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On the Conversion of Bulk Polycrystalline Y_2O_3 into the Nanocrystalline State

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A reversible phase transformation (RPT) process is observed that converts fully dense polycrystalline Y_2O_3 directly into the nanocrystalline state. The process involves a *forward* transformation from cubic-to-monoclinic symmetry under a high pressure and a *reverse* transformation from monoclinic-to-cubic symmetry under a lower pressure. An example is given of a reduction in grain size of cubic-Y_2O_3 from 300 to 0.1 μm in a single pressure-induced RPT at 1000°C.

I. Introduction

Yttrium Oxide (Y_2O_3) displays excellent optical transmittance in the mid-IR range,[1] representing a potential replacement for aluminum oxide (Al_2O_3) in key applications. However, there is a need to increase the hardness of Y_2O_3 without comprising optical transmittance, which should be possible by reducing the grain size of the material to nanoscale dimensions.[2]

Attempts to obtain fully dense nanocrystalline (single component) oxide ceramics by hot pressing of nanopowder compacts have been met with limited success, owing to the difficulty of mitigating grain growth during sintering. In general, little grain growth is experienced during the early stages of nanopowder consolidation, due to the presence of a uniform distribution of growth-limiting nanopores. However, when the pores begin to disappear, typically at >90% theoretical density, rapid grain growth sets in, resulting in a micrograined sintered product. To circumvent this problem, we investigate the potential for conversion of coarse-grained polycrystalline Y_2O_3 directly into the nanocrystalline state, utilizing a reversible phase transformation (RPT) process.

The RPT process involves two steps: (i) a *forward* phase transformation from cubic symmetry to monoclinic symmetry under a high pressure followed by a (ii) *reverse* phase transformation from monoclinic symmetry to cubic symmetry under a lower pressure, with both steps performed at the same temperature. An example is given of a reduction in grain size of cubic system-Y_2O_3 from 300 to 0.1 μm in a single pressure-induced RPT at 1000°C. Previous work[3–6] has shown that nanocrystalline oxide ceramics can be produced by high pressure sintering of metastable nanopowders, taking advantage of metastable-to-stable phase transformations during sintering to mitigate grain growth. However, there exists concern that the properties of the final consolidated ceramics may be compromised by impurities introduced during processing and handling of the high surface area nanopowders. The present approach should mitigate this problem, particularly when the starting material is produced by a melt-processing technique, such as plasma or laser melting under a reduced pressure. Conceivably, the grain refinement effect should also occur in a single phase crystalline oxide, provided that the material is susceptible to a pressure-induced phase transformation.

An on-going investigation examines mechanisms and kinetics involved, with a view toward establishing the optimal parameters (i.e., pressure, temperature, and time) to achieve the finest possible nanograin size for Y_2O_3.

II. Experimental Procedure

Disk-shaped samples (4 mm × 4 mm) of coarse-grained (~300 μm) polycrystalline Y_2O_3, prepared by sinter-HIP of powder compacts, are obtained from Raytheon. The samples are subjected to various high pressure–high temperature (HPHT) treatments using a HPHT device.[7] Prestressed 4340-steel rings encasing WC/6%Co anvils enable pressures up to 8 GPa to be achieved, without causing anvil cracking. Resistive heating of a graphite crucible, which contains the sample, allows heating up to the desired temperature. Pressure is calibrated via known data for pressure-induced phase transitions in Ce, Bi, and PbSe. Temperature is calibrated via known values of melting points of Sn, Al, and Cu under high pressure. In a typical experiment, the sample is placed in the graphite crucible, subjected to high pressure, heated to high temperature, held for a specific time, and cooled under pressure. Heating and cooling rates are set at ~65°C/min.

The RPT processing is performed in two steps. First, each sample is subjected to a forward phase transformation under a specified set of HPHT conditions, cooled down under pressure, unloaded at ambient temperature, removed from its graphite crucible, and investigated. Second, the sample is placed again in a graphite crucible and subjected to a reverse phase transformation, using a similar procedure. Each sample is examined before and after RPT processing for dimensional, structural, and properties changes. For example, from the observed changes in sample dimensions at the same weight, an estimate can be made of changes in sample density.

