ABSTRACT

Structural analysis by time-of-flight neutron diffraction is presented for both ErD$_2$ powders and film samples. Rietveld refinement results demonstrated sensitivity to deuterium site occupancy and distribution within the fluorite-type lattice. Powder refinements showed that the presence of 10% D at the octahedral site caused detectable contraction in the unit cell volume. XRD analysis revealed strong bi-axial texture in the ErD$_2$ thin films. With a sufficient number of films present, neutron diffraction analysis and refinement of the ErD$_2$ structure could be achieved.

INTRODUCTION

Neutron Generators (NG) have a wide variety of applications. Homeland security applications include use at airports and military bases for the purpose of screening checked/carry-on baggage and/or suspicious packages.[1] Applications in the field of energy include minerals exploration and oil-well logging.[2] NG also have applications in the medical field for Boron-Neutron-Capture Therapy (BNCT)[3] and In-Vivo measurement of body composition.[4] However, the great functionality of NG is off-set by the problematic degradation of the target component. This component which contains tritium (a $\beta$-emitter) degrades due to helium bubble formation as $^3$T decays to $^3$He. Bubble formation and growth ultimately results in component failure. Our research objective is to obtain a scientific and technical basis for understanding tritium decay in Er-tritide target components. In this way we hope to improve the lifetime and functionality of NG. We are focusing on several aspects of the target, one of which is structural analysis of the ErT$_2$ (fluorite-type) phase. Structural analysis of the fluorite-type structure shall be the focus of this manuscript, with the caveat that we have performed measurements on the non-radioactive ErD$_2$ prototype system. ErD$_2$ is an ideal prototype for ErT$_2$ because they both have fluorite structures of essentially the same unit-cell size. Additionally, the neutron-scattering-lengths for D (6.67 fm) and T (4.79 fm) are similar, making both atoms easily detectable via neutron diffraction. Therefore, these initial experiments on ErD$_2$ yield important information concerning the site locations and occupancies of the atoms, and simultaneously serve to establish measurement protocols for future ErT$_2$ samples. We report Rietveld structural refinement results for both ErD$_2$ powders and films.
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EXPERIMENTAL

Sample Preparation

Er chunks (99.8% Er) and 1 µm Er thin films (supported on thin Mo foils of 25 µm thickness, 1 cm dia.) were placed in a Sievert’s type apparatus and heated to 450°C for 1 hour to partially reduce the oxide layer/activate the Er metal. Samples were then ramped to the desired hydriding temperature: 350°C or 450°C. For hydriding reactions, research grade, 99.99% deuterium (D₂) was passed through a Pd based purifier and a LN₂ trap before exposure to the activated metal chunks/films. For the metal chunks, D₂ gas (room temperature gauge pressure prior to expansion = 500 torr) was pulsed in the system until an equilibrium pressure was achieved at 350°C and 450°C for the respective powder samples. Similar 450°C processing was performed for a batch of 40 Er films. After reaction, D₂ gas was evacuated at temperature and samples were cooled to room temperature. Final powders and films are nominally ErD₂±x; ongoing tests are being performed to determine exact stoichiometry.

XRD Data Collection

X-ray powder diffraction patterns were collected on a Scintag Pad X θ−θ diffractometer equipped with a sealed-tube copper X-ray source, and a Peltier-cooled solid-state detector. The instrument was configured with an Eulerian cradle for the purposes of measuring the texture of the ErD₂ films. Typical θ−2θ diffraction patterns were collected using a 2θ-80° 2θ range, 0.04° step-size and 1 sec count-time. Pole figures (measured out to 80° chi) were collected in reflection mode using 5° steps in chi-tilt and phi-rotation with a count-time of 0.5 sec/step.

Neutron Data Collection

Specimen powders were loaded into vanadium canisters with approximately 20 wt. % silicon powder (NIST standard 640c) added as an internal standard. Time-of-flight (TOF) neutron diffraction data were collected at room temperature on the HIPD spectrometer at the Los Alamos Neutron Science Center (LANSCE). Data collection required 8 hrs for each specimen and resulted in four neutron diffraction histograms from the different detector banks (±153°, ±90°). To prepare the thin film specimens for neutron diffraction, 40 ErD₂ films were stacked into a vanadium canister. Vanadium spacers were placed on top of the films to hold them in place within the canister. The total volume of ErD₂ in the beam was 4 x 10⁻³ cc and was roughly 3 weight % of the volume compared to the Mo substrate foil. TOF neutron diffraction data for the films were collected on the HIPPO spectrometer.[5] Four rotations of the sample were collected (phi = 0°, 45°, 67.5°, 90°) and histograms were collected at 90° and 40° detector banks. The total count time for the film measurement was 24 hrs (4 x 6 hours/phi angle).

