Journal of Alloys and Compounds 508 (2010) 457–462

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Structures and solid solution mechanisms of pyrochlore phases in the systems Bi_2O_3–ZnO–$(Nb, Ta)_2O_5$

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ARTICLE INFO

Article history:
Received 16 March 2010
Received in revised form 19 August 2010
Accepted 24 August 2010
Available online 27 September 2010

Keywords:
Ceramics
Solid state reaction
Crystal structure
Pyrochlore
X-ray and neutron diffractions

ABSTRACT

The crystal structures of two pyrochlore phases have been determined by Rietveld refinement of combined X-ray and neutron powder diffraction data. These are stoichiometric, $Bi_{1.5}ZnTa_{1.5}O_7$ and non-stoichiometric $Bi_{1.56}Zn_{0.92}Nb_{1.44}O_{6.86}$. In both structures, Zn is distributed over A- and B-sites; Bi and Zn are displaced off-centre, to different *96g* A-site positions; of the three sets of oxygen positions, O(1) are full, O(2) contain vacancies and O(3) contain a small number of oxygen, again in both cases. Comparisons between these structures, those of related Sb analogues and literature reports are made.

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1. Introduction

The pyrochlore structure, of general formula $A_2B_2O_7$, is found with a wide-variety of oxides containing a large cation A that typically prefers a site coordination number of eight and a smaller cation B that typically occurs in octahedral sites [1–7]. These cations are commonly comprised of A^{3+} and B^{4+} cations, A^{2+} and B^{5+} cations or other combinations with required average mixed valency. Large numbers of compounds have been discovered with this type of cubic crystal structure with space group Fd3m, (no. 227). An early, comprehensive review of pyrochlore phases is given in Ref. [1].

Oxides in the pyrochlore systems have considerable compositional and structural flexibility, including the possibility to incorporate a wide range of dopant ions [1,7–11]. The electrical properties, including oxide-ion conductivity, permittivity and temperature coefficient of permittivity, can be fine-tuned by compositional control, giving the possibility to design materials to meet specific property requirements. One of the promising pyrochlore oxide systems is bismuth-based, due to their low firing temperature and ability to accommodate different kinds of chemical substituents. The Bi_2O_3–Sb_2O_5–MO (M = Cd, Zn) materials were reported as pyrochlores with permittivities of approximately 20 and modest dielectric losses ($\tan\delta = 7–19 \times 10^{-4}$). Significantly higher permittivities were reported for the $Bi_2(M'M'')O_7$ and $Bi_2(M'_{2/3}M''_{4/3})O_7$ systems (M′ = Zn, Mg, Ni, Sc, In and Cu and M″ = Nb, Ta) [10–16]. By far the most extensively studied Bi-based pyrochlores are the two ternary phases in the Bi_2O_3–ZnO–Nb_2O_5 ternary system: the cubic pyrochlore $Bi_{3/2}ZnNb_{3/2}O_7$ ($k' = 150$, $t_k = -400$ ppm/°C) and the monoclinic zirconolite phase ($k' = 80$, $t_k = +200$ ppm/°C). With the opposite signs for the temperature dependence of permittivity, they are considered a good pair that provides temperature compensated dielectric properties because it is possible to control the temperature coefficient of permittivity by adjusting the pyrochlore phase content [2,5–7,10–15].

Because of the technological interest in dielectric applications, several studies have been reported on phase formation, crystallography and electrical properties of pyrochlore phases in the ternary systems Bi_2O_3–ZnO–$(X)_2O_5$: X = Nb, Ta, Sb. In these systems the ideal pyrochlore stoichiometry, *P* appears to be $Bi_{1.5}ZnX_{1.5}O_7$ (or $Bi_3Zn_2X_3O_{14}$); however, phase diagram studies show considerable compositional complexity with different behaviour in the three systems, X = Nb, Ta, Sb. In addition to the pyrochlore phase, a second anion-deficient fluorite phase, of probable stoichiometry $Bi_4Zn_{4/3}Nb_{8/3}O_{14}$ has been reported to exist in the Nb system. However, there is uncertainty in the literature as to its precise crystal symmetry and stoichiometry. It has been described as an orthorhombic phase, but recent studies indicated it has a mon-

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doi:10.1016/j.jallcom.2010.08.093

oclinic unit cell, space group C2/c with a zirconolite-like crystal structure [14–15,17].