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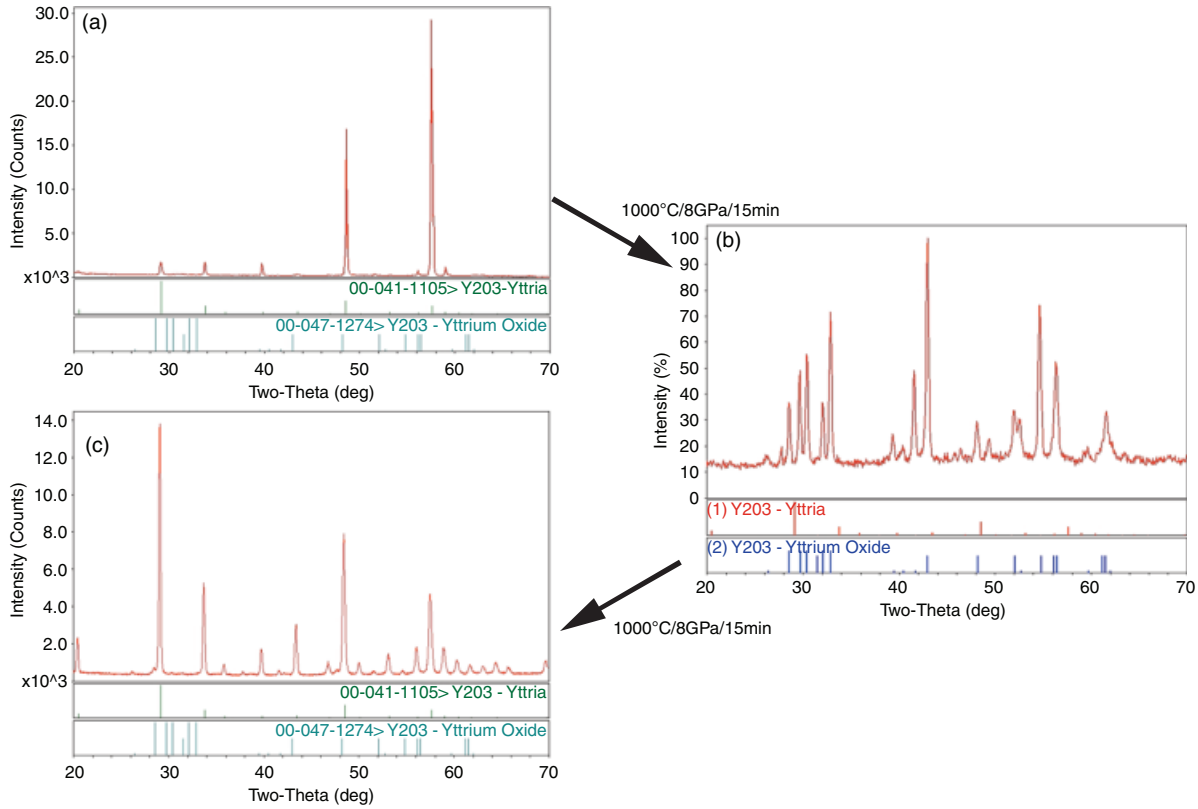

Fig. 1. XRD spectra showing a significant reduction in grain size (300–0.1 μm) for Y_2O_3, when subjected to a pressure-induced reversible phase transformation (cubic system → monoclinic system → cubic system).

Samples are characterized using conventional analytical electron microscopy techniques. Samples for SEM observation are fractured just before insertion into the microscope to minimize surface reaction with the environment. Thin foils for TEM examination are prepared by the wedge technique. EDS spectral analysis is used to determine the concentrations of elements present. Hardness is measured using both Vickers and nanoindentation methods. Density measurements are made using the standard Archimedes technique.

