



Synthesis and characterization of dense Gd₂Ti₂O₇ pyrochlore thin films deposited using RF magnetron sputtering



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ABSTRACT

Thin films of phase-pure pyrochlore Gd₂Ti₂O₇ have been synthesized by RF magnetron sputtering. The films were prepared from oxide targets in 50%O₂/Ar atmosphere and deposited on 111 yttria-stabilized zirconia (YSZ) substrates at a temperature of 800 °C. The pyrochlore structure was confirmed via grazing angle X-ray diffraction and selected area electron diffraction (SAED). Transmission electron microscopy (TEM) analysis also showed that the films were dense and of uniform thickness with surface roughness of approximately 8 nm. The total conductivity measured with AC impedance spectroscopy was found to be independent of thickness and comparable in magnitude to that of bulk Gd₂Ti₂O₇. Differences were observed in the Arrhenius behavior between the bulk and thin film samples and are attributed to varying states of order in the crystalline lattice compounded by different levels of background impurities.

1. Introduction

The solid solution Gd₂Zr_xTi_{1-x}O₇ has been studied extensively for its properties of fast ion conduction and radiation tolerance [1–3]. For both applications, a key enabling property is the ability for the cations to disorder. The ordered pyrochlore end member Gd₂Ti₂O₇ (GTO) is generally regarded as an insulating extrinsic ionic conductor, while the more easily disordered Gd₂Zr₂O₇ (GZO) exhibits intrinsic fast ion conduction.

The pyrochlore structure A₂³⁺B₂⁴⁺O₇ can be regarded as a defect-fluorite type structure with ordering on both the cation and anion sublattice yielding a superstructure with twice the lattice constant of the parent fluorite. The A and B site cations order in the <110> directions with each cation occupying alternate rows with the larger A³⁺ cation 8-fold coordinated and the smaller B⁴⁺ cation 6-fold coordinated. The structure consists of three distinct oxygen sites: 48f with two A and two B nearest neighbors, 8a with four A nearest neighbors and a vacant 8b site with four B nearest neighbors [4]. Previous studies have shown that, generally, the pyrochlore structure forms when 1.46 < R_A/R_B < 1.80. Below 1.46 the cation radii are of similar enough size that anti-site order is introduced giving rise to the defect fluorite phase [5]. Disorder on the cation sublattice is accompanied, or

perhaps preceded by [6], disorder on the anion sublattice. Disorder on the anion sublattice serves to increase the number of mobile oxygen vacancies through the formation of Frenkel defects consisting of a vacancy on the 48f site and an oxygen interstitial ion on the 8b site [7].

Numerous works have correlated increasing disorder with increasing ionic conductivity. For example, Moon and Tuller have shown that the isovalent substitution of Zr for Ti in Gd₂Zr_xTi_{1-x}O₇ results in an approximately 4 order of magnitude increase in conductivity at 600 °C between x = 0 and x = 1.0 [8]. Recent modeling results have indicated that cation disorder enhances ionic conductivity by increasing both the concentration of mobile charge carriers and their individual mobility [9]. Conversely, other researchers have shown that disorder serves to increase the amount of mobile oxygen in the lattice, i.e. carrier concentration, but that order actually provides a preferential pathway for transport and thus a reduced activation energy. This is supported by the work of Diaz-Guillen et al. who examined the effect of homovalent lanthanide (Ln) A-site substitution on the pyrochlore phase of Gd_{2-y}Ln_yZr₂O₇ and demonstrated that activation energy decreased and conductivity increased, albeit slightly, with larger cations on the A-site (i.e. increasing order) [10].

Quantifying the extent of disorder in pyrochlore materials can be challenging. XRD patterns consist of two subsets of patterns. The first

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set arises from the defect fluorite structure, which is present in all materials regardless of order. The second subset is attributable to the pyrochlore superstructure. A common method for defining the extent of disorder is to use the ratio of the intensities of pyrochlore to fluorite peaks to calculate the cation order parameter [8,11]. The superstructure peaks, however, are much weaker than those of the fluorite phase even in a fully ordered material, and decrease rapidly with increasing disorder [6]. Thus, the unambiguous determination of order is difficult from XRD data alone. Another factor complicating structural analysis in polycrystalline samples is the possibility of locally ordered phases in a matrix exhibiting long-range disorder [12,13], or vice versa. An early study by van Dijk et al. used selected area electron diffraction (SAED) to identify ordered pyrochlore microdomains in a disordered fluorite structure [13]. A recent study by Blanchard et al. coupled neutron and X-ray powder diffraction with X-ray absorption near edge structure analysis of the Zr L-edge across the lanthanoid series of $\text{Ln}_2\text{Zr}_2\text{O}_7$ [14]. This study showed increasing local disorder with decreasing R_A/R_B across the compositions identified as pyrochlore via neutron and X-ray diffraction, demonstrating the gradual nature of the transition from ordered pyrochlore to defect fluorite phase.

Unlike bulk polycrystalline materials, thin films provide a platform for precise phase control through epitaxial growth on substrates with appropriate lattice match. While the use of thin films to explore and exploit properties of fast ion conductors has gained a great deal of interest in recent literature [15,16], and some thin film pyrochlore compositions have been previously synthesized [17,18], this platform has not yet been utilized to control the structure and study the conductivity of pyrochlore materials. In this work, epitaxial growth on single crystal (111) YSZ substrates is used to obtain the fully ordered pyrochlore structure of $\text{Gd}_2\text{Ti}_2\text{O}_7$ (GTO). We report on the conductivity of thin films of the pyrochlore $\text{Gd}_2\text{Ti}_2\text{O}_7$ (GTO) and how this compares with the bulk material.

