Phase Composition and Mechanical Properties of Sm$_2$O$_3$ Partially Stabilized Zirconia Crystals

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Abstract: The mechanical properties, phase composition and luminescence of (ZrO$_2$)$_{1-x}$(Sm$_2$O$_3$)$_x$ (x = 0.02–0.06) crystals synthesized using directional melt crystallization were studied. The regularities of changes in the phase composition of the crystals depending on samaria concentration were analyzed. Optical spectroscopy showed that Sm ions were incorporated into the ZrO$_2$ crystal lattice in the form of Sm$^{3+}$. The microhardness of the crystals was shown to increase with Sm$_2$O$_3$ concentration and reached 12.45 GPa for (ZrO$_2$)$_{0.94}$(Sm$_2$O$_3$)$_{0.06}$ crystals. The highest fracture toughness of 14.2 MPa·m$^{1/2}$ was observed for the crystals containing 3.7 mol.% Sm$_2$O$_3$. The experimental results were analyzed in order to understand the effect of phase composition on the mechanical properties of the crystals. The effect of ionic radii of stabilizing oxide cations (i.e., Y$^{3+}$, Gd$^{3+}$ and Sm$^{3+}$) on the mechanical properties of the materials on the basis of partially stabilized zirconia was also discussed.

Keywords: partially stabilized zirconia; skull melting; solid solutions; mechanical properties

1. Introduction

Materials based on partially stabilized zirconia (PSZ) exhibit excellent mechanical and friction properties and are resistant to high temperatures and corrosive media. These materials find broad applications as construction materials, thermal barriers and protective coatings, orthopedic and dental implants, solid state electrolytes and solid oxide fuel cells [1–4].

PSZ is recognized as having good mechanical properties, for example, fracture toughness that originates from transformation hardening. The mechanism of transformation hardening is based on a tetragonal to monoclinic phase transition induced by mechanical stress [5,6]. For this reason, the study of phase transformations in ZrO$_2$–R$_2$O$_3$ binary systems (R being a rare-earth element) as well as factors affecting the phase composition of zirconia-based solid solutions has attracted great interest from researchers [7–14]. Most of the works published on the topic so far have dealt with yttria-stabilized zirconia. However, of interest are also materials partially stabilized by Nd, Sm, Gd, Dy and Yb oxides. Studies of the phase diagrams of ZrO$_2$–R$_2$O$_3$ systems (R being Y, Nd, Sm, Gd, Dy, Yb) have shown that the ZrO$_2$-rich side of the diagrams contains not only thermodynamically stable monoclinic (m), tetragonal (t) and cubic (c) phases but also metastable t′ and t′′ tetragonal ones [15–19]. Under specific conditions of material synthesis, these phases can be retained at room temperature. However, the abovementioned phase diagrams have differences because of the different ionic radii of trivalent stabilizing cations. For example, in binary ZrO$_2$–R$_2$O$_3$ systems (R being Y, Gd, Sm, Nd), an increase in the trivalent cation radius shifts the t/t + c phase boundary towards lower stabilizing oxide concentrations, whereas the
t + c/c phase boundary shifts towards higher stabilizing oxide concentrations [16,17]. This causes broadening of the t + c two-phase region where most of the high fracture toughness compositions are located.

We previously studied the structural and mechanical properties of zirconia crystals partially stabilized by yttria or gadolinia [20–22]. Comparison of the structural and mechanical properties of these crystals showed that an increase in the ionic radius of the trivalent cation (R\(_{\text{Gd}^3+}\) = 1.053 Å, R\(_{\text{Y}^3+}\) = 1.019 Å) changes the ratio of the metastable tetragonal phases and leads to an increase in the fracture toughness of the material at comparable stabilizing oxide concentrations. Sm\(^{3+}\) ions (R\(_{\text{Sm}^{3+}}\) = 1.079 Å) are larger than Gd\(^{3+}\) ones, and therefore one can expect that the use of Sm\(_2\)O\(_3\) as a stabilizing oxide will further improve the mechanical properties of the crystals.

