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Transformation plasticity in $TbPO_4$ and $(Gd,Dy)PO_4$ orthophosphates during indentation of polycrystalline specimens

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Abstract

Phase transformations and deformation mechanisms were characterized in polycrystalline rare-earth orthophosphates by SEM and TEM after indentation. Xenotime-phase pellets with $TbPO_4$ and $(Gd_X,Dy_{1-X})PO_4$ compositions close to the monazite stability field were softer than $DyPO_4$ compositions far from the monazite stability field, or monazite-phase $GdPO_4$ compositions. Transformation to monazite was observed by TEM beneath indents in $TbPO_4$. Grains with alternating (0 1 0) anhydrite and {0 1 0} xenotime lamellae were adjacent to areas that transformed to monazite. Pressure and/or shear stress in xenotime may cause three phase transformations: xenotime → monazite, xenotime → anhydrite, and anhydrite → monazite. These transformations were not observed in indented $DyPO_4$ xenotime. Large displacement rebounds in some indentation load–displacement curves suggest that at least one of these transformations is ferroelastic. The phase transformations and material softening are consistent with previous observations made for sheared $(Gd_{0.4},Dy_{0.6})PO_4$ xenotime fiber coatings.
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1. Introduction

Transformation plasticity occurs when atomic rearrangements during a phase transformation simultaneously accommodate stress and weaken the material.[1–5] It is common in steel, and has been proposed to weaken geological materials.[3,6] Transformation plasticity is beneficial for refractory ceramics if it enables machinability, or reduces friction during fiber pull-out in ceramic fiber-matrix composites (CMCs). Rare-earth orthophosphate ($REPO_4$) fiber-matrix interphases such as monazite ($LaPO_4$) have been successfully demonstrated in CMCs by several research groups,[7–12] but fiber pull-out stresses that are significantly higher than those for carbon and BN coated fibers are a major concern.[12–16] Mechanisms for reduction of the friction in $REPO_4$ during fiber pull-out are therefore of interest.

The structural relationships between the monazite and xenotime structures are reviewed elsewhere.[17–20] Rare-earth orthophosphates form both monazite and xenotime structures, and at high pressures form scheelite and fergusonite. The anhydrite structure (orthorhombic – Amma) has also been recently reported.[21,22] Light, larger rare-earths from La to Gd form monoclinic (Space Group $P2_1/c$) monazite,[23,24] and heavier, smaller rare-earths from Tb to Lu (including Sc and Y) form tetragonal (Space Group $I4_1/amd$) xenotime.[23–25] Dimorphism has been reported for $GdPO_4$ and $DyPO_4$. $TbPO_4$[26] and $DyPO_4$[26,27] form metastable monazite, and metastable $GdPO_4$ xenotime has been reported.[26,28,29] $GdPO_4$, $TbPO_4$, and $DyPO_4$ transform from xenotime to monazite under pressure. The volume loss of the xenotime → monazite transformation is ~5.8 vol%. Extended solid-solubility is predicted between $GdPO_4$ and $DyPO_4$,[30] so formation of metastable xenotime solid-solutions is quite likely. Solid-solution alternatives to $TbPO_4$ are attractive because of the relatively high cost and low crustal abundance of terbium compared to most other rare-earths, including gadolinium and dysprosum.[31,32] Pressures necessary to induce the xenotime → monazite transformation can be estimated from existing thermodynamic and crystal structure data,[22,26,33–36] and are on the order of 1 GPa for $TbPO_4$, but are lower for $REPO_4$ solid-solutions near monazite–xenotime equilibrium.[22]

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Transformation to monazite in shear bands formed during fiber push-out was confirmed by TEM.[21] $REPO_4$ grains with fine lamellae were prevalent in the deformed zones.[21] The surfaces of these sheared grains were often stepped where there were high lamellae concentrations, suggesting shear by large slip displacements along the lamellae planes. Selected area electron diffraction (SAED) patterns along $\langle 0\,k\,l\rangle_{XENOTIME}$ zones were extensively streaked in the (1 0 0) direction from lamellae along $\{1\,0\,0\}_{XENOTIME}$.[21] The diffraction patterns could not be indexed as either monazite or xenotime, but were consistent with anhydrite (orthorhombic – Amma).[22] Transformation of xenotime to anhydrite after grinding or polishing was also inferred from X-ray diffraction.[21]

Phase transformations in xenotime rare-earth orthophosphates with compositions close to the monazite stability field are explored by indentation of bulk polycrystalline $TbPO_4$, $DyPO_4$, and $(Gd_X,Dy_{1-X})PO_4$. The difficulty of densifying and polishing these compositions makes conventional analysis of indentation data for hardness and modulus problematic. Indentation, with subsequent TEM characterization, is instead used as a tool to gather evidence for phase transformations and material deformation mechanisms. Phase transformations and deformation mechanisms are characterized by TEM after indentation. This work complements other recent work on transformation plasticity in rare-earth orthophosphate fiber coatings during fiber push-out, and detailed TEM characterization of rare-earth orthophosphate transformation mechanisms, which are discussed in other papers.[21,22] Some preliminary results have been reported elsewhere.[37–39]

