_2\text{O}_3)_{0.08}(\text{CeO}_2)_{0.01}$	5.850 ± 0.003	1660 ± 20
8.5Sc0.5CeSZ	$(\text{ZrO}_2)_{0.91}(\text{Sc}_2\text{O}_3)_{0.085}(\text{CeO}_2)_{0.005}$	5.776 ± 0.002	1570 ± 50
8.5Sc1.5CeSZ	$(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.085}(\text{CeO}_2)_{0.015}$	5.787 ± 0.001	1560 ± 50
9Sc1CeSZ	$(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.09}(\text{CeO}_2)_{0.01}$	5.791 ± 0.004	1680 ± 20
9.5Sc0.5CeSZ	$(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.095}(\text{CeO}_2)_{0.005}$	5.778 ± 0.004	1585 ± 50
9.5Sc1CeSZ	$(\text{ZrO}_2)_{0.895}(\text{Sc}_2\text{O}_3)_{0.095}(\text{CeO}_2)_{0.01}$	5.763 ± 0.003	1690 ± 60
10Sc0.5CeSZ	$(\text{ZrO}_2)_{0.895}(\text{Sc}_2\text{O}_3)_{0.1}(\text{CeO}_2)_{0.005}$	5.738 ± 0.001	1695 ± 30
10Sc1CeSZ	$(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.10}(\text{CeO}_2)_{0.01}$	5.757 ± 0.004	1720 ± 20
10ScSZ	$(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.10}$	5.763 ± 0.002	1580 ± 20

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