III. Results and Discussion

(1) Grain Size Reduction

When subjected to HPHT treatments in the 5–8 GPa range, the initial coarse-grained polycrystalline Y_2O_3 invariably experiences a cubic-to-monoclinic phase transformation, accompanied by a significant reduction in grain size. An example is presented in Fig. 1, where such a transformation at 1000°C/8 GPa/15 min reduces the grain size from 300 μm to <100 nm. Moreover, when the pressure is relaxed to 1.0 GPa at the same temperature, a transformation back to cubic symmetry occurs, yielding a final grain size of <100 nm. In other words, a single pressure-induced RPT reduces the grain size of the original micrograined Y_2O_3 by a factor of at least 3000. Note that in Fig. 1(a) all the expected peaks for cubic-Y_2O_3 are present, but their relative intensities do not match that of a standard powder pattern because only a few surface grains are in favorable orientations for diffraction. On the other hand, Fig. 1(c) shows all the characteristics of a powder pattern, indicating that the final nanocrystalline c-Y_2O_3 has no preferred orientation. Apparently, this is a consequence of random nucleation of c-Y_2O_3 nanoparticles within the intermediate nanograined m-Y_2O_3 structure (Fig. 1(b)), during the reverse phase transformation.

In agreement with the XRD data, SEM micrographs of fractured samples before and after RPT processing (Figs. 2(a)–(c)), show a large decrease in grain size accompanying the forward transformation, but little further change upon the reverse transformation. The forward transformed material consists of fully-transformed m-Y_2O_3, formed by the pressure-induced forward phase transformation. Confirmation is provided by TEM analysis (Fig. 2(d)), which shows an HRTEM image and an electron diffraction pattern, (Fig. 2(d), inset) that indexes as the monoclinic phase.

A TEM analysis of the reversible transformed material also confirms that the grain size of the transformed cubic phase is <100 nm as can be observed from the HRTEM micrograph (Fig. 2(e)). On closer examination, however, it appears that there is a thin transition layer (arrow) between the well-defined c-Y_2O_3 nanograins where the transformation is incomplete. In addition, the electron diffraction pattern (Fig. 2(e) inset) confirms the presence of randomly oriented c-Y_2O_3 nanograins in the reverse transformed material. The spotty ring pattern, while displaying all major reflections for c-Y_2O_3, also shows a weak (310) ring for m-Y_2O_3. A rough estimate of the retained m-Y_2O_3 phase is 1–3%.

(2) Materials Properties

Measured changes in sample dimensions during RPT processing showed that the forward transformation is accompanied by ~6% decrease in volume, whereas the reverse transformation is accompanied by ~6% increase in volume. Measured densities of transformed monoclinic system- and cubic system-Y_2O_3 samples, Table I, gave values that are comparable to the theoretical densities of 5.03 and 5.41 g/cm^3, respectively. Data also show that the forward transformation from cubic-to-monoclinic symmetry increases hardness by ~35%, whereas the reverse transformation from monoclinic-to-cubic symmetry reduces hardness by ~15%. Hence, the net resultant increase in Vickers microhardness (1 kg load) of c-Y_2O_3 by reducing its grain size from 300 to 0.1 μm is about 20%. This is indicative of a trend of increase in hardness with decrease in grain size for c-Y_2O_3.