In the Ta system, a pyrochlore phase of ideal *P* stoichiometry exists, but it is one member of a solid solution area with both variable Bi:Ta ratio and a deficiency of Zn. The compositional extent of the pyrochlore solid solutions in the ternary system Bi_2O_3–ZnO–Ta_2O_5 is shown in Fig. 1a superposed on a grid with variables *x* and *y* in the general formula, $Bi_{3+y}Zn_{2-x}Ta_{3-y}O_{14-x-y}$ [16]. The range of cation contents in the single phase area, given by *x* and *y*, was determined by a detailed phase diagram study. The oxygen contents, also given by *x* and *y*, were not determined directly but are derived by assuming that the cations have the oxidation states 3+(Bi), 2+(Zn) and 5+(Ta).

In the Nb system, a rather similar solid solution area for the pyrochlore phase also exists, but in this case, a pyrochlore with the ideal *P* stoichiometry appears not to exist [4,15]. In Fig. 1b, the solid solution area in the system Bi_2O_3–ZnO–Nb_2O_5 is shown and as can be seen, the ideal composition *P* lies outside this area. The location of the solid solutions was determined by two independent research groups: the trapezoidal shape in bold lines is from our own studies [15]; in Ref. [5], the shape of the solid solution area was not determined exactly, but the single phase compositions that were studied coincide closely with the solid solution area determined by ourselves, as shown in Fig. 1b.

In the Sb system, there are two closely related pyrochlore phases, neither of which has the ideal pyrochlore, *P*, stoichiometry. These are shown in Fig. 1c using a similar compositional grid to that in Fig. 1a and b. Both phases, P_1, and P_2, may be derived from the ideal *P* stoichiometry, but with different Bi:Sb ratios; in one case, the P_1 phase forms a solid solution containing excess Zn balanced by a deficiency of Bi and Sb [3,7].

Several structural reports on the pyrochlore phases in the three systems have been given; although there is general agreement that the structures are pyrochlore-like, there is considerable disagreement over certain details. Structure determination is complicated for several reasons. First, as shown by the phase diagram results, the ideal *P* stoichiometry exists only in the Ta system [16] and in all three systems, the pyrochlores have the possibility of variable stoichiometry [3,5–7,15]. Second, the general formula of the ideal pyrochlore in these systems, $Bi_{1.5}ZnX_{1.5}O_7$ means that the cation distribution must be more complex than given by the general formula, $A_2B_2O_7$. All reports do agree, however, that Bi is located exclusively on the larger A-sites with X exclusively on the smaller B-sites and with Zn distributed over both sets of sites.

The details of the A-site occupancy are unclear and indeed, appear to differ in the different systems. Probably this is because Zn is considerably smaller than Bi and would not normally be expected to occur in large, 8-coordinate sites. In the two pyrochlore structures in the Sb system, refinement of combined X-ray and neutron powder diffraction data indicated that, whereas Bi remained in the central A-site positions, Zn was displaced off-centre into *96g* positions with shorter bond lengths and smaller coordination number [4]. In several reports of analogous Zn-, Mg-, Ni-, Mn- and Ti-containing pyrochlores with X = Nb, both Bi and the divalent ion are displaced off the centre of the A-sites [18–25]. The nature of the B-site occupancy is less controversial; since Zn^{2+} is similar in size to the X^{5+} ions, it appears possible for joint occupancy of the 6-coordinate B-sites to occur, with similar Zn–O and X–O bond distances and regular octahedral coordination.

