

Synthesis and characterization of a new pyrochlore solid solution for actinide immobilization: $Y_2Ti_{2-2x}Fe_xNb_xO_7$

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ABSTRACT

The synthesis and structure of a new pyrochlore solid solution formulated $Y_2Ti_{2-2x}Fe_xNb_xO_7$ is reported. This solid solution is a model host for trivalent actinide species by substitution at the Y^{3+} site. Compositions in this solid solution were prepared by a solid state reaction and sintering method, affording ceramic specimens of > 95% theoretical density. Compositions with $0.0 < x < 0.4$ adopt the pyrochlore structure with substitution of Fe^{3+} on the octahedral Ti site confirmed by Mossbauer spectroscopy. In contrast, compositions with $0.7 < x < 0.9$ adopt a new monoclinic structure which appears to be stabilised by Fe^{3+} in 5-fold co-ordination, as demonstrated by Mossbauer spectroscopy. Compositions $0.4 < x < 0.7$ and $x > 0.9$ were found to comprise a mixture of pyrochlore, new monoclinic and at least one other phase.

INTRODUCTION

Metal oxides with a pyrochlore structure ($A_2B_2O_7$) have generated interest for application as actinide host phases for radioactive waste immobilisation, and, more widely, for application in fuel cells and catalysis. Pyrochlore oxides are known to exhibit high ionic and electrical conductivity [1], magnetic ordering [2], [3], as well as luminescence properties [4], [5]. This diversity in application is associated with the chemical flexibility of the pyrochlore structure, which may accept substitution on both the A and B site, by cations of appropriate size and charge.

Pyrochlore ceramics tolerate both cation and anion disorder and are known for their resistance to chemical corrosion and radiation damage, which is the primary requirement for application as an actinide host, e.g. as within Synroc (SYNthetic ROCK) [6].

The Pyrochlore structure

The ideal pyrochlore structure adopts the $Fd\bar{3}m$ space group; with eight formula units per unit cell. The ideal $A_2B_2O_7$ pyrochlore structure is derived from fluorite (AO_2) via an ordered removal of one eighth of the oxygen atoms, combined with an ordered arrangement of A and B cations.

The ordered arrangement of cations and anion vacancies yields two distinct cation polyhedra: the A site is 8-fold co-ordinate, in the form of a distorted cube; whereas the B-site is 6-fold co-

ordinate, in the form of a distorted octahedron (effectively, a trigonal prism) [7]. The A site is typically occupied by +2 and +3 cations, and the B site by +4 and +5 cations.

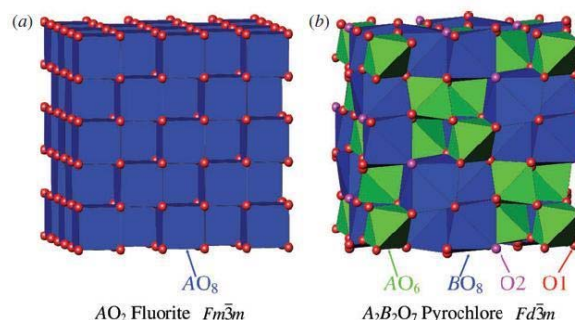


Figure 1 Relationship between the crystal structures of a fluorite structured oxide and of a pyrochlore structured oxide of $A_2B_2O_7$ stoichiometry

There are three unique oxygen positions, in the pyrochlore structure: the 48 f position ($x, 1/8, 1/8$), the 8b position ($3/8, 3/8, 3/8$) and the 8a position ($1/8, 1/8, 1/8$) which is vacant. The pyrochlore structure can then therefore be defined by two parameters: the 48f x oxygen position and the cubic unit cell parameter (a). All atoms, except the 48f oxygen, adopt special symmetry defined positions.

The stability of the pyrochlore structure depends on the relative sizes of A and B cations. In general, the pyrochlore structure is stable for the

radius ratio: $1.46 < r_A/r_B < 1.78$ [8]. Below $r_A / r_B = 1.46$ we observe a defect fluorite structure with both anion and cation disorder. Above $r_A / r_B = 1.78$ a variety of more complex phases are formed.

The $Y_2Ti_{2-2x}Fe_xNb_xO_7$ solid solution

The $Y_2Ti_{2-2x}Fe_xNb_xO_7$ solid solution is a model host for trivalent actinide species by substitution at the Y^{3+} site. Fe^{3+} is a common contaminant in nuclear waste streams (arising from corrosion of steel containment vessels) and could be potentially accommodated on the Ti^{4+} site, with charge compensation by Nb^{5+} . However, solid solutions of the type $Y_2Ti_{2-2x}Fe_xNb_xO_7$ have not been previously investigated. Moreover, the co-substitution of Fe and Nb for Ti, could offer a route to improving the radiation tolerance of titanate pyrochlores, which are known to be sensitive to composition. Thus, the synthesis of the $Y_2Ti_{2-2x}Fe_xNb_xO_7$ solid solution was attempted to determine the potential existence of a new family of pyrochlore compositions of this type.