The aim of this work is to carry out melt synthesis of zirconia crystals partially stabilized by samaria and to study the phase composition and mechanical properties of this new material.

2. Materials and Methods

A series of (ZrO\(_2\))\(_{1-x}\)(Sm\(_2\)O\(_3\))\(_x\) (x = 0.02–0.06) crystals were grown using directional melt crystallization from a 130-mm-diam. water-cooled copper crucible. The heater was a high-frequency (5.28-MHz) 60-kW generator. Directional melt crystallization was achieved by lowering the crucible relative to the induction heater at a 10-mm/h speed. Detailed description of zirconia-based crystal growth using this method was published earlier [23]. The raw materials were at least 99.99% purity ZrO\(_2\) and Sm\(_2\)O\(_3\) powders. The charge was prepared for melting by mechanical mixing of the raw oxide powders in the required ratio.

The phase composition was studied using X-ray diffraction on a Bruker D8 instrument in CuK\(_\alpha\) radiation and Raman spectroscopy on a Renishaw inVia microscope-spectrometer. The luminescence spectra were recorded at 300 K using an FHR 1000 spectrometer (Horiba) and a Hamamatsu R928 photomultiplier as a light detector. The luminescence spectra are presented in relative units ignoring the instrumental spectral sensitivity. The microhardness and fracture toughness of the crystals were measured by microindentation with a DM 8 B AUTO microhardness tester having Vickers indenters and a Wolpert Hardness Tester 930. The microhardness and fracture toughness measurements were carried out at loads of 5 and up to 200 N, respectively. The specimens for the measurements were in the form of polished wafers cut from the middle parts of the crystals oriented in the (100) plane. The indenter diagonals were oriented in the <100> and <110> directions in the specimen plane, the angle between these directions being 45 arc deg. The fracture toughness (K\(_{1c}\)) was calculated using the Niihara equation for the Palmqvist crack system [24].

\[
K_{1c} = 0.035(L/a)^{-1/2}(CE/H)^{2/5}Ha^{1/2}C^{-1}
\]

where K\(_{1c}\) is the stress intensity factor (MPa m\(^{1/2}\)); L is the radial crack length (m); a is the indentation halfwidth (m); C is the constraint factor (=3); E is the Young modulus (Pa); and H is the microhardness (Pa). K\(_{1c}\) was calculated for the radial cracks around the indentation, the length of which met the criterion 0.25 ≤ l/a ≤ 2.5 for Palmqvist cracks.

3. Results and Discussion

Figure 1 shows photographic images of crystals with different compositions. The crystals had a yellow color with the color intensity increasing with the Sm\(_2\)O\(_3\) concentration. Furthermore, the crystals exhibited differences in their surface morphology. For example, the crystals containing 2.0 mol.% Sm\(_2\)O\(_3\) (Figure 1a) had a matted rough surface, whereas the surfaces of the crystals containing 2.9 mol.% Sm\(_2\)O\(_3\) (Figure 1c) were smooth and semitransparent. The surface morphology of the crystals containing 2.0 mol.% Sm\(_2\)O\(_3\) (Figure 1b) varied along the crystal, from the matted bottom part of the crystal to the semitransparent top.
whereas the surfaces of the crystals containing 2.9 mol.% Sm$_2$O$_3$ (Figure 1c) were smooth and semitransparent. The surface morphology of the crystals containing 2.0 mol.% Sm$_2$O$_3$ (Figure 1b) varied along the crystal, from the matted bottom part of the crystal to the semitransparent top.

Figure 1. Photographic images of (ZrO$_2$)$_{1-x}$(Sm$_2$O$_3$)$_x$ crystals: (a) (ZrO$_2$)$_{0.98}$(Sm$_2$O$_3$)$_{0.02}$, (b) (ZrO$_2$)$_{0.097}$(Sm$_2$O$_3$)$_{0.03}$ and (c) (ZrO$_2$)$_{0.96}$(Sm$_2$O$_3$)$_{0.04}$.

