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The fluorite–pyrochlore transformation of $Ho_{2-y}Nd_yZr_2O_7$

Richard Clements [a,b], James R. Hester [a], Brendan J. Kennedy [b,*], Chris D. Ling [a], Anton P.J. Stampfl [a,b]

[a] School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia
[b] Bragg Institute, Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2234, Australia

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ABSTRACT

Twelve members of the $Ho_{2-y}Nd_yZr_2O_7$ series, prepared using conventional solid state methods, have been characterised by neutron powder diffraction. $Ho_2Zr_2O_7$ has a defect fluorite structure whereas $Nd_2Zr_2O_7$ is found to adopt the ordered pyrochlore structure with the composition induced fluorite–pyrochlore transformation occurring near $y=1$. Rietveld analysis on the neutron data for all the compositions reveals an increase in lattice parameter as a function of y across the entire series, with a small discontinuity associated with the transformation. The neutron profile results suggest that domains of pyrochlore-type initially begin to form before crystallising into a separate phase, and therefore that anion and cation ordering processes are distinct. There is a strong correlation between the extent of disorder in the anion sublattice and the x-parameter of 48f oxygen. These results point the way to a better understanding of the stability observed in pyrochlore structures.

1. Introduction

The remarkable stability of the pyrochlore structure type allows for numerous chemically distinct materials to be prepared, some of which display properties that are technologically important including catalytic activity, piezoelectricity, ferro- and ferri-magnetism, luminescence and giant magnetoresistance [1,2] The electronic properties of pyrochlores vary from being superconducting, metallic, or semiconducting to having a high ionic conductivity [2].

Lanthanide zirconates, $Ln_2Zr_2O_7$, are being developed for use in solid oxide fuel cells [3], in thermal barrier coatings (TBCs) that are employed to extend the practical lifetime of devices such as turbine blades as well as allowing these to operate at higher temperatures [4] and for the storage of nuclear waste [5,6]. While the titanate pyrochlores transform to an amorphous structure upon irradiation, the zirconate pyrochlores remain crystalline to very high doses [5]. The effect of ion bombardment on tin pyrochlores has also been studied [6].

Pyrochlore oxides have the general formula $A_2B_2X_6Y$, where A, B are cations and X, Y are anions. Most pyrochlore oxides ($X=Y=$oxygen) crystallise in space group $Fd\overline{3}m$ (#227). Of the four possible choices of origin in this space group, the most commonly used places the smaller B-type cation at the 16c site with the larger A-type cation at 16d. There are two anion sites, with O (or X) at 48f, and O′ (or Y) at 8b. There are only two variable structural parameters, the cubic lattice parameter, a, and the positional parameter, x, for the O atom in 48f. The pyrochlore structure can be described in several ways, most commonly as interpenetrating BX_6 octahedra and A_2Y chains [1,7]. The structure may also be described as an anion deficient fluorite, since the coordination polyhedra around the A and B cations change shape with the value of the O 48f positional parameter, x. In the pyrochlore phase, the smaller B-type cation is coordinated to the six O-type anions in a distorted octahedron. The larger A-type cation is in a distorted cube that is best described as consisting of a puckered six membered ring of O atoms with two O′ atoms forming linear O′–A–O′ chains, reminiscent of the Cu_2O structure, that are normal to the average plane of the six-membered ring [1]. The A–O and A–O′ bond distances are very different. Typically the A–O distances are around 2.4–2.5 Å, in accord with the sum of the ionic radii, whilst the A–O bonds are among the shortest known for any rare-earth oxide, ~2.2 Å. Vacancies in the A_2O′ are relatively common, and even when the A-site is fully occupied the O′ anion site (8b) may be only partially occupied. The pyrochlore structure can also be considered as a fluorite superstructure in which the 8a sites are vacant and there is an ordering of the two cations. A final description of the structure depicts the cations at the 16c and 16d sites forming a three-dimensional array of corner-sharing tetrahedra, where both types of cations are magnetic giving rise to a geometrically frustrated lattice [2]. The fluorite structure is in space group $Fm\overline{3}m$ and since both the cations and anions occupy general positions it does not have any variable atomic positional parameters.