EXPERIMENTAL PROCEDURE

Synthesis of $Y_2Ti_{2-2x}Fe_xNb_xO_7$ was achieved by several consecutive solid state reactions: 1573 K for 8h, and twice at 1673 K for 8 h, with intermittent regrinding. The temperature ramp was 5 K/min. The reactions were carried in air, under atmospheric pressure. The reaction completion was followed by XRD. Ceramic bodies were also sintered. Approximately 1 g of the material was pressed in a 10 mm diameter die at ~ 1 ton. Pellets were sintered at up to 1898 K for 8h. Compositions became less refractory with increasing Fe / Nb substitution. Final sintered densities of > 95% theoretical were achieved, microstructure was investigated using SEM / EDX with a Jeol 6400 microscope.

For XAS experiments, ~10 mg of sample was ground with ~100 mg of polyethylene glycol and pressed to form pellets for analysis in transmission mode at the Fe K-edge. The energy scale was calibrated by reference to Fe foil with $E_0 = 7112$ eV. Experiments were undertaken at beamline BL11.1 at the Elettra light source.

Specimens for Mossbauer spectroscopy were prepared by dilution of 50 - 100 mg of sample in 100 mg of graphite. Data were acquired at room temperature using a Wissel Mossbauer Spectrometer with a $^{57}Co:Rh$ source. Data analysis was performed using the RECOIL software package.

RESULTS

X-ray diffraction data

The XRD patterns of $Y_2Ti_{2-2x}Fe_xNb_xO_7$ phases with compositions $0.0 < x < 0.4$, could be indexed on

the basis of the aristotype pyrochlore space group $Fd-3m$, with a cubic cell parameter of $a = 10.1$ Å. Figure 2a shows the index diffraction of the $x = 0.3$ composition. The X-ray diffraction patterns of compositions in the range $0.7 < x < 0.9$ could be indexed on a monoclinic cell, space group $C2/c$, with unit cell parameters $a = 11.8$ Å, $b = 7.3$ Å, $c = 11.4$ Å, and $\beta = 103.3^\circ$. Figure 2b shows the X-ray diffraction pattern of the composition with $x = 0.7$. Compositions in the range $0.4 < x < 0.7$ comprised a mixture of both cubic pyrochlore and the new monoclinic phase.

The unit cell parameters of the pyrochlore structured compositions showed a linear dependence on the weighted mean radius of the B site cation, as shown in Figure 3.

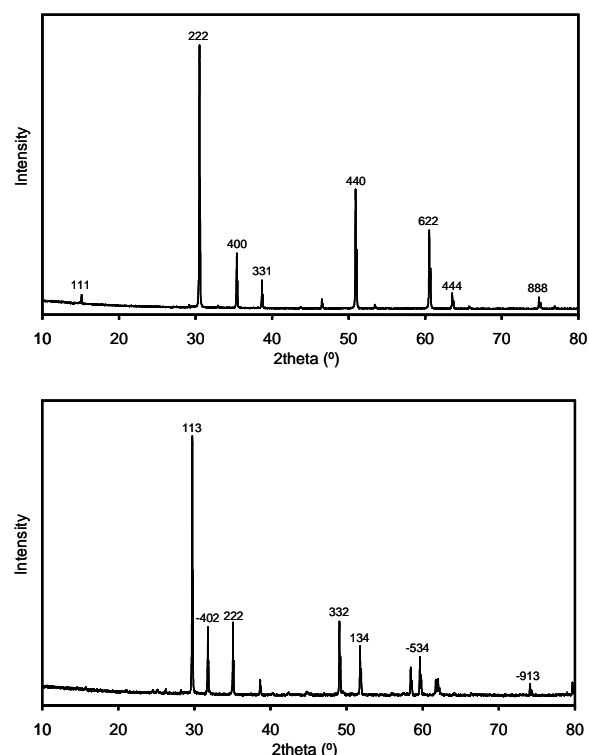


Figure 2 XRD patterns of a) $x = 0.4$ (top) and b) $x = 0.7$ (bottom), compositions in $Y_2Ti_{2-2x}Fe_xNb_xO_7$ system