An earlier study of ZrO$_2$ crystals partially stabilized with Y$_2$O$_3$ showed that the observed evolution of the appearance and surface morphology of the crystals stems from the difference in the concentration of the stabilizing oxide, which determines the crystalline structure [25]. One can assume that the same is true for the (ZrO$_2$)$_{1-x}$(Sm$_2$O$_3$)$_x$ crystals. To check this assumption, we carried out a local Raman study of the phase composition at different points of the crystals containing 2, 3 and 4 mol.% Sm$_2$O$_3$ (Figure 2).

The spectra of the (ZrO$_2$)$_{0.98}$(Sm$_2$O$_3$)$_{0.02}$ crystals exhibit monoclinic phase bands and weak tetragonal phase bands along the whole crystal (Figure 2a). The spectra of the (ZrO$_2$)$_{0.96}$(Sm$_2$O$_3$)$_{0.04}$ crystals (Figure 2c) exhibit tetragonal phase bands only. For a Sm$_2$O$_3$ concentration of 3 mol.% (Figure 2b), the monoclinic phase dominates in the bottom part of the crystal, whereas the spectra for the rest of the crystal have patterns similar to those typical of the tetragonal phase [26].

These experimental results suggest a possible composition variation in the length of the crystals, potentially causing errors in the results of further studies. To rule out any composition indeterminacy, we conducted further studies for specimens cut from the middle parts of the test crystals.

Sm cations are known to exist in crystals and glasses in the form of Sm$^{3+}$ and Sm$^{2+}$ [27–29]. To determine the charge state of Sm cations in partially stabilized ZrO$_2$, we studied luminescence spectra of the (ZrO$_2$)$_{0.96}$(Sm$_2$O$_3$)$_{0.04}$ crystals using optical spectroscopy. Figure 3 shows the luminescence spectra of these crystals.
Figure 2. Raman spectra of \((\text{ZrO}_2)_{1-x}(\text{Sm}_2\text{O}_3)_x\) crystals: (a) \((\text{ZrO}_2)_{0.98}(\text{Sm}_2\text{O}_3)_{0.02}\), (b) \((\text{ZrO}_2)_{0.97}(\text{Sm}_2\text{O}_3)_{0.03}\) and (c) \((\text{ZrO}_2)_{0.96}(\text{Sm}_2\text{O}_3)_{0.04}\); (1) crystal bottom, (2) crystal middle part and (3) crystal top.
The luminescence spectra exhibited bands in the green, yellow and red regions, corresponding to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions of Sm$^{3+}$ ions, respectively. However, the spectra did not contain 675–775 nm bands that are typical of Sm$^{3+}$ ions. Annealing of the crystals at 1200 °C in air for 2 h did not cause any visible changes to the luminescence spectra. Thus, Sm cations are mainly present in the ZrO$_2$ lattice in the trivalent charge state.

X-ray diffraction data for the crystals containing 2.0 mol.% Sm$_2$O$_3$ suggest that the crystals contained the monoclinic ZrO$_2$ modification (Figure 4a). At $2.8 \leq$ Sm$_2$O$_3 \leq 3.2$ mol.% concentrations the crystals contained a mixture of the monoclinic and tetragonal ZrO$_2$ modifications, the quantity of the monoclinic phase decreasing with an increase in the Sm$_2$O$_3$ concentration. The crystals containing Sm$_2$O$_3 \geq 3.7$ mol.% did not contain the monoclinic phase. In the $3.7 \leq$ Sm$_2$O$_3 \leq 6.0$ mol.% concentration range, the X-ray diffraction spectra of the crystals only exhibited reflections of two tetragonal phases differing in the tetragonality degree. Figure 4b shows the X-ray diffraction pattern of the (ZrO$_2$)$_{0.96}$(Sm$_2$O$_3$)$_{0.04}$ crystal, this pattern being typical of the two other crystals containing only two tetragonal phases.

