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Energetics of stepwise disordering transformation in pyrochlores, $RE_2Ti_2O_7$ (RE = Y, Gd and Dy)

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Abstract

The capacity to incorporate actinide cations makes pyrochlore titanates first-choice phases in titanate-based waste form ceramics. Despite broad interest in the pyrochlore order–disorder transformation due to the cumulative effects of ^{238}U, ^{235}U and ^{232}Th radioactive decay and their daughter products, only limited thermodynamic data, mainly based on simulations of ion-beam irradiation experiments, have been reported. In this work, for the first time, heavily disordered pyrochlores, $RE_2Ti_2O_7$ (RE = Y, Gd and Dy), from mechanical milling of their constituent oxides, were thermochemically investigated. Two types of thermal events were identified using high-temperature differential scanning calorimetry and correlated to the structural disorder in the cation and anion sublattices. Moreover, the excess formation energy measured by oxide melt solution calorimetry shows that the smaller the ionic radius of the RE, the easier it is to remove damage domains.

Keywords: Pyrochlore; Formation enthalpy; Diffusionless transformation; Disordering transformation

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1. Introduction

The capacity to incorporate actinide cations [1] makes the pyrochlore and structurally related monoclinic zirconolite the first-choice phases in titanate-based waste form ceramics [1–5]. In order to mimic and clarify the damage due to radioactive decay (disordering and amorphization) due to the cumulative effects of the radioactive decay of ^{238}U, ^{235}U and ^{232}Th and their daughter products [6], theoretical simulations and experimental ion-beam irradiation have been conducted [7,8]. Despite broad interest in the pyrochlore order–disorder transformation, only limited thermodynamic data, mainly based on simulations of ion-beam irradiation experiments, have been reported. While irradiation produces direct physical damage, disorder can also be induced by doping, including the chemical introduction of the decay and fission products. However, the thermodynamic effects of radiation damage, of introducing a new cation species and of the concomitant increase in structural disorder cannot be separated. In 2005 Fuentes et al. [9] reported a method to prepare disordered pyrochlores, $RE_2Ti_2O_7$ (RE = Y, Gd and Dy) by mechanical milling of the constituent oxides; this gave access to both ordered and disordered pyrochlores of the same composition. In the present work, we report the results of a detailed thermochemical investigation of these disordered rare earth (RE) titanate pyrochlores.

2. Experimental methods

2.1. Sample synthesis and characterization

Rare earth titanate pyrochlores prepared by mechanochemical synthesis were provided by one of the authors

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(A.F.F.). Briefly, mixtures of RE_2O_3 (RE = Y, Gd, and Dy) and TiO_2 powders were ball milled using a container and balls made from zirconia for 19 h, and then different fractions were fired at 650, 800 and 1200 °C for 12 h. The structural and microstructural features of the materials were published by Fuentes et al. [9]. In the present work, complementary characterizations, primarily thermochemical measurements, were conducted to support the previously published results. The as-received samples were characterized by powder X-ray diffraction (XRD) and electron microprobe analysis using energy and wavelength dispersive spectroscopy (EDS, WDS). Powder XRD patterns were taken using a Bruker-AXS D8 Advance diffractometer (Bruker-AXS, Inc.) operating at an accelerating voltage of 40 kV and an emission current of 40 mA with Cu Kα radiation ($\lambda = 0.15406$ nm). Data were acquired from 20° to 80° 2θ with a step size of 0.02°. Surface area was measured by the Brunauer–Emmett–Teller (BET) method using a Micromeritics ASAP 2020 (Micromeritics, Norcross, GA) instrument. Thermogravimetric analysis/differential scanning calorimetery (TGA/DSC) were performed on a Netzsch STA 449 system (Netzsch GmbH, Selb, Germany) from 30 to 1200 °C in Ar with a heating rate of 10 °C min $^{-1}$. A buoyancy correction was made by subtracting the baseline collected by performing a blank TGA/DSC run with an empty platinum crucible. The total water content was determined from the TGA weight loss curve. The gases evolved during thermal analysis were analyzed by infrared (IR) spectroscopy using a Bruker Equinox 55 FTIR spectrometer (Bruker Optics Inc., Billerica, MA) coupled to the TGA/DSC by a transfer line heated to 150 °C. The chemical composition of the samples was determined using a Cameca SX-100 electron microprobe (Nampa, ID) at an accelerating voltage 15 kV, and a 10 nA beam current. The Y, Gd and Dy contents of the samples were determined using YPO_4, $DyPO_4$ and $GdPO_4$ standards, respectively.