Additional complexities occur with the oxygen positions and occupancies. In a pyrochlore oxide, $A_2B_2O(1)_6O(2)$, A- and B-cations make up the fcc array but are ordered in the ⟨1 1 0⟩ directions to create three crystallographically distinct tetrahedrally co-ordinated anion sites. There is general agreement that O(1)

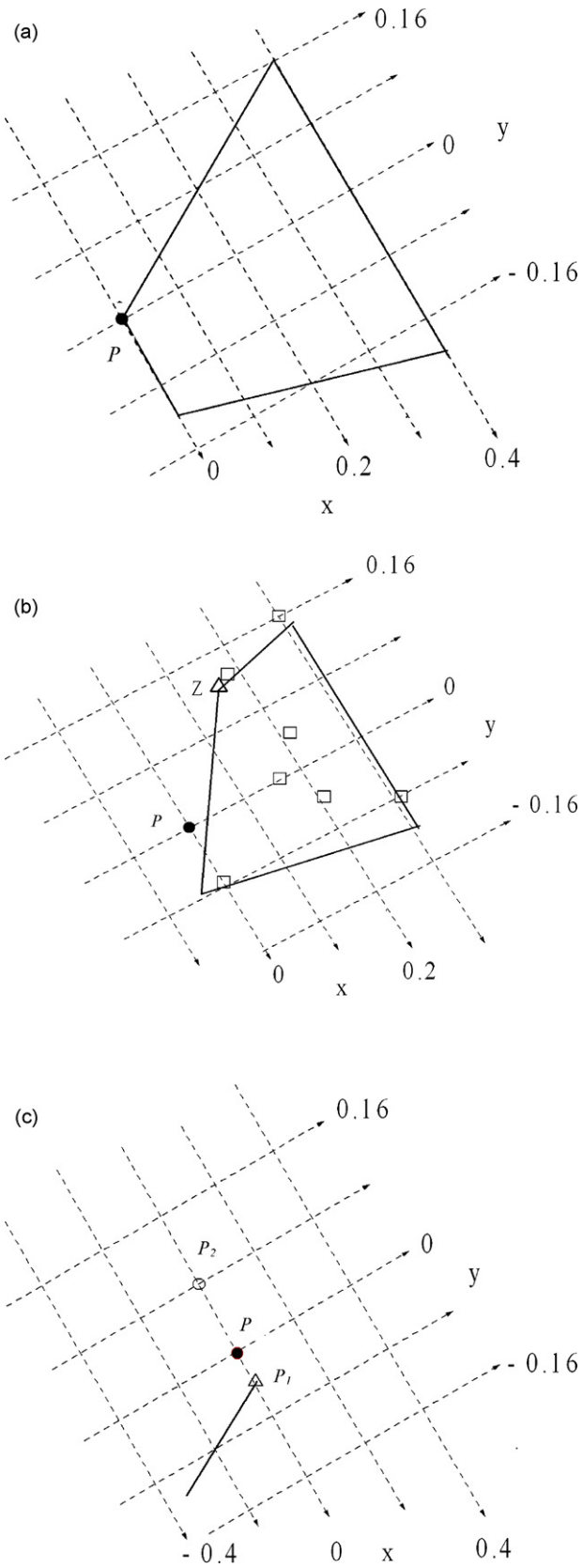

Fig. 1. (a) Solid solution area of pyrochlore phase with *x* and *y* as variables in the formula, $Bi_{3+y}Zn_{2-x}Ta_{3-y}O_{14-x-y}$. (b) Solid solution area of Nb-pyrochlore with general formula. $Bi_{3+y}Zn_{2-x}Nb_{3-y}O_{14-x-y}$. Open squares – compositions studied by Vanderah et al (2005). Open triangle (marked as Z) – composition used for Rietveld refinement. (c) Compositions of Sb pyrochlore phases, P_1 and P_2, superposed on the same compositional grid to that used for Nb and Ta pyrochlores.

Table 1
Starting structural model of cubic pyrochlore.

