



Cation antisite disorder in uranium-doped gadolinium zirconate pyrochlores



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ABSTRACT

The incorporation of uranium into gadolinium zirconate ($Gd_2Zr_2O_7$) is investigated by synchrotron X-ray powder diffraction and X-ray absorption near-edge structure (XANES) spectroscopy. The results suggest that the uranium cation is largely located on the pyrochlore B-site instead of the targeted A-site. Cation disorder in $Gd_2Zr_2O_7$ and U-doped $Gd_2Zr_2O_7$ is investigated by positron annihilation lifetime spectroscopy (PALS) which demonstrates the absence of cation vacancies in these systems. This work provides direct evidence for cation antisite (A- and B-site mixing) disorder in U-doped and off-stoichiometric $Gd_2Zr_2O_7$ pyrochlore.

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1. Introduction

Compounds with the pyrochlore structure have been proposed for use as electrolytes in solid oxide fuel cells and as hosts for the disposal and storage of long-lived isotopes such as uranium, plutonium and the minor actinides (e.g., neptunium, americium and curium) generated as part of the nuclear fuel cycle [1–3]. In particular, zirconate ceramics with the pyrochlore and related fluorite structures are promising waste form candidates due to their chemical durability and remarkable resistance to amorphization under ion beam irradiation [4,5]. Within this family, $Gd_2Zr_2O_7$ is the focus of significant interest not only because of its strong resistance to amorphization but also due to its high ionic conductivity (La-doped $Gd_2Zr_2O_7$ has conductivity values similar to those of Y-doped ZrO_2) [1,5]. To understand the feasibility of incorporating long-lived radioactive elements in ceramics, it is essential to gain a clear understanding of the crystal chemistry and speciation within the potential waste form ceramic, as this may have significant bearing on its behavior in the repository environment. Developing an understanding of how to suppress higher actinide valence states, which can form water-soluble actinyl ions and potentially enhance aqueous leaching in geological repositories, is essential. In this regard we investigate here the cation distribution in uranium-doped $Gd_2Zr_2O_7$ pyrochlore using Rietveld refinement of

synchrotron X-ray diffraction data, X-ray absorption near-edge structure (XANES) and positron annihilation lifetime spectroscopy (PALS).

The pyrochlore crystal structure has the general formula $A_2B_2X_6Y$ (cubic with space group $Fd-3m$) where A and B are cations, e.g., Gd^{3+} and Zr^{4+} respectively, and X (O^{2-}) and Y (O^{2-} , OH^- , F^-) are anions. Pyrochlore is often described as a superstructure of the fluorite structure; in which the A and B cations are ordered on two distinct cation sites, and one-eighth of the oxygen anions are absent. In origin choice 2, the 8-coordinate A- and 6-coordinate B-type cations occupy the $16d$ ($1/2, 1/2, 1/2$) and $16c$ ($0, 0, 0$) sites, respectively, the X-anion occupies the $48f$ ($x_{48f}, 1/8, 1/8$) position, the Y-anion occupies the $8b$ ($3/8, 3/8, 3/8$) site, and the $8a$ ($1/8, 1/8, 1/8$) is a vacant site [6]. $Gd_2Zr_2O_7$ has an r_A/r_B cation radius ratio of 1.46, the 8-coordinate ionic radius of Gd^{3+} is 1.053 Å, and that of 6-coordinate Zr^{4+} is 0.72 Å, and is right on the boundary of the stable III/IV pyrochlore region of 1.46–1.78; the disordered fluorite structure is expected to form when $r_A/r_B < 1.46$ [6]. Pyrochlore-type ordering in the ZrO_2 – $GdO_{1.5}$ system is reported to exist between 44 and 54 mol% $GdO_{1.5}$ following heat treatment at 1400 °C and this region is temperature dependent [7]. The formation of the non-stoichiometric phase $Gd_{2-x}Zr_{2+x}O_{7+0.5x}$ is thought to occur with either substitution between Gd^{3+} and Zr^{4+} or by introducing point defects (vacancies or interstitials) into the pyrochlore structure [7].