2. Experiment procedure

2.1. Powder and pellet processing

Reagent grade lanthanum nitrate hydrate, dysprosium nitrate hydrate, gadolinium nitrate hexahydrate, terbium nitrate pentahydrate, phosphoric acid, (Aldrich Chemical Co., Milwaukee, WI) and citric acid (Fisher Scientific Co., Pittsburgh, PA) were used without further purification. The water of hydration of $Dy(NO_3)_3{\cdot}xH_2O$ was determined to be 0.5 and for $Gd(NO_3)_3{\cdot}xH_2O$ was 0.6. Water was purified with the nanopure system (Model D4744, Barnstead/Thermolyne Corp., Dubuque, IA) for all powder synthesis.

Rare-earth orthophosphate ($REPO_4$) powders with $GdPO_4$, $TbPO_4$, $DyPO_4$ and $(Gd,Dy)PO_4$ compositions were made by forced precipitation with phosphoric acid at a pH = ~10, as previously reported.[39] Rare-earth solid solutions of $(Gd,Dy)PO_4$ corresponding to Gd:Dy molar ratios of 40:60, 50:50, and 60:40 were formed by mixing Gd and Dy nitrates and subsequently precipitating their phosphates.[39] The particles were washed sequentially with water, ethanol and isopropanol.

Hydrated $REPO_4$ powders were dried at 120 °C/18 h and ball-milled in isopropanol for 4 h using alumina balls. A 3% polyvinyl butryal resin was added as a binder. The milled slurry was separated and dried at 120 °C for 18 h. The dried powder was uniaxially pressed into pellets and isostatically cold pressed at ~300 MPa. The pellets were then heat-treated in air at a rate of 1 °C/min to 700 °C/1 h to degas organics from the binder, and then sintered at 1600 °C/20 h and 1700 °C/1 h in a $MoSi_2$ furnace with a heating rate of 3 °C/min. After sintering, samples were cooled at 3 °C/min to room temperature and polished with 3 M diamond films (30 μm to 1/2 μm) at low speeds using distilled water to prepare surfaces for nano-indentation. The $REPO_4$ phase was determined by X-ray diffraction. Pellets were characterized by optical microscopy and SEM.

2.2. Indentation

The hardness, modulus, and load–displacement curves of sintered, polycrystalline $TbPO_4$ (xenotime), $DyPO_4$ (xenotime), $GdPO_4$ (monazite), and $(Gd_{0.4}Dy_{0.6})PO_4$, $(Gd_{0.6}Dy_{0.4})PO_4$, and $(Gd_{0.5}Dy_{0.5})PO_4$ (xenotime) pellets were measured using a Nanoindenter II (Nano Instruments Inc., Oak Ridge, TN) with a Vickers indenter. Indentation was done on the most dense, pore-free areas in the samples to a maximum penetration of about 1500 nm using a 50 g load. Indented samples were examined with FEI (Hillsboro, Oregon) scanning electron microscopes (Models Sirion and Quanta) with an X-ray energy dispersive spectroscopy systems operating at 5–20 kV. The ease of inducing the xenotime–monazite phase transformation was assessed from the load–displacement curves during instrumented indentation by a method that is widely applied to silicon.[40–43] Cracking during indentation makes modulus determination from load–displacement curves problematic, but for comparison between $REPO_4$ compositions, moduli were determined by the Oliver–Pharr method.[44] Foils for transmission electron microscopy (TEM, Philips CM200 and FEI Titan) were cut from areas directly beneath the tips of the Vickers indentations in $DyPO_4$ and $TbPO_4$ samples using FEI (Hillsboro, Oregon) Focused Ion Beam (FIB) Dual Beam DB 235 workstation equipped with Omniprobe (Dallas, TX) AutoProbe™ 200 micromanipulator. Deformation mechanisms and phase transformation extent beneath indentations were characterized by TEM.

3. Results and discussion

3.1. Densification

Past research has found xenotime much more difficult to densify than monazite. $LaPO_4$ and $CePO_4$ monazite sintered to 97% density after heat-treatment at 1400 °C/1 h, but YPO_4 xenotime sintered to 62% density.[45] Even at 1500 °C/1 h YPO_4 did not significantly densify, possibly because of elongated particle morphology.[45] Large (~5 μm) particles of (RE = Y, Er, Yb, Lu) $REPO_4$ xenotime did not densify after heat-treatment at 1700 °C/5 h.[27] However, ~200 nm particles sintered to 98% density at 1500 °C/2 h.[27] In this work, the original particle size was ~30 nm, so xenotime was expected to densify at 1700 °C. However, pellets of xenotime with compositions close to the monazite stability field could not be well polished over large areas, which also made it difficult to assess densification of these pellets by optical and SEM characterization.