Model atom	Site	"*P*" atom	Wyckoff	*x*	*y*	*z*	Starting occupancy	U_{iso} (Å^2)
Bi	A	Zn(1)	*16d*	0.5	0.5	0.5	0.25	0.025
		Bi		0.5	0.5	0.5	0.75	0.025
Nb/Ta	B	Zn(2)	*16c*	0	0	0	0.25	0.025
		Nb/Ta		0	0	0	0.75	0.025
O	O(1)	O(1)	*48f*	*x*	0.125	0.125	1	0.025
O′	O(2)	O(2)	*8b*	0.375	0.375	0.375	1	0.025

which is co-ordinated by two A- and two B-cations is fully occupied in a *48f* position together with one positional variable *x*. Meanwhile, O(2) is co-ordinated by four A cations and appears to be either fully or partially occupied, as well as being displaced from the *8b* special positions to either *32e* or *96g* positions. In addition to these two oxygen sites, a third oxygen site, O(3), which is co-ordinated by four B-cations is also partially occupied in several structure reports. The occupancy of O(3) serves to compensate, at least partially, for vacancies in O(2), but the partial occupancies of O(2) and O(3) also provide a mechanism for accommodating variable oxygen content associated with the non-stoichiometric pyrochlores.

At present, there appears to be no real rationale behind the differences in the various structure reports. In some cases, it is assumed that the phases have the ideal *P* stoichiometry; in others, it is often not clear how the variable composition is accommodated within the crystal structure. The purpose of this paper is to report combined X-ray and neutron powder diffraction data on two pyrochlore compositions, the stoichiometric *P* phase in the Ta system and a non-stoichiometric pyrochlore in the Nb system and to compare the results with those reported in the literature and with those for the Sb system.

2. Experimental

Starting materials were reagent grade oxides, which, prior to weighing, were dried at the following temperatures: Bi_2O_3, 300 °C; ZnO, Nb_2O_5, Ta_2O_5: 600 °C. Samples, totaling approximately 15 g, were weighed out, mixed into a paste with acetone with an agate mortar and pestle, dried and fired in a muffle furnace in Pt crucibles. In order to avoid loss of Bi_2O_3 by volatilisation, the samples were heated slowly in stages, initially at 300 °C for 3 h, 600 °C for 3 h and then overnight at 800 °C. They were then removed from the furnace, cooled, reground and returned to the furnace in Pt crucibles, at either 950 °C (Nb) or 1050 °C (Ta) for a total of 2 days with regrinding after 1 day. These conditions had been shown by the phase diagram study to yield high-quality single phase samples.

Phase purity was checked by X-ray powder diffraction using a Stoe Stadi P powder diffractometer, CuKα_1, radiation, using a small linear position sensitive detector. For neutron diffraction, samples were loaded into V sample cans. Neutron diffraction data were collected on the POLARIS diffractometer at the Rutherford Appleton Laboratory, ISIS facility, using high-resolution back-scattered detectors arranged into four discrete resolution focused banks over the Time of Flight (ToF) range 2000–19,500 μs [26]. Polaris instrument parameters were constant for all data collected; data sets shown here are presented on a d-spacing scale. Rietveld refinement of combined XRD and ND data was carried using the General Structure Analysis System (GSAS) programme

3. Results and discussion

3.1. $Bi_3Zn_2Ta_3O_{14}$

The starting model for both this and the Nb-containing structure refinement was that of a simple ideal pyrochlore, Table 1, in which no displacement of cations from the centres of the A-sites was presumed, oxygen sites O(1) and O(2) were assumed to be full, again with no site displacement and oxygen site O(3) was assumed to be empty. Zn was assumed to be distributed randomly over both A and B-sites, according to the ideal P stoichiometry, with the occupancies shown in Table 1.

The combined XRD and ND data sets were used for refinement from the outset. In the first stage, the *x* parameter of O(1), together with U_{iso} of all atoms were refined. U_{iso} values for the A-site cations and O(2) were high. Since it was expected that there could be vacancies on the O(2) sites, as a result of refinements reported in the literature (especially in Zn-deficient compositions), a default value for U_{iso} of O(2) was selected and the occupancy refined, giving a reduced value of 0.52 instead of 1.0. Oxygen O(3) was then added, with a default U_{iso} and its occupancy refined to 0.25. These oxygen parameters were then fixed and the parameters of the A-site investigated. Various strategies were tried; by allowing Zn to displace either to a *32e* or *96g* site, its U_{iso} refined to a more realistic value, but that of Bi, remained high. Instead, on allowing Bi to displace to a *32e* site, U_{iso} values of both Zn and Bi remained high. After various attempts to obtain a satisfactory refinement with reasonable U_{iso} values, it was clear that both Zn and Bi are displaced off the central A-site position, but that they are displaced into separate sites: combined displacement of Zn and Bi onto a single off-centre site did not yield a satisfactory refinement. Both Zn and Bi were therefore displaced to *96g* sites, giving reasonable U_{iso} parameters for both.