Previous work has demonstrated extensive solubility of uranium in $Gd_2Zr_2O_7$ [8,9]. Govindan Kutty et al. [8] prepared two series of U doped $Gd_2Zr_2O_7$ oxides, targeting substitution on

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both the A-site in $Gd_{2-x}U_xZr_2O_{7+y}$ and B-site in $Gd_2Zr_{2-x}U_xO_{7+y}$. Both series were sintered in air and were postulated to be oxygen hyperstoichiometric and presumably with the nominally vacant 8b site partially occupied by anions. These workers concluded that U^{6+} and U^{4+} formed in both series. In the former series the pyrochlore structure persisted to $x \sim 0.25$, with high doping levels resulting in the formation of a fluorite phase, whereas for the B-site doped series U doping levels of $x \sim 0.20$ were sufficient to stabilize the fluorite phase.

Uranium in the 6+ oxidation state has an ionic radius of 0.73 Å and 0.86 Å in 6- and 8-fold coordination, respectively [10]. The ionic radii of the 8-fold coordinated A-site cations in III/IV pyrochlores are typically in the range of $r_A = 0.87\text{--}1.51$ Å and the 6-fold coordinated B-site cations are typically $r_B = 0.40\text{--}0.78$ Å [11]. Considering size alone, U^{6+} ions are a closer match for Zr^{4+} (0.72 Å in 6-fold coordination) than Gd^{3+} and since this also minimizes the charge heterogeneity in the system it is likely that any U^{6+} present will predominantly reside in the 6-coordinate B-sites. Such an arrangement was observed in some U-doped titanate pyrochlores [12] but is in contrast to the recent suggestion of Govindan Kutty et al. [8] that in U-doped $Gd_2Zr_2O_7$ the U^{6+} substitutes for the Gd^{3+} on the 8-coordinate A-site. It is of course, possible that the U ions may be present in lower oxidation states. We have previously observed mixed U oxidation states in samples sintered under either Ar (U^{5+}/U^{6+}) or mildly reducing $N_2\text{--}3.5\%H_2$ (U^{4+}/U^{5+}) atmospheres [9]. However our recent XANES study of various U-doped $Gd_2Zr_2O_7$ samples sintered in air [9] showed that only U^{6+} was formed even when Ca^{2+} was added in an attempt to encourage the formation of lower uranium oxidation states. It was hypothesized that crystal-chemical stabilization, through substitution of uranium onto the smaller B-site, rather than the larger A-site, was the driving factor for the presence of U^{6+} in air-sintered samples and that no U^{4+} was present. Since the pyrochlore structure is well known to tolerate degrees of non-stoichiometry, it was postulated that if the U^{6+} was located on the B-site the compositions with nominal formula $Gd_{2-x}U_xZr_2O_7$ were off-stoichiometric and deficient in A-site cations [9]. As there was no evidence in the scanning electron microscope (SEM) results for the presence of a second phase along with the pyrochlore main phase, then one would expect either A-site cation vacancies or cation antisite disorder within the U-doped $Gd_2Zr_2O_7$ compositions. The pyrochlore lattice is known to tolerate vacancies in the A_2Y sublattice. Using positron annihilation lifetime spectroscopy (PALS), Vance et al. demonstrated that ceramics based on the pyrochlore $Gd_2Ti_2O_7$ tolerate Gd deficiency by incorporating Gd vacancies [13]. Computational studies by Stanek et al. [14] suggested that A-site cation vacancies are the principal defects in $BO_2\text{--}excess A_2B_2O_7$ pyrochlores. Alternative arguments however suggest that off-stoichiometric pyrochlores can be accommodated by a degree of cation disorder [15–17].

In the present work we have investigated the cation distribution in air-sintered uranium-doped $Gd_2Zr_2O_7$ pyrochlore using synchrotron XRD and XANES. PALS was used to detect the presence or absence of cation vacancies in off-stoichiometric $Gd_2Zr_2O_7$ and U-doped $Gd_2Zr_2O_7$.

2. Experimental

The samples used were those previously studied by Gregg et al. [9]. A summary of the preparation is presented here, and more detail is available [9]. The samples were prepared by a modified nitrate alkoxide route. Stoichiometric amounts of tetrabutyl zirconate were dissolved in isopropanol and intimately mixed with an aqueous solution containing the other metal nitrates ($Gd(NO_3)_3 \cdot 6H_2O$ and $UO_2(NO_3)_2 \cdot 6H_2O$) in a stainless-steel beaker. The mixture was heated to dryness on a hot plate at $\sim 110^\circ C$.