The crystal lattice parameters and the tetragonality degrees of the crystals containing only two tetragonal ZrO$_2$ modifications are summarized in Table 1. The t phase has a tetragonality degree of 1.017–1.016, the tetragonality degree of the t’ phase being slightly greater than 1. The presence of the metastable tetragonal t phase with a large tetragonality degree in the ZrO$_2$-R$_2$O$_3$ systems is an indispensable condition determining the good mechanical properties of the materials [5,6]. Due to the ability to undergo a tetragonal to monoclinic phase transformation under mechanical loads, this phase is referred to as transformable. It can be seen from Table 1 that an increase in the Sm$_2$O$_3$ concentration leads to a decrease in the content of the transformable t phase and, hence, an increase in the content of the non-transformable phase. It is worth mentioning that an increase in the Sm$_2$O$_3$ concentration is also accompanied by a slight decrease in the tetragonality degree of both phases.
![X-ray diffraction patterns](image)

**Figure 4.** X-ray diffraction patterns of (a) (ZrO$_2$)$_{0.98}$(Sm$_2$O$_3$)$_{0.02}$ and (b) (ZrO$_2$)$_{0.96}$(Sm$_2$O$_3$)$_{0.04}$ crystals.

**Table 1.** Phase composition and lattice parameters in different tetragonal phases of (ZrO$_2$)$_{1-x}$(Sm$_2$O$_3$)$_x$ crystals.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Phase</th>
<th>Wt. %</th>
<th>$a$, Å</th>
<th>$c$, Å</th>
<th>$c/\sqrt{2a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ZrO$<em>2$)$</em>{0.963}$(Sm$_2$O$<em>3$)$</em>{0.037}$</td>
<td>t'</td>
<td>85 ± 5</td>
<td>3.6062(1)</td>
<td>5.1866(2)</td>
<td>1.0170</td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{0.96}$(Sm$_2$O$<em>3$)$</em>{0.04}$</td>
<td>t'</td>
<td>15 ± 5</td>
<td>3.6426(2)</td>
<td>5.1695(5)</td>
<td>1.0035</td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{0.96}$(Sm$_2$O$<em>3$)$</em>{0.04}$</td>
<td>t'</td>
<td>75 ± 5</td>
<td>3.6063(1)</td>
<td>5.1854(2)</td>
<td>1.0167</td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{0.95}$(Sm$_2$O$<em>3$)$</em>{0.05}$</td>
<td>t'</td>
<td>25 ± 5</td>
<td>3.6629(2)</td>
<td>5.1692(5)</td>
<td>1.0134</td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{0.95}$(Sm$_2$O$<em>3$)$</em>{0.05}$</td>
<td>t'</td>
<td>70 ± 5</td>
<td>3.6068(1)</td>
<td>5.1815(2)</td>
<td>1.0158</td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{0.94}$(Sm$_2$O$<em>3$)$</em>{0.06}$</td>
<td>t'</td>
<td>30 ± 5</td>
<td>3.6434(2)</td>
<td>5.1683(5)</td>
<td>1.0031</td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{0.94}$(Sm$_2$O$<em>3$)$</em>{0.06}$</td>
<td>t'</td>
<td>60 ± 5</td>
<td>3.6073(1)</td>
<td>5.1767(2)</td>
<td>1.0147</td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{0.94}$(Sm$_2$O$<em>3$)$</em>{0.06}$</td>
<td>t'</td>
<td>40 ± 5</td>
<td>3.6438(2)</td>
<td>5.1672(5)</td>
<td>1.0028</td>
</tr>
</tbody>
</table>