RESULTS AND DISCUSSION

Neutron Rietveld structure refinements on the ErD₂ powders were performed using GSAS.[6] The histograms were fit as a two-phase refinement of ErD₂ and silicon, using the silicon as a calibration standard and the instrument calibration parameters variable. The ErD₂ fluorite structures were refined by placing the Er at the (0,0,0) site at full occupancy (fixed) and the D on the tetrahedral (¼ ¼ ¼) site (D₄). Subsequent refinements included the possible occupation of D
at the octahedral ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) site ($D_o$). To improve stability of the refinements, the $B_{iso}$ values for $D_t$ and $D_o$ were constrained to be equivalent. Four observed histograms were used simultaneously for structural refinements. The refined data sets for the fluorite $Fm\overline{3}m$ structures fit well to the observed data with very little residual intensity observed in the difference patterns. Refined structural parameters for the powders are shown in Table 1.

Table 1. Structural parameters for ErD$_2$ powders with statistical uncertainties in parentheses. Temperatures indicate D-loading conditions, neutron measurements were made at RT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>350°C</th>
<th>450°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.1166(1)</td>
<td>5.1187(2)</td>
</tr>
<tr>
<td>cell volume (Å$^3$)</td>
<td>133.95(1)</td>
<td>134.11(1)</td>
</tr>
<tr>
<td>Er occ.</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$D_t$ occ.</td>
<td>1.01(1)</td>
<td>1.00(1)</td>
</tr>
<tr>
<td>$D_o$ occ.</td>
<td>0.10(1)</td>
<td>0.02(1)</td>
</tr>
<tr>
<td>Er $B_{iso}$ (Å$^2$)</td>
<td>0.28(2)</td>
<td>0.15(2)</td>
</tr>
<tr>
<td>$D_t$ $B_{iso}$ (Å$^2$)</td>
<td>1.25(3)</td>
<td>1.01(2)</td>
</tr>
<tr>
<td>$D_o$ $B_{iso}$ (Å$^2$)</td>
<td>1.25(3)</td>
<td>1.01(2)</td>
</tr>
<tr>
<td>$R_p$ combined</td>
<td>0.0179</td>
<td>0.0349</td>
</tr>
</tbody>
</table>

As one can see from Table 1, the ErD$_2$ lattice parameter and unit-cell volume shrink as D begins occupation of the octahedral site, as expected.[7-8] From the refined data, it appears that there is significant octahedral site occupancy for the 350°C sample, whereas the 450°C sample displays only slight $D_o$ occupancy (if at all). The initial results on the powder specimens were very encouraging in that we could detect the D site distribution in ErD$_2$ using neutron diffraction analysis.

However, since analysis of thin film ErT$_2$ specimens by neutron diffraction is our long-term goal, it is of great importance that we be able to characterize thin film samples. There are several problems with this type of analysis. Although film characterization with respect to Er location is quite easy by XRD due to Er being a good X-ray scatterer and the penetration depth being small, quantification of D site occupancies is next to impossible due to the very low X-ray scattering of D (and T). The above results for powder samples demonstrate that, in principle, neutron scattering can be used for D site occupancy distribution of ErD$_2$. However, an individual thin film is not sufficient to obtain adequate neutron diffraction signal from ErD$_2$. A rule of thumb regarding material quantity for neutron diffraction measurements is that one needs $\sim$1x10$^{-3}$ cc (1 mm$^3$) of material to generate sufficient detect-ability for a compound. To meet this threshold, we determined that we would need a minimum of ten Mo substrates with ErD$_2$ films deposited on both sides of each substrate. With a thin enough substrate, this could be easily achieved. The analysis of the thin films became challenging due to the high degree of texture existent in the thin films and the existence of very strong Bragg peaks from the substrate (Mo) which sometimes overlapped those of the ErD$_2$ films.

We took the following approach to cope with these significant challenges regarding neutron diffraction of ErD$_2$ films. We characterized the ErD$_2$ thin film specimens using XRD and texture analysis to determine the type and extent of texture in the films. From the XRD analysis, we found that the severity of the texture would make structure analysis of ErD$_2$ via neutron
diffraction very difficult indeed. Therefore, the neutron diffraction histograms would require randomization of the highly-orientation-dependent intensities for structural refinement. To generate a randomized dataset, the histograms for each set of banks would be ‘binned’ over the entire circle of detectors. In order to maximize ErD₂ signal all 40 double-sided ErD₂ thin-films (deposited on thin Mo foils) we stacked into a V sample canister and we used neutrons to characterize the ensemble. We also simulated neutron diffraction patterns for ErD₂ with different D₁/D₀ site distributions to determine which hkl’s were most sensitive to D site occupancy. Lastly, we used the structural parameters obtained from the powder data as starting parameters for the Rietveld refinement of the thin film histograms, fixing the Biso values for ErD₂ to reasonable values based on the powder analysis. The results of this approach to ErD₂ analysis are discussed below.

