An interstitial pyrochlore formed by chemical intercalation of oxygen

James B. Thomson, A. Robert Armstrong and Peter G. Bruce*

School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, UK KY16 9ST

Oxygen is intercalated, using a solution-based route at ambient temperature, into a pyrochlore oxide, thus establishing a new class of pyrochlore-based interstitial solid solutions: the specific system studied is $Ce_2Zr_2O_7$ and compositions in the range $Ce_2Zr_2O_{7+x}$, $0 < x < 0.36$ are obtained; the structure of the most oxygen rich composition has been elucidated by powder neutron diffraction.

The pyrochlore structure type is associated with the general formula $A_2B_2X_7$. The A and B cations form an ordered cubic close packed array within which the X anions occupy tetrahedral sites. The structure is related to that of fluorite but with 1/8 of the anions missing. Many important compounds adopt the pyrochlore structure, these include catalysts, piezoelectrics, ferroelectrics and oxide-ion conductors such as $Gd_2Zr_2O_7$.[1–3]

Pyrochlore oxides may readily be prepared as vacancy solid solutions, *e.g.* $(Gd_{2-x}Ca_x)Zr_2O_{7-x/2}$.[4] In comparison, the formation of oxygen interstitial solid solutions based on the pyrochlore structure has, as far as we are aware, received less attention. In this paper we describe the formation of such a solid-solution series $Ce_2Zr_2O_{7+x}$. Furthermore, these solid solutions have not been prepared by conventional high-temperature solid-state reaction but by the intercalation of oxygen at room temperature using a chemical route. This is the first example of such room-temperature oxygen intercalation into a pyrochlore. Only a few research groups have investigated oxygen intercalation by chemical or electrochemical means, mainly involving the Brownmillerite and K_2NiF_4 structure types.[5–9]

The stoichiometric $Ce_2Zr_2O_7$ was prepared by reacting appropriate proportions of $Zr(OEt)_4$ (Aldrich 97%) and $Ce_2(C_2O_4)_3$ (Aldrich 99.9%) in water. After rotary evaporation and freeze drying, the resulting powder was reacted initially at 250 °C for 30 min then at 1300 °C for 18 h in an atmosphere composed of 95% argon–5% hydrogen. The basic pyrochlore structure of the resulting compound was confirmed by powder X-ray diffraction using a Stoe STADI/P diffractometer with Cu-$K\alpha_1$ radiation. Chemical intercalation of oxygen into $Ce_2Zr_2O_7$ was carried out by the action of a 0.5 mol dm^{-3} solution of NaOBr in water for periods between 30 min and 72 h depending on the desired degree of oxygen insertion. During the reaction the solution was subjected to vigorous stirring. The reaction was carried out under argon and in deoxygenated water to avoid any possibility of oxidising the starting material from a source other than the NaOBr since this could have led to irreproducibility in the degree of intercalation. The resulting powders were dried and then characterised by powder X-ray diffraction.

In order to demonstrate that oxygen intercalation had taken place and to establish the positions occupied by the interstitial oxide ions, neutron diffraction was carried out on the most highly oxidised sample. Neutron data were collected on the POLARIS diffractometer at ISIS, Rutherford Appleton Laboratory. The powder diffraction pattern is shown in Fig. 1 and the refined crystallographic data are presented in Table 1. An excellent fit to the data was obtained for a structure based on pyrochlore but with interstitial oxygen, R_{wp} = 2.94%, R_e = 1.96% and χ^2 = 2.25. Compounds with the pyrochlore structure belong to space group $Fd\bar{3}m$ (no. 227). The starting model for refinement was the structure of stoichiometric $Ce_2Zr_2O_7$. The cubic close packed Ce/Zr ions adopt an ordered arrangement with the A-site, Ce ions, occupying 16c and the B-site, Zr ions, the 16d positions. Attempts to refine anti-site disorder, *i.e.* the presence of Zr on Ce sites and *vice versa*, yielded occupancies of zero within two e.s.d.s, indicating that no such disorder exists. In stoichiometric pyrochlores, 6 of the oxide ions occupy tetrahedral 48f positions with the remaining oxide ion located in a tetrahedral 8a site. This oxygen order is also found in the interstitial pyrochlore solid solutions. Attempts to refine the occupancies of oxygen in the 48f and 8a sites yielded values of 1 for each within two e.s.d.s. In the final refinement, the occupancies of the 48f and 8a sites were set to unity. Two interstitial positions exist in the pyrochlore structure, one, an 8b tetrahedral site and the other, an octahedral site at the 32e position. The extra oxide ions associated with the interstitial

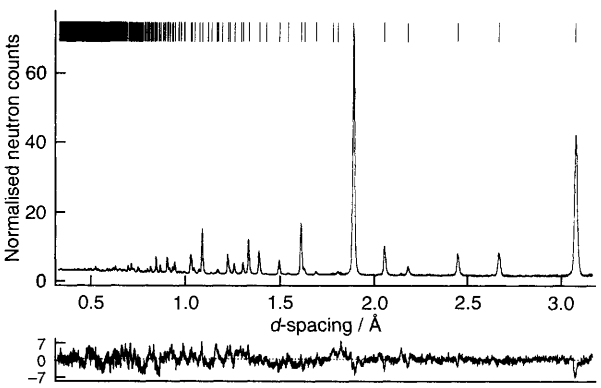

Fig. 1 Observed (dots) and calculated (solid line) diffraction profiles for $Ce_2Zr_2O_{7.36}$. The lower plot shows the difference/e.s.d.