At this stage, the U_{iso} for O(2) remained high at 0.051 and it was allowed to displace off-centre onto a *32e* site, giving a more reasonable U_{iso} value. It was clear, then, that both Zn and Bi were displaced off-centre in the A-sites, that site O(2) was partially occupied but also displaced off-centre and that site O(3) was partially occupied. To carry out further refinements and obtain a satisfactory structural model, the expected stoichiometry, especially the oxygen contents, was used to fix certain of the occupancies. Specifically, the occupan-

Table 2
Refined structural parameters for *P*, $Bi_3Zn_2Ta_3O_{14}$.

Atom	Wyckoff	*x*	*y*	*z*	Occupancy	U_{iso} (Å^2)
Zn(1)	96*g*	0.4984(11)	0.4984(11)	0.4490(13)	0.0417	0.0177(28)
Bi	96*g*	0.5165(4)	0.5165(4)	0.4708(5)	0.125	0.0127(7)
Zn(2)	16*c*	0	0	0	0.25	0.0051(1)
Ta		0	0	0	0.75	0.0051(1)
O(1)	48*f*	0.3195(1)	0.125	0.125	1	0.0172(1)
O(2)	32*e*	0.3931(2)	0.3931(2)	0.3931(2)	0.2	0.0438(12)
O(3)	8*a*	0.125	0.125	0.125	0.2	0.0312
	wRp XRD: 16.57		Rp XRD: 13.02			
	ND: 5.44		ND: 7.36			Chi^2 = 5.31
	Combined: 5.92		Combined: 12.53			

Table 3
Bond distances for *P*, $Bi_3Zn_2Ta_3O_{14}$.

Cation site	Bond	Bond length (Å)
A′	Zn(1)–O(1)	2.32
		2.45 × 2
	Zn(1)–O(2)	2.19 × 2
		2.10 × 2
		2.32 × 2
		1.67
A	Bi–O(1)	2.27
		2.50 × 2
		2.87 × 2
	Bi–O(2)	2.44 × 2
		2.45 × 2
		2.37, 2.52
		1.97, 2.01
B	Ta/Zn(2)–O(1)	2.00 × 6
	Ta/Zn(2)–O(3)	2.28 × 2

cies of O(2) and O(3) were adjusted to give fixed values, consistent with the overall stoichiometry. Thus, after the various refinement stages, the refined occupancy of O(2) was 0.203 and was therefore fixed at 0.2; the occupancy of O(3) had refined to 0.152 and was also given a fixed value of 0.2. In the final refinement, with these fixed occupancies, the variable positional parameters of all atoms were refined, together with U_{iso} values of all atoms apart from O(3): refinement of U_{iso} for O(3) together with the other parameters, gave a negative value which was discounted. Final refined parameters are given in Table 2, with selected bond lengths in Table 3. Profile plots are shown in Fig. 2.

3.2. $Bi_{3.12}Zn_{1.84}Nb_{2.88}O_{13.72}$

A similar strategy was used to that for refinement of $Bi_3Zn_2Ta_3O_{14}$. In this case, although the cation stoichiometry was different to the ideal, Fig. 1b, it was assumed initially that the stoichiometry was that of ideal *P*. Two alternative strategies were used in the refinement sequence. In one, oxygen O(3) was introduced with reduced occupancy of O(2), before the cations on the A-site were allowed to displace. In the second, the A-site cations were allowed to displace before oxygen O(3) was introduced, together with reduced occupancy of O(2). Both strategies yielded essentially similar results in that: the A-site cations, Zn and Bi, were both displaced, but to different positions; there were vacancies on the O(2) site; the O(2) site was displaced off-centre, probably into a *32e* site; there was a small partial occupancy of the O(3) site.