2. Experimental methods

2.1. RF magnetron sputtering

Thin films were prepared using RF magnetron sputtering on 111 oriented single-crystal YSZ substrates (8 mol% Y_2O_3 -stabilized ZrO_2 , one-side polished, MTI corporation). The substrates were ultrasonically cleaned in DI water and acetone and dried in air at 150 °C for several hours. The YSZ substrates were affixed to the Ni faceplate of a heater box using silver epoxy (AREMCO). A stoichiometric $\text{Gd}_2\text{Ti}_2\text{O}_7$ target was synthesized from high purity Gd_2O_3 and TiO_2 powders. Powders were mixed in an inert atmosphere glove box, milled for 6 h in a Retsch rotary mill, dried on a Shlenk line, and then calcined as a loose powder for 10 h under 25% O_2 /Ar gas flow at 700 °C. Powder was loaded into a 2.125-in. die and pressed at 15 lbs. This target was then sintered at 1575 °C for 100 h in an oxygen atmosphere furnace on a bed of loose powder in a high purity alumina boat. Shrinkage during the sintering cycle resulted in an approximately 2 in. diameter target. Before use, the target was sanded to remove any adhered powder from the sintering process. Phase purity of the $\text{Gd}_2\text{Ti}_2\text{O}_7$ target was confirmed by XRD. The sintered target was mounted in a 2-in. diameter copper RF magnetron sputter cup using Ag epoxy (Ted Pella). The heater box with the affixed substrate was mounted off-axis 3.5 in. from the target. The substrate was maintained at 800 °C using a photo lamp heater bulb (Wiko). The films were grown in 50% O_2 /balance Ar atmosphere with total pressure maintained at 25 mTorr and at a power setting of 100 W. These sputtering conditions yielded a deposition rate of roughly 17 Å/min. Films with thicknesses of 480 nm and 850 nm were produced by 5 h and 8-h deposition times, respectively.

2.2. Film characterization

Films were characterized by grazing incidence X-ray diffraction

(GIXRD) and transmission electron microscopy (TEM). GIXRD measurements were performed using a Bruker AXS D8 Advance X-ray diffractometer, with a Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$) X-ray source operating in θ - 2θ geometry, and at the fixed angle of incidence (γ) of 1° relative to the specimen surface. The X-ray diffractometer exit source was equipped with a Göebel mirror diffraction optic used to achieve a parallel beam condition that is highly sensitive to near surface features in thin films. The θ - 2θ scans were performed using a step size of 0.02° and a dwell time of 4 s per step. Diffracted intensities from the specimens were collected using a solid-state detector to suppress fluorescence from the rare-earth gadolinium constituent.

The structure of the films was examined in a FEI Titan 300 kV image corrected (scanning) transmission electron microscope (S/TEM). Specimens for S/TEM analysis were prepared via a focused ion beam (FIB) process. The specimen was cut from the film, plucked and attached to a copper FIB grid, and then thinned to electron transparency.

2.3. Electrochemical measurements

Platinum ink (Heraeus 6082) was painted onto the unpolished side of the YSZ and used to adhere the substrate to a Pt foil counter electrode. The ink was cured at 950 °C for 30 min. A shadow mask (Photo Etch) was used to sputter platinum electrodes ranging from 0.1 to 1 mm in diameter onto the GTO film, or directly onto the YSZ substrate. A microprobe station (Cascade Microtech) equipped with a high temperature furnace stage (Linkham) was used to collect the impedance spectra in the through-plane configuration. Gold-coated tungsten probe tips were contacted to the Pt foil counter electrode and a Pt working electrode on the surface of the GTO film. AC impedance measurements were performed using a PARSTAT 2273 potentiostat/FRA in the frequency range of 10⁶–0.1 Hz as a function of temperature (500–900 °C) in ambient gas environment.

2.4. Bulk powder synthesis and characterization

In order to compare the epitaxial thin films to bulk measurements, powders of GTO were synthesized from the oxide precursors Gd_2O_3 (Alfa Aesar, 99.999% purity) and TiO_2 (Alfa Aesar, 99.995% purity), by conventional ceramic solid state processing. The oxide powders were first calcined at 1000 °C for 24 h, then ball-milled in a Spex Certiprep 8800 high energy ball-mill for 12 h in ZrO_2 vials with ZrO_2 balls using a 10:1 ball to powder ratio for optimum milling and blending. The resulting powders were then pressed at a pressure of 440 MPa in a 13 mm diameter stainless steel die. The resulting pellets were then sintered at 1200 °C for 24 h, then re-milled (same routine previously discussed), re-pressed and re-sintered at 1600 °C for 24 h. The measured (geometric) density of the final $\text{Gd}_2\text{Ti}_2\text{O}_7$ pellets was 80% of the theoretical values. Sections of ~1 mm thickness were then polished to a mirror finish using diamond impregnated lapping films and oil as lubricant followed by a final polishing step using SYTON® HT-50 on a flocked twill cloth. X-ray diffraction measurements obtained from the samples showed them to be phase-pure with the pyrochlore structure belonging to space group Fd-3m. Despite best efforts to minimize contamination, the final cation stoichiometry was 0.04:0.96 Zr:Ti as identified by X-ray fluorescence (XRF) (Thermo Scientific Quant'x) using a fundamental parameters model. Al was also identified as a minor impurity via XRF. Platinum ink (Heraeus 6082) electrodes were painted on opposite sides of the pellet and cured at 950 °C according to the manufacturer's firing schedule. The pellets were compressed between two sheets of Pt foil using a standard spring-compression set-up. The assembly was placed inside a quartz tube and electrochemical measurements were made as a function of temperature (600–1000 °C) under ambient conditions in a tube furnace.

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