Table 1 Structural and thermal parameters for $Ce_2Zr_2O_{7.36}$ [cubic, space group $Fd\bar{3}m$, a = 10.6440(1) Å]

Atom	Wyckoff symbol	X/a	Y/a	Z/a	Occupancy	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ce	16c	0.0	0.0	0.0	1	0.42(3)	0.42	0.42	−0.08(3)	−0.08	−0.08
Zr	16d	0.5	0.5	0.5	1	0.68(2)	0.68	0.68	0.32(3)	0.32	0.32
O(1)	48f	0.40586(11)	0.125	0.125	1	2.54(5)	0.52(2)	0.52(2)	−0.28(3)		
O(2)	8a	0.125	0.125	0.125	1.007(17)	0.92(5)					
O(3)	8b	0.375	0.375	0.375	0.357(12)	0.92(5)					

R_{wp} = 2.9%, R_e = 2.0%, B_{ij} in Å^2

solid solution are located exclusively in the tetrahedral 8b sites, attempts to refine oxygen in the 32e positions proved unstable, consistent with the site being vacant. Therefore we can conclude there is no evidence of octahedrally coordinated oxygen in the interstitial pyrochlores. The refined occupancy of the 8b site leads to an overall composition for this compound of $Ce_2Zr_2O_{7.36}$. A model of the structure is shown in Fig. 2. Refinement with powders exposed for more than 72 h to the NaOBr solution showed no evidence of further oxygen insertion, therefore this represents the highest oxygen content obtainable under the conditions used in the study. Associated with this oxygen content is an oxidation of 0.72 Ce^{3+} ions to Ce^{4+} *i.e.* the explicit formula for the compound is $(Ce^{3+}{}_{1.28}Ce^{4+}{}_{0.72})Zr_2O_{7.36}$. It should be noted that the stoichiometry of the $Ce_2Zr_2O_7$ starting material was also verified using powder neutron diffraction.

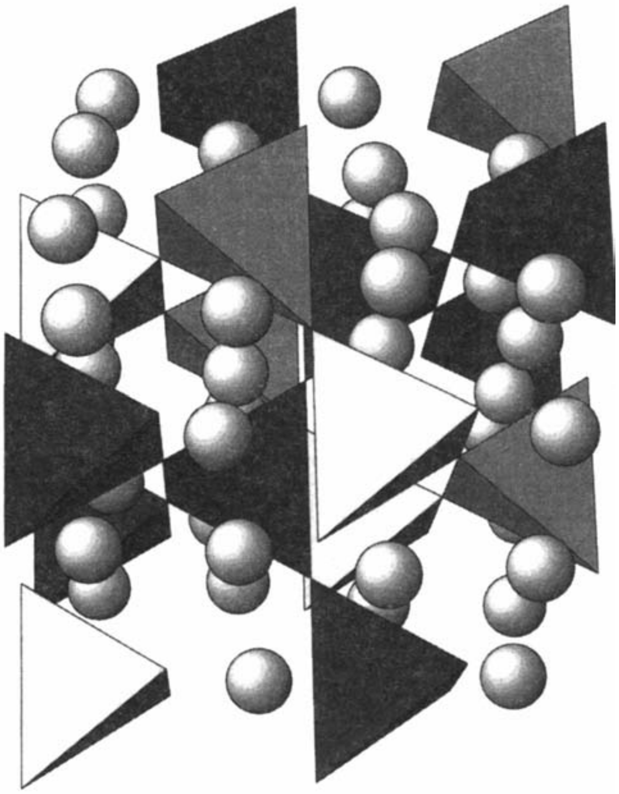

Fig. 2 Structure of $Ce_2Zr_2O_{7+x}$. Pale tetrahedra represent O(2) (8a) coordinated by 4 Ce. Dark tetrahedra represent O(3) (8b) coordinated by 4 Zr. Pale circles represent O(1) (48f) sites.

Powder diffraction patterns for samples exposed to the oxidising solution for various lengths of time exhibited only the reflections corresponding to the pyrochlore structure but a continuous contraction of the lattice parameter was evident with increasing reaction time up to 72 h. This confirms the existence of a continuous range of solid solutions. The reduction in lattice parameter with increasing oxygen content illustrates the fact that conversion of the Ce^{3+} to the smaller Ce^{4+} ion more than compensates for any expansion of the lattice due to the additional oxygen content. Further discussion of the changes which occur throughout the solid solution range must await a detailed analysis of neutron powder data for these intermediate compositions. This and the structure refinement of the $Ce_2Zr_2O_7$ will be reported in a subsequent paper.

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