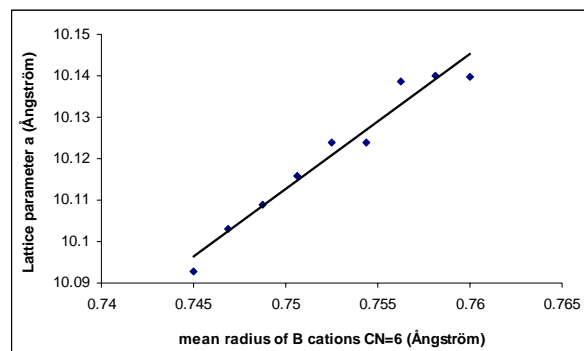


Figure 3 Dependence of unit cell parameters of $Y_2Ti_{2-2x}Fe_xNb_xO_7$ solid solution on weighted mean B site cation radius; for $0 < x < 0.4$

SEM / EDX analysis

SEM combined with quantitative EDX analysis confirmed the formation of single phase ceramic

specimens in accordance with XRD data. Figure 4 shows electron micrographs of the $x = 0.4$ specimen, which are broadly representative of all compositions. The secondary electron image (Figure 4a) shows a small volume fraction of porosity, consistent with the average sintered density of $95 \pm 2 \%$ of theoretical. The back-scattered electron micrograph (Figure 4b) shows equiaxed grains of ~ 1 micron in size with uniform contrast demonstrating the homogeneity in chemical composition. Quantitative EDX confirmed synthesis of phases with the target stoichiometry as given in Table 1.

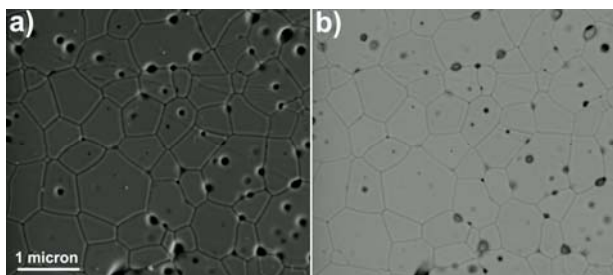


Figure 4 a) Secondary and b) Back-scattered electron micrographs $x = 0.3$ ceramic

Table 1 Quantitative elemental analysis of ceramic specimens with pyrochlore structure

Nominal Composition	Measured composition
0.0	$Y_{2.14}Ti_{1.90}O_7$
0.1	$Y_{2.06}Ti_{1.76}Fe_{0.10}Nb_{0.09}O_7$
0.2	$Y_{2.06}Ti_{1.56}Fe_{0.20}Nb_{0.19}O_7$
0.3	$Y_{2.06}Ti_{1.36}Fe_{0.29}Nb_{0.30}O_7$
0.4	$Y_{2.05}Ti_{1.17}Fe_{0.39}Nb_{0.40}O_7$

⁵⁷Fe Mossbauer Spectroscopy

Figure 5a shows the ⁵⁷Fe Mossbauer spectrum of the composition with $x = 0.3$ which is typical of compositions with the pyrochlore structure in the $Y_2Ti_{2-2x}Fe_xNb_xO_7$ system. The spectrum presents a single doublet with a centre shift of $0.36(1)$ and quadrupole splitting of $0.76(1) \text{ mm s}^{-1}$. These values are typical of Fe^{3+} in an octahedral site. In particular, spectra showed no evidence of Fe^{2+} , which would be associated with an additional doublet with considerably larger centre shift and different quadrupole splitting – this was not observed.

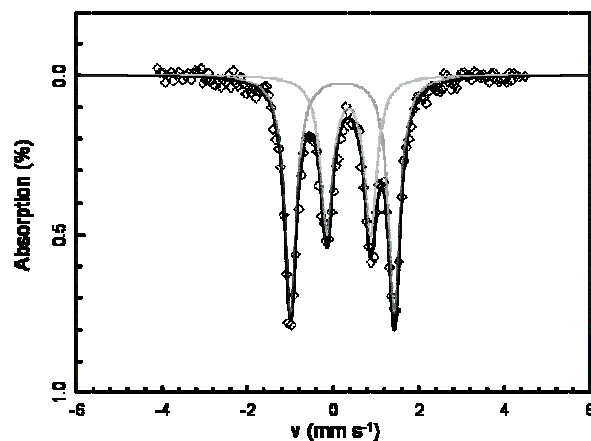
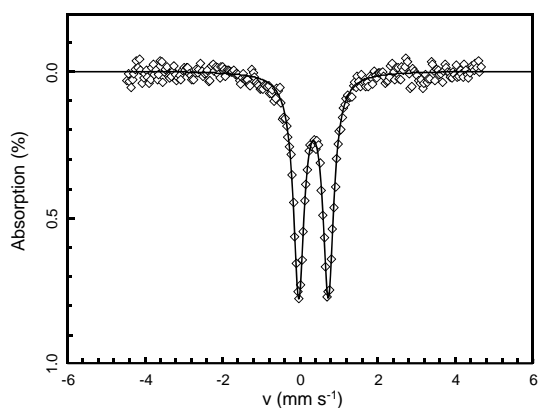