Table 2 shows the microhardness and fracture toughness of the (ZrO$_2$)$_{1-x}$(Sm$_2$O$_3$)$_x$ crystals. The lowest microhardness and fracture toughness are observed in the crystals containing 2.0 and 2.8 mol.% Sm$_2$O$_3$. With an increase in the Sm$_2$O$_3$ concentration from 3.0 to 6.0 mol.% the microhardness grows in a monotonic manner. The change in the fracture toughness of the crystals in this concentration range has a more complex pattern. The fracture toughness initially increases, reaching a peak at 3.7 mol.% Sm$_2$O$_3$, and then sees a gradual decline. This behavior of the fracture toughness remains the same for different indenter diagonal orientations, but the fracture toughness for the <100> indenter diagonal orientation is higher than that for the <110> orientation.

Figure 5 shows indentations for the <100> and <110> indenter diagonal orientations. It can be seen that the indentation produces a surface pile-up in the <110> direction regardless of indenter diagonal orientation.
indenter diagonal orientations, but the fracture toughness for the <100> indenter diagonal orientation is higher than that for the <110> orientation.

<table>
<thead>
<tr>
<th>Sm₂O₃ Content, mol.%</th>
<th>Microhardness HV, GPa</th>
<th>Fracture Toughness, MPa·m¹/²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;100&gt;</td>
<td>&lt;110&gt;</td>
</tr>
<tr>
<td>2.0</td>
<td>8.65 ± 0.30</td>
<td>5.0 ± 0.5</td>
</tr>
<tr>
<td>2.8</td>
<td>8.75 ± 0.30</td>
<td>8.5 ± 0.5</td>
</tr>
<tr>
<td>3.0</td>
<td>9.50 ± 0.30</td>
<td>10.0 ± 0.5</td>
</tr>
<tr>
<td>3.2</td>
<td>10.75 ± 0.30</td>
<td>11.5 ± 0.5</td>
</tr>
<tr>
<td>3.7</td>
<td>11.30 ± 0.30</td>
<td>14.2 ± 0.5</td>
</tr>
<tr>
<td>4.0</td>
<td>12.15 ± 0.30</td>
<td>13.5 ± 0.5</td>
</tr>
<tr>
<td>5.0</td>
<td>12.30 ± 0.30</td>
<td>11.5 ± 0.5</td>
</tr>
<tr>
<td>6.0</td>
<td>12.45 ± 0.30</td>
<td>8.0 ± 0.5</td>
</tr>
</tbody>
</table>

Study of the specimen containing 4.0 mol.% Sm₂O₃ by local Raman spectroscopy showed the presence of the monoclinic phase inside the indentation (Figure 6). This suggests the occurrence of the tetragonal to monoclinic phase transformation initiated by the mechanical loads during the indentation.

These experimental data are in agreement with X-ray phase analysis data for the specimens of different compositions. The crystals containing 2.0 and 2.8 mol.% Sm₂O₃ consist of the monoclinic ZrO₂ modification with a small quantity of the tetragonal phase. The monoclinic phase does not exhibit good mechanical parameters [30], and therefore these crystals have relatively low fracture toughness. The crystals containing 3.0 and 3.2 mol.% Sm₂O₃ retain a small quantity of the monoclinic phase, which is completely eliminated at 3.7 mol.% Sm₂O₃. The absence of the monoclinic phase in combination with the highest concentration of the transformable t phase seems to determine the highest fracture toughness of the crystals of these compositions. The following decline in the fracture toughness of the crystals with an increase in the Sm₂O₃ concentration within a range of 3.7–6.0 mol.% originates from a decrease in the content of the transformable t phase.
Figure 6. Raman spectra of (ZrO$_2$)$_{0.96}$(Sm$_2$O$_3$)$_{0.04}$ crystal: (a) near the indentation, (b) inside the indentation.