Figure 1 shows the XRD patterns obtained for the ErD₂ powder as compared to the ErD₂ film. Pole figures are also shown for various hkl’s of the ErD₂ film sample. The powder pattern for ErD₂ looks consistent with that of the PDF entry[9] in terms of peak location and intensity. However, the XRD pattern for the film shows very strong (111) preferred orientation. This strong (111) plane orientation is confirmed in the (111) pole figure by the strong intensity at the center of the pole figure as well as additional intensity observed at 70° chi (polar angle). Intensity observed at 70° chi in the (111) pole figure demonstrates that the unit cell is likely to be cubic. However, instead of the typical three spots rotated by 120° phi which correspond to the other cubic (111) poles, six spots were observed. This indicates that there is bi-axial in-plane texture of the ErD₂ grains with two possible in-plane grain orientations for ErD₂ related by a 60° rotation in phi. This is confirmed in the ErD₂ (200) and (220) pole figures by the presence of six spots at 54° and 35° chi, respectively. These results illustrate the severity of the film orientation and the need for proper handling of the neutron diffraction data for accurate structural modeling.

![Figure 1. ErD₂ powder and film XRD scans. Pole figures were from ErD₂ film sample.](image)
To model the change in neutron diffraction intensities based on D site occupancy, calculated patterns were generated using the program PowderCell v2.4 [10]. Based on this detailed analysis, it was determined that the following ErD$_2$ hkl’s were the most sensitive to D site occupancy/distribution: (111), (200), (220), and (311). Of particular interest was the ratio of the (111) intensity to (220) intensity. The (220) peak is the 100% peak in the neutron diffraction pattern and is strongly affected by D$_t$ site occupancy. The (111) peak is sensitive to both D$_t$ and D$_o$ occupancy. Therefore, to simplify the structure refinement of the neutron diffraction data, a range of d-spacing was selected (1.4 < d < 3.4 Å) to encompass only these ErD$_2$ hkl’s. Additional peaks in this range included the Mo (110) and (200) peaks, which were used as an internal standard, and weak V (110) and (200) peaks from the Vanadium spacers. To perform the refinement on the thin film data, binned histograms were used from both the 90° and 40° banks. An example histogram is shown in Figure 2. Note that the signal from the ErD$_2$ (220) is the strongest peak for the ErD$_2$ phase and has reasonably good intensity considering the small quantity of material present. The major peaks are from the Mo substrate, but over this range of d-spacings there is not a severe overlap with the ErD$_2$ peaks and the relative intensity ratio between the Mo (110) and (200) is approximately that of a randomized pattern. The refined lattice parameter is similar to that obtained for the ErD$_2$ 450°C powder.

Refined site occupancies for the D$_t$ and D$_o$ sites are also shown in Figure 2. The refined quantity of D at the D$_t$ site is consistent with full occupancy. The fact that it exceeds unity by 4% could indicate that the level of uncertainty for this refinement is likely higher than the error reported in the numerical fit, most likely due to the unaccounted texture. The refinement also displayed the presence of D on the D$_o$ site at ~15% occupancy. This was not expected based on lattice parameter and site occupancy results from the powder samples, and therefore is viewed with suspicion. Perhaps the thin film nature of the ErD$_2$ could stabilizes D on the D$_o$ site. However, as mentioned earlier, the ratio of the (220) and (111) hkl’s is highly dependant on the D$_o$ site occupancy. It is plausible that the low intensity of these peaks limits the level of quantification that can be achieved. It could also be an artifact of incomplete texture correction of the ErD$_2$ histograms during binning. The encouraging aspect of the overall result is that qualitatively we
have demonstrated that site occupancy determination in a film is not beyond the reach of current neutron scattering capabilities. This was particularly apparent for the $D_t$ site. A more sophisticated analysis, including in particular a texture description by the spherical harmonics method, is ongoing. Systematic studies of film specimens with varying $D$ site occupancy could substantially aid in determining the necessary protocols for analysis of tritiated films.

CONCLUSION

We have successfully obtained structural data for $\text{ErD}_2-x$ powders using TOF neutron powder diffraction methods. These results show variability in the deuterium octahedral-site occupancy as a result of changes in processing conditions (i.e. temperature). With the use of parameters obtained from the powder refinements, we measured/refined textured $\text{ErD}_2$ thin films by neutron diffraction, with mixed results. While the observed lattice parameter value for the $\text{ErD}_2$ films was similar to that of the $450^\circ C$ $\text{ErD}_2$ powder specimen, the $D_o$ site occupation showed inconsistent results compared to the powder sample. To address these inconsistencies, further detailed and systematic studies are required to refine protocols for thin-film TOF neutron diffraction analysis.

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REFERENCES