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* Corresponding author. Fax: +61 2-9351 3329.
E-mail address: B.Kennedy@chem.usyd.edu.au (B.J. Kennedy).

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In the pyrochlore structure the presence of a lone-pair active *A* cation, such as Pb^{2+} or Bi^{3+} results in off centring, through incoherent local displacements of the *A*-type cation, which can couple with the disorder of the anions. As a consequence of the relatively weak interaction between the B_2O_6 and A_2O sublattices of the pyrochlore [1] the structure can tolerate a large degree of substitutional [8] and displacive disorder on the *A*-cation site [9,10].

Naively the stability of the pyrochlore superstructure in the lanthanide zirconates may be thought to be linked to the ratio of the *Ln* and Zr cation radii [11–13]. It is now well established that when the lanthanide radius is larger than Gd, the ordered pyrochlore structure is generally encountered, while the smaller and hence higher *f*-electron containing lanthanides form fluorite-type structures [1]. Under certain conditions, including high temperature or after ion beam irradiation, the *Ln* and Zr cations are disordered over the *A* and *B* sites, and 48*f*, 8*b* and the normally unoccupied 8*a* anion sites can be occupied by both anions and vacancies [1]. Under extreme conditions an order–disorder transition from the pyrochlore to defect-fluorite structure is observed [14]. This transition is a very rare example of simultaneous disordering of both anions and cations. Those oxides with *Ln*=Nd–Gd all display a pyrochlore–fluorite transition upon heating with the transition temperature rapidly decreasing as the ionic radii of the lanthanide cation decreases and number of 4*f*-electrons increase from 2300 °C in $Nd_2Zr_2O_7$ to 1530 °C in $Gd_2Zr_2O_7$ [15]. Complex transformations can also occur upon the application of pressure [16].

There have been numerous studies of the effect of chemical substitution on the structural transformation from the perfect pyrochlore to defect fluorite [17–19]. This transformation can be induced by substitution at the *B*-site as illustrated by the work of Glerup et al. [20] on the series $Y_2Ti_{2-y}Zr_yO_7$. A feature of this work was the observation of an intermediate disordered phase. Mandal et al. [21] studied the same transformation in $Nd_{2-y}Y_yZr_2O_7$ series. Given the importance of the anion disorder in the transformation it is surprising that very few neutron diffraction studies of this transformation have been reported. Two notable exceptions are the early work of Heremans et al. [22] on $Y_2Ti_{2-y}Zr_yO_7$ and the recent study of Whittle et al. [23] on $Y_{1.2}La_{0.8}Zr_2O_7$. A further challenge in the study of the pyrochlore to defect fluorite transformation in the zirconates is that it occurs near *Ln*=Gd. Gd has an extremely large thermal neutron absorption coefficient 49,700 barn for $\lambda=1.798$ Å that effectively precludes neutron diffraction studies.

The aim of the present work is to establish if anion disorder existed in the pyrochlore type zirconates poised near the fluorite–pyrochlore transformation, and if so what if any correlation existed between the disorder in the anion sublattice and the *x*-parameter of 48*f* oxygen in the pyrochlore phase. To do this a number of samples of the type $Ho_{2-y}Nd_yZr_2O_7$ were prepared and their structures examined using high resolution powder neutron diffraction.

2. Experimental

Twelve samples in the series $Ho_{2-y}Nd_yZr_2O_7$ $(0 \le y \le 2)$ were prepared using conventional solid state methods. The appropriate stoichiometric quantities of Ho_2O_3, Nd_2O_3 and ZrO_2 (calcined at 1000 °C overnight before use), sufficient to prepare ~20 g of material, were finely mixed before being fired at 1200 °C for 24 h. The resulting powders were then re-ground, under acetone, for 10 min in an agate jar in a planetary ball mill at 350 rpm for 15 min. The ground powders were hydrostatically pressed into rods and heated at 1450 °C for 85 h. This process was then repeated to yield single phase samples as established using a Shimadzu S-6000 X-ray diffractometer. Scanning Electron Micrographs were measured using a Carl Zeiss Evo 50 scanning electron microscope with LaB_6 filament operated at 25 kV equipped with an IXRF System energy dispersive spectroscopy (EDS) detector (EDS2006 version 1.0). The exception was the sample of $Nd_2Zr_2O_7$ used in the synchrotron measurements, which was found to contain a small amount of Nd_2O_3. This was not evident in the neutron diffraction profile of this material.

