

Radiation Response and Recovery of $\text{Gd}_2\text{Ti}_2\text{O}_7$ Pyrochlore

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Materials with the general formula $\text{A}_2\text{B}_2\text{O}_7$ that are isostructural with the mineral $(\text{Na,Ca})_2\text{Nb}_2\text{O}_6(\text{OH,F})$ are known as pyrochlores, and this class of materials has attracted interest for nuclear waste form and ionic conduction applications (among others; e.g., [1]). The pyrochlore structure is a 2×2 superlattice of the fluorite structure, with A and B atoms in alternating positions on the cation sublattice and a systematic oxygen vacancy due to the trivalent A atoms; the B atoms are tetravalent. The presence of both 3^+ and 4^+ cations also results in a slight displacement of the oxygen atoms from the diamond sites.

Upon exposure to radiation, pyrochlores respond structurally by amorphization, a transition to the so-called “defect fluorite” structure, or some combination of the two. The cation sites are randomized in the defect fluorite structure, and the oxygen atoms sit on the diamond sites with random vacancies. Some pyrochlores, like $\text{Gd}_2\text{Zr}_2\text{O}_7$, are ready fluorite-formers and resist amorphization; others, like $\text{Gd}_2\text{Ti}_2\text{O}_7$, are easily amorphized with little trace of fluorite [2]. Understanding defect kinetics in these materials, particularly on the cation sublattice, is critical. The more cation disorder a given pyrochlore chemistry will tolerate, the more resistant the structure is to amorphization [3]. The ionic conductivity of pyrochlores has also been related to the degree of disorder on the cation sublattice, although there is not always agreement in the literature on whether conductivity increases or decreases with increasing disorder [4, 5]. Computer simulations have suggested that there may be a threshold for disorder on the cation sublattice above which the ionic conductivity will increase, related to the connectivity of disordered domains [6].

Here we report preliminary results from in-situ and ex-situ TEM experiments designed to probe the defect kinetics of the $\text{Gd}_2\text{Ti}_2\text{O}_7$ (GTO) system. The (re)crystallization process was targeted as a means of illuminating the reverse (i.e., amorphization) process indirectly. Amorphous GTO films deposited by pulsed laser deposition on polycrystalline yttria-stabilized zirconia substrates were prepared for TEM using an FEI Helios dual-beam focused ion-beam (FIB)/scanning electron microscope (SEM), loaded in a Gatan model 628 double-tilt heating holder, and heated to 900 °C in an FEI Titan 80-300 TEM operated at 300 kV in conventional imaging mode. The results of this process are briefly summarized in Figure 1.

Additionally, FIB lamellae were selected from a single-crystal sample of GTO produced by the floating zone technique. The crystal was oriented using a Laue diffractometer and sectioned with a $\{110\}$ surface normal, mechanically ground and polished, and irradiated with He ions at 200 kV at a fluence of $1 \times 10^{17} \text{ cm}^{-2}$. The He ion irradiation produced an amorphous damage layer just below the surface of the crystal; the FIB lift-outs from the single-crystal were then heated in a similar manner to the thin film specimens and the recrystallization was observed. Particular attention was paid to the cation distribution at the interfaces during this process.

References:

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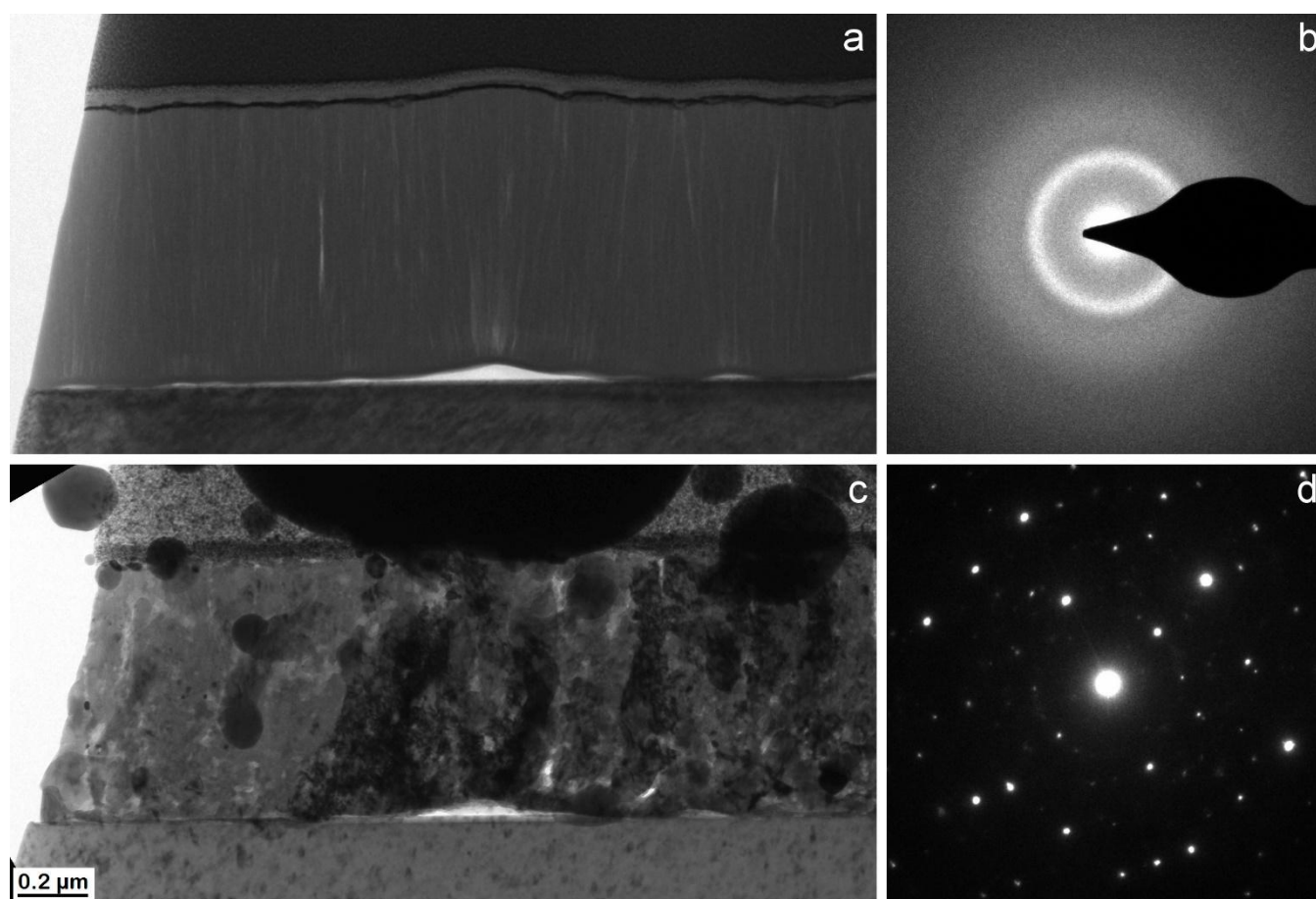


Figure 1. a) Bright-field TEM image of the as-deposited GTO film with b) a corresponding diffraction pattern demonstrating the initial amorphous structure; c) shows the film after heating with d) the corresponding diffraction pattern indicating the crystallization of the film. The scale of (a) is identical to (c).