2.2. Calorimetry

2.2.1. Differential scanning calorimetry

DSC was conducted in Ar using a Netzsch high-temperature DSC 404 (Netzsch GmbH) [10]. Sample temperature calibration was performed by melting Sn, Ag and Au standards in alumina crucibles. Sensitivity calibration was performed using single-crystal Al_2O_3 as a heat capacity standard. The measurements were carried out by continuous heating at 10 °C min^{-1} with 5 min isothermal holds at 25 and 1300 °C in the heating direction. A typical sample mass of 30 mg was used. After the completion of the first run, a second run was performed under identical conditions, without lifting the furnace or disturbing the sample, in order to serve as a material baseline. For some of the samples, a third run was performed to confirm that no detectable thermal events occurred after the second measurement. The uncertainty in excess enthalpy was determined to be 5% from the difference in integration results of the second and third heating cycles. This uncertainty includes both instrumental reproducibility, caused by possible changes in the sample configuration, and any coarsening-related DSC signal during the second heating.

2.2.2. Oxide melt solution calorimetry

High-temperature oxide melt solution calorimetry was performed in a custom-built Tian-Calvet twin calorimeter at 810 °C. Details of the equipment and experimental procedure are described elsewhere [11,12]. For the measurements, pelletized samples (~10 mg) were dropped into a platinum crucible containing 20 g of sodium molybdate ($3Na_2O\cdot 4MoO_3$) solvent. Oxygen gas was flushed through the calorimeter assembly and bubbled through the solvent in order to enhance dissolution and to sweep out evolved gases. Prior to calorimetry, the RE-titanate samples were equilibrated at 25 ± 1 °C and 50 ± 2% humidity. The drop solution enthalpy values for the end-member oxides (TiO_2, Y_2O_3, Gd_2O_3 and Dy_2O_3) are a necessary component of the thermochemical cycle. Since the formation of more than one polymorph is possible, the sesquioxides of Y, Gd and Dy (Alfa Asar, 99.99 wt.% metal basis) and the TiO_2 (Alfa Asar, 99.997 wt.% metal basis) were dried and stabilized in the cubic (bixbyite type) and rutile forms, respectively, at 1000 °C for 12 h.

3. Results

3.1. Characterization

It should be mentioned that in this work, the data related to the structural and microstructural features of these samples (i.e. structure refinements, IR spectroscopy, Raman spectroscopy and transmission electron microscopy) were derived from the published work of Fuentes et al. [9]. The Y-, Gd- and Dy-titanate samples fabricated by mechanochemical synthesis were white in color, indicating no oxygen deficiency within the samples. The XRD patterns of the Y-, Gd- and Dy-titanate samples—after 19 h of high-energy ball milling (HEBM) and heat treatments at 650, 800 and 1200 °C for 12 h—confirmed that all samples were single-phase pyrochlores (PDFs Nos. Y-85-1584, Gd-73-1698 and Dy-17-0453) (Fig. 1). The pyrochlore phases have the compositions $Y_{1.98}Ti_{2.02}O_{7.00}$, $Gd_{2.02}Ti_{1.98}O_{7.00}$ and $Dy_{2.00}Ti_{2.00}O_{7.00}$ as determined by microprobe analysis. Moreover, the elemental analysis of the samples indicated no major contamination. TGA together with evolved gas analysis indicated only the presence of water.

The crystallite size and the root mean square strain (ε_{rms}) from Ref. [9] and the calculated surface area for all samples are summarized in Table 1. The calculated surface area (SA) (based on the crystallite size and assuming spherical particles) ranges from 227 ± 18 to 9 ± 0.4 m^2 g^{-1}, 96 ± 7 to 4.8 ± 2.5 m^2 g^{-1} and 132 ± 8 to 16.5 ± 0.2 m^2 g^{-1} for the Y-, Gd- and Dy-titanate samples, respectively. The exposed surface area for nitrogen adsorption, as measured by the BET method (Table 1), was found to be 90–99% lower, with the maximum values being 2.9 ± 0.1, 4.3 ± 0.3