The dried powder was subsequently calcined in air for 10 h at $700^\circ C$. The calcined powder was then milled, using yttria-stabilized zirconia media, in cyclohexane for 16 h and dried at $\sim 110^\circ C$. The powder was then pelletized using a uniaxial press and sintered in air at $1450^\circ C$ for 50 h. Off-stoichiometric $Gd_{(2-x)}Zr_2O_{(7-3x/2)}$ samples were synthesized using the same procedure.

The sintered pellets, ~ 12 mm in diameter and 2 mm thick, were characterized using SEM and X-ray diffraction (XRD). XRD patterns were measured using a PANalytical Xpert Pro diffractometer (PANalytical Ltd., Almelo, The Netherlands) with $Cu K\alpha$ radiation, in an angular range of $10\text{--}110^\circ 2\theta$, with a step size of 0.03° and a counting time of 5 s per step. A Zeiss Ultra Plus scanning electron microscope operating at 15 kV and equipped with an Oxford Instruments X-Max 80 mm² SDD X-ray microanalysis system was used for microstructural and semi-quantitative phase-composition analysis. Samples were mounted in epoxy resin and polished to a 1 μm diamond finish for SEM analysis. A carbon film (~ 5 nm) was deposited onto the polished surface for charge neutralization.

Synchrotron X-ray powder diffraction data were collected using the powder diffractometer at the beamline 10-BM of the Australian Synchrotron [18]. Each sample was finely ground and contained in a 0.2 mm diameter quartz capillary that was rotated during the measurements. The wavelength was set at ~ 0.825 Å, and the precise value of this was determined using a NIST LaB₆ 660b standard reference material as 0.82518 Å. The structures described here were refined by the Rietveld method using the program RIETICA (version 1.7.7) [19]. The peak shape was modeled using a pseudo Voigt function and the background was estimated by interpolating between up to 40 selected points. The scale factor, detector zero point, lattice parameters, atomic coordinates and isotropic atomic displacement parameters were refined together with the peak profile parameters.

X-ray absorption near edge structure (XANES) spectra were collected at the U L_2 -edge for both U-doped $Gd_2Zr_2O_7$ samples and U^{4+} (UO_2), U^{5+} ($Ca_{0.6}Y_{1.1}U_{0.3}Ti_2O_7$) [20] and U^{6+} ($SrCa_2UO_6$ and $CaUO_4$) standards, on beamline 12-ID of the Australian Synchrotron [21]. The beam intensity (I_0) was monitored by an ionization chamber (Ar) located upstream from the sample. XANES spectra were collected by a second ionization chamber (Ar) placed immediately after the sample. A third ionization chamber (Ar) was placed downstream to simultaneously measure a reference spectrum of UO_2 . The monochromator was detuned by 50% for harmonic rejection. Energy steps as small as 0.4 eV were employed near the absorption edge with a counting time of 1 s per step. The energy scale of the monochromator was calibrated using the K-edge of a Mo foil at 20,000 eV. Analysis was carried out using the software package ATHENA [22].

The PALS apparatus was a fast-fast coincidence spectrometer, with scintillation detectors based on Hamamatsu H3378-51 (25SE25) photomultiplier tubes and BaF₂ scintillators (Nucletron, Newtown, Australia). A 30 μCi ²²NaCl source was used for collecting spectra; the source was encapsulated in 8 μm Kapton foil. Experiments were carried out in the usual sandwich geometry between two identical samples. The time resolution of the instrument was determined to be 265 ps from the FWHM of a ⁶⁰Co prompt peak under actual experimental conditions. Whereas the “prompt width” is a measure of the time resolution of the spectrometer, it does not represent the minimum lifetime that can be measured. Each spectrum had $>10^6$ counts and was analyzed using PALSfit Version 1.64 [23]. For all samples, after subtraction of the source contribution and a constant background, a one- or two-component analysis gave satisfactory fits (a variance close to unity). The average experimental errors are of the order of 2 ps for the lifetime results and $<1\%$ for the intensities. Measurements were conducted at room temperature in air.

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