Neutron powder diffraction (NPD) data were obtained over the angular range $10 < 2\theta < 160°$ using the high resolution powder diffractometer Echidna at ANSTO's OPAL facility at Lucas Heights [24]. The wavelength of the incident neutrons, obtained using a Ge (331) monochromator, was 1.299 Å. For these measurements the sample was contained in a 12 mm diameter vanadium can. Synchrotron X-ray powder diffraction (S-XRD) data were collected at ambient temperature in the angular range $5 < 2\theta < 85°$, using X-rays of wavelength 0.94814 Å on the powder diffractometer at

Table 1
The results of the Rietveld refinements for the $Ho_{2-y}Nd_yZr_2O_7$ series as a function of composition. Selected bond-distance are given. The structures were refined using neutron diffraction data measured with $\lambda=1.299$ Å.

y	2.0	1.8	1.6	1.4	1.2	1.1	1.0[a]	0.9	0.6	0.4	0.2	0.0
a	10.6424(1)	10.6049(2)	10.5871(1)	10.5652(2)	10.5607(3)	10.5563(3)	10.5093(3)	5.2521(1)	5.2429(1)	5.2317(2)	5.2283(1)	5.2213(2)
x	0.3365(1)	0.3406(3)	0.3396(2)	0.3409(2)	0.3419(3)	0.3402(4)	0.3516(5)					
NdU11	1.76(5)	1.36(7)	1.27(3)	1.27(4)	1.63(6)	1.30(7)	2.35(15)	2.12(3)	2.29(3)	2.20(3)	1.92(2)	2.28(3)
U12	0.29(3)	0.29(10)	0.31(4)	0.35(5)	0.27(8)		0.04(18)					
Zr11	1.31(3)	0.39(2)	2.13(5)	2.43(6)	3.11(11)	2.66(13)	2.22(17)					
Zr12	0.15(4)	0.06(2)	0.36(6)	0.54(9)	0.53(16)		0.03(20)					
O111	2.31(5)	4.20(21)	3.13(8)	3.32(11)	4.6(2)	2.78(11)	7.8(4)	5.89(7)	5.88(7)	5.31(6)	5.24(6)	5.40(7)
O122	1.30(3)	1.78(9)	2.11(5)	2.37(6)	2.81(10)		3.89(14)					
O123	0.32(5)	0.46(13)	0.63(6)	0.82(8)	0.98(14)		1.5(2)					
O211	1.25(6)	2.40(22)	1.30(7)	1.48(10)	1.84(17)	1.38(15)	3.6(4)					
Nd–O(1)	2.5626(9)	2.525(2)	2.525(2)	2.513(1)	2.504(2)	2.515(2)	2.426(3)	2.2742(1)	2.2703(1)	2.2655(1)	2.2639(1)	2.2609(1)
Nd–O(2)	2.3041(1)	2.2959(1)	2.2922(1)	2.2874(1)	2.2865(1)	2.2855(1)	2.2753(1)					
Zr–O(1)	2.0945(6)	2.106(1)	2.100(1)	2.100(10)	2.104(2)	2.095(1)	2.142(3)					
*n*8*a*	0.0061(5)	0.008(1)	0.010(1)	0.0123(8)	0.0115(12)	0.006(1)	0.0182(19)					
R_p	4.68	7.71	4.57	4.37	5.76	4.33	5.52	5.82	4.25	5.16	5.66	5.14
R_{wp}	6.01	10.35	5.94	5.53	7.50	5.44	7.07	7.40	5.40	6.56	7.21	6.59
χ^2	1.97	7.12	2.37	1.26	2.16	1.38	2.73	3.51	2.55	2.73	3.35	2.72

[a] This sample contained both pyrochlore and fluorite phases. The refined lattice parameter for the fluorite phase was 5.26056(16).