It is of interest to compare these experimental results with earlier data for (ZrO$_2$)$_{3−x}$(Y$_2$O$_3$)$_x$ [20] and (ZrO$_2$)$_{1−x}$(Gd$_2$O$_3$)$_x$ [21] crystals (Figure 7). This comparison seems to be justified since all the crystals were grown by directional melt crystallization under similar process conditions (crystallization and cooling rates and temperature regimes), and the measurement methods used were also the same.

Figure 7. Fracture toughness of (1) (ZrO$_2$)$_{1−x}$(Sm$_2$O$_3$)$_x$, (2) (ZrO$_2$)$_{1−x}$(Y$_2$O$_3$)$_x$, and (3) (ZrO$_2$)$_{1−x}$(Gd$_2$O$_3$)$_x$ crystals as a function of stabilizing oxide concentration.

The concentration dependences of the fracture toughness of the (ZrO$_2$)$_{1−x}$(Y$_2$O$_3$)$_x$ and (ZrO$_2$)$_{1−x}$(Gd$_2$O$_3$)$_x$ crystals have similar patterns. The highest fracture toughness is observed at a Y$_2$O$_3$ or Gd2O3 content of 2.8 mol.%. At a comparable stabilizing oxide concentration, the fracture toughness of the (ZrO$_2$)$_{1−x}$(Gd$_2$O$_3$)$_x$ crystal proves to be higher than that of the (ZrO$_2$)$_{1−x}$(Y$_2$O$_3$)$_x$ one. The concentration dependence of the fracture toughness of the (ZrO$_2$)$_{1−x}$(Sm$_2$O$_3$)$_x$ crystals also exhibits a peak, but it is shifted towards higher stabilizing oxide concentrations. The highest fracture toughness of the (ZrO$_2$)$_{1−x}$(Sm$_2$O$_3$)$_x$
crystals is higher than that of the (ZrO$_2$)$_{1-x}$(Sm$_2$O$_3$)$_x$ crystals, which is in turn higher than that of the (ZrO$_2$)$_{1-x}$(Y$_2$O$_3$)$_x$ ones. This dependence correlates well with the growth of the ionic radius in the sequence R$_{3+}$ $>$ R$_{3+}$ $>$ R$_{3+}$.

4. Conclusions

(ZrO$_2$)$_{1-x}$(Sm$_2$O$_3$)$_x$ crystals (x = 0.02–0.06) were grown using directional melt crystallization in a cold skull. A local Raman spectroscopic study of the crystals showed that, in some cases, the phase composition of the crystals changes along the crystal, probably because of a variable quantity of cations with a larger ionic radius being incorporated into the crystal lattice. Optical spectroscopy showed that Sm ions were incorporated into the ZrO$_2$ crystal lattice mainly in the form of Sm$^{3+}$. The evolution of the phase composition of the crystals depending on the Sm$_2$O$_3$ concentration was studied using X-ray phase analysis. The phase composition proved to change with an increase in the Sm$_2$O$_3$ concentration in the sequence m$\rightarrow$m + t $\rightarrow$m + t + t$'$ $\rightarrow$t + t$. The monoclinic phase was completely eliminated at a concentration of Sm$_2$O$_3$ $\geq$ 3.7 mol.%. The microhardness of the crystals grew monotonically with an increase in the Sm$_2$O$_3$ concentration, reaching 12.45 GPa for the (ZrO$_2$)$_{94}$(Sm$_2$O$_3$)$_{0.06}$ crystals. The highest fracture toughness of 14.2 MPa m$^{1/2}$ was observed in the crystals containing 3.7 mol.% Sm$_2$O$_3$. The high fracture toughness of the crystals of this composition seems to originate from a combination of several factors: the highest concentration of the transformable t phase, and the high transformability and the absence of the monoclinic phase. A comparison of these experimental results with earlier data for (ZrO$_2$)$_{1-x}$(Y$_2$O$_3$)$_x$ and (ZrO$_2$)$_{1-x}$(Gd$_2$O$_3$)$_x$ crystals showed that the maximum fracture toughness increases with the ionic radius of the stabilizing oxide.

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