Figure 5 ⁵⁷Fe Mossbauer spectrum of: a) $x = 0.3$ composition with pyrochlore structure (top); b) $x = 0.7$ composition with new monoclinic structure. Grey lines show fits of Lorentzian line shapes to individual doublets

Figure 5b shows the ⁵⁷Fe Mossbauer spectrum of the composition with $x = 0.7$ which is typical of compositions with the new monoclinic structure in the $Y_2Ti_{2-2x}Fe_xNb_xO_7$ system. This spectrum presents two doublets: the first with a centre shift of $0.37(1)$ and quadrupole splitting of $1.02(2) \text{ mm s}^{-1}$; the second with a centre shift of $0.23(1)$ and quadrupole splitting of $2.42(2) \text{ mm s}^{-1}$. The relative areas of these two doublets were $41.2(1)\%$ and $58.8(1)\%$, respectively. The first doublet is again typical of Fe^{3+} in an octahedral site. The second doublet is characteristic of Fe^{3+} in 5-fold coordination. Again, spectra showed no evidence of Fe^{2+} species.

Fe K-edge XANES data

Figure X compares the Fe K-edge XANES spectra of the $x = 0.3$ composition and with those of Fe_2O_3 and FeO standards. The data are consistent with the presence of Fe^{3+} in a high symmetry (octahedral) site, as determined by Mossbauer spectroscopy.

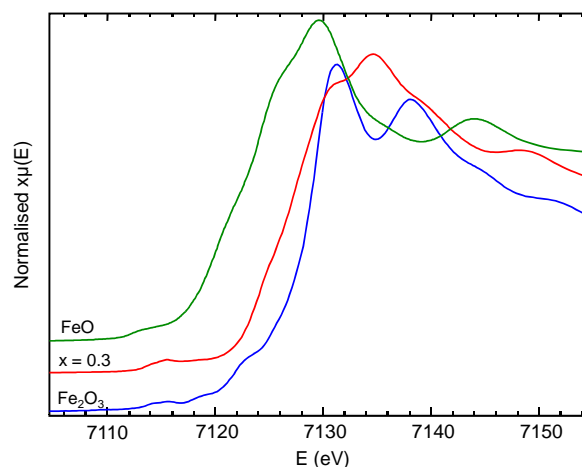


Figure 6 Fe K-edge XANES spectra of FeO , Fe_2O_3 and $x = 0.3$ composition

DISCUSSION

Powder X-ray diffraction and SEM / EDX data confirmed the synthesis of a new pyrochlore solid

solution $Y_2Ti_{2-2x}Fe_xNbO_7$ with $0.0 < x < 0.4$. The unit cell parameters scale with the weighted mean radius of the B site cations, as expected. ^{57}Fe Mossbauer spectroscopy and Fe K-edge XANES data demonstrated the presence of only Fe^{3+} species, as targeted. Furthermore, Mossbauer spectroscopy demonstrated the presence of Fe^{3+} in an octahedral site, consistent with substitution at the pyrochlore B-site.

Investigation of the solid solution $Y_2Ti_{2-2x}Fe_xNb_xO_7$ with $0.7 < x < 0.9$, by X-ray diffraction, revealed the synthesis of a new monoclinic phase of unknown structure. Mossbauer spectroscopy confirmed the presence of Fe^{3+} species, as targeted, but present in both 6- (59 %) and 5-fold co-ordination environments (41 %). Thus, it would appear that the new monoclinic phase is stabilised by formation of FeO_5 species. Determination of this new structure, and investigation of radiation and corrosion tolerance, is currently underway. The observation of a two phase region in the phase diagram of $Y_2Ti_{2-2x}Fe_xNb_xO_7$, between $0.5 < x < 0.7$, implies that the free energy of the pyrochlore and monoclinic phase must be similar.

CONCLUSION

The synthesis and characterisation of a new solid solution, $Y_2Ti_{2-2x}Fe_xNb_xO_7$ was achieved. Pyrochlore structured materials were obtained for $0.0 < x < 0.4$, whereas a new monoclinic structure was obtained for $0.7 < x < 0.9$. The structure and suitability of this new structure as a potential actinide host is under further investigation.

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