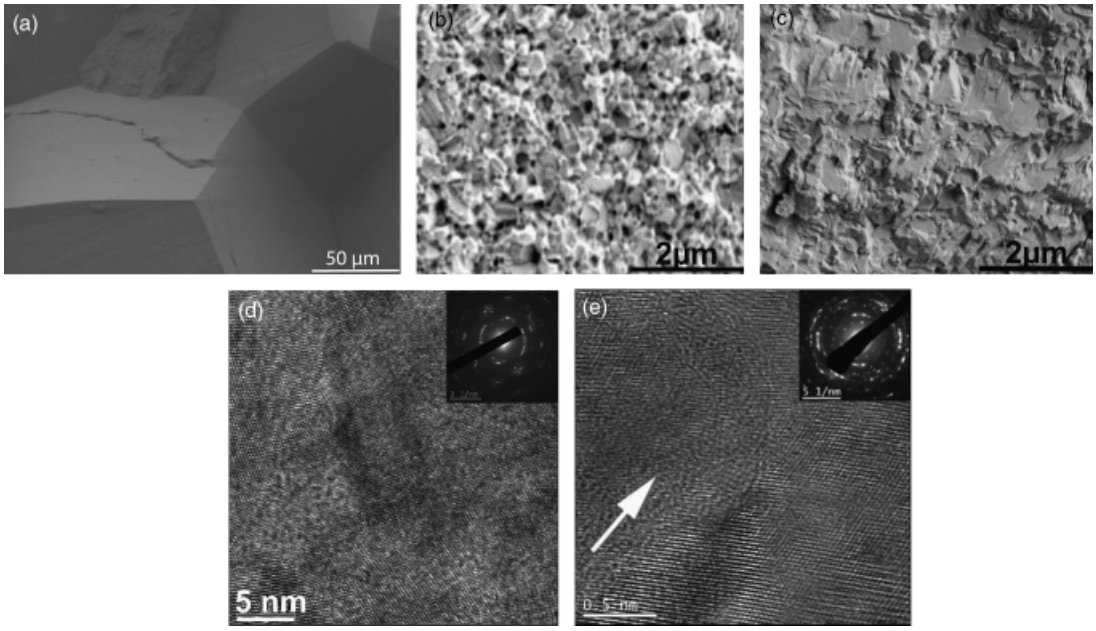

Fig. 2. SEM and TEM micrographs of fractured Y_2O_3 samples, showing significant reduction in grain size due to RPT processing: (a) coarse-grained starting material; (b) nanograined monoclinic phase after forward phase transformation at 1000°C/8 GPa/15 min; and (c) nanograined cubic phase after a reversible phase transformation at 1000°C/1 GPa/15 min; (d) HRTEM micrograph and diffraction pattern (inset) of Y_2O_3 material after forward transformation showing nanograined *m*-Y_2O_3; (e) HRTEM micrograph, and diffraction pattern (inset) of nanograined *c*-Y_2O_3 after reversible transformation.

IV. Summary

A pressure-induced RPT (i.e., a combination of forward and reverse transformations) in bulk polycrystalline Y_2O_3 accompanied by reduction in grain size from micro- to nanoscale dimensions has been demonstrated. Accompanying the forward transformation from cubic-to-monoclinic symmetry, the micro hardness increases by ~35%, whereas the reverse transformation decreases hardness by ~15%.

Based on observations made to date, we conclude that it should be possible to generate even finer nanograined structures by reducing the reverse transformation temperature and increasing time, while maintaining 1.0 GPa pressure. Without the application of pressure during the reverse phase transformation, the sample disintegrates. This is attributed to the large internal strains developed when the material experiences ~6% volume increase. A similar effect is observed in polycrystalline ZrO_2 when cooled from a high temperature, where a transformation from tetragonal-to-monoclinic symmetry, involving a significant volume increase, causes disintegration of the material. As is well known,[8] this effect can be avoided by the use of additives to stabilize or partially stabilize the tetragonal phase, or its high temperature cubic polymorph. There may be similar alloying consequences that apply to RPT processing, which are being investigated in the Y_2O_3–MgO system.

Table I. Density, Hardness, and Grain Size of As-Received, Nanograined *m*-Y_2O_3, and Nanograined *c*-Y_2O_3 after Forward and Reverse Phase Transformations

	Hardness (GPa)	Density (gm/cm^3)	Grain size (nm)
As-received	6.35±0.15	5.03±0.001	300 000±500
Forward transformation	8.6±0.45	5.38±0.03	98±8
Reverse transformation	7.45±0.55	4.985±0.015	91±8

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