At this stage, the cation non-stoichiometry was taken into consideration, with the expectation that the resulting model should be deficient in Zn and the Nb content should be reduced, to be compensated by an increase in Bi content, Fig. 1b. Given the difficulty of refining both occupancies and cation displacement parameters on the A-site, attention was focused first on the B-site. It was assumed that all of the Nb in the structure was located on the B-site, giving

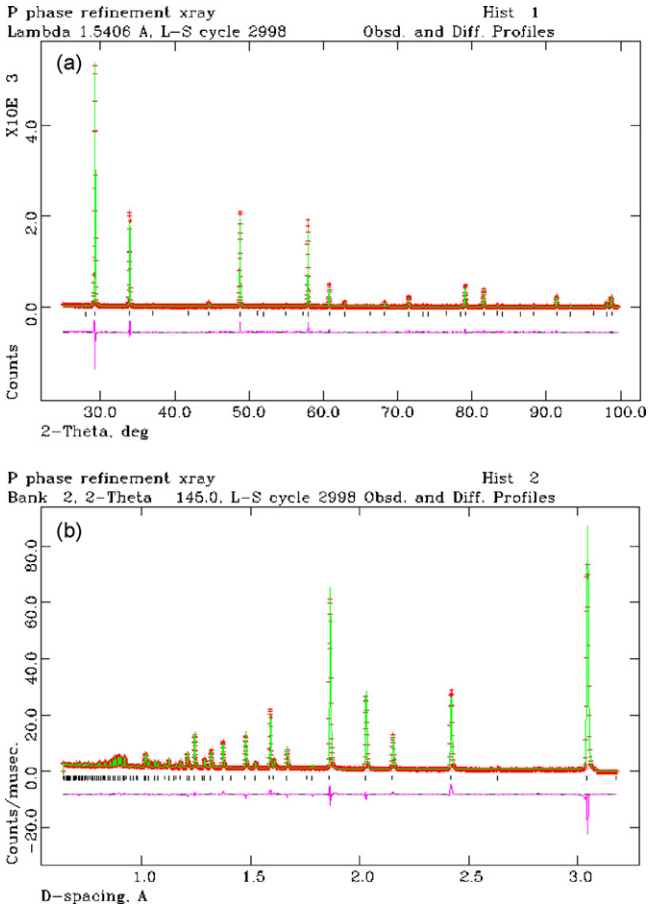

Fig. 2. Experimental, calculated and difference plots for (a), XRD data, and (b) ND data of composition, $Bi_3Zn_2Ta_3O_{14}$.

an occupancy of 0.71, instead of a value of 0.75 in the ideal *P* stoichiometry. The U_{iso} was given a default value for Nb. The occupancy of Zn on the B-site was then refined, giving a value somewhat less than expected for full occupancy of the B-site. Since the remaining Zn was located on the A-site, calculations showed that, from the amount of Zn on the A-site, together with the Bi content from the sample composition, the A-site was effectively fully occupied by a combination of Zn and Bi. This gave a strong indication, therefore, that the Nb deficiency was accommodated by an excess of Bi on the A-site and the Zn deficiency was accommodated by vacancies in the B-site.

In the final stage of refinement, the B-site occupancies were fixed using the previously refined value for Zn, the A-site occupancies were fixed, to give overall full occupancy, and all positional parameters and U_{isos} were allowed to refine. A satisfactory refinement was achieved, apart from the U_{iso} value of O(3), which went

Table 4
Refined structural parameters for non-stoichiometric cubic pyrochlore, $Bi_{3.12}Zn_{1.84}Nb_{2.88}O_{13.72}$.

Atom	Wyckoff	*x*	*y*	*z*	Occupancy	U_{iso} (Å^2)
Zn(1)	96*g*	0.5284(12)	0.5284(12)	0.4747(25)	0.0355*	0.0025(35)
Bi	96*g*	0.5115(6)	0.5115(6)	0.4652(2)	0.13	0.0159(11)
Zn(2)	*16c*	0	0	0	0.247	0.0095(1)
Nb		0	0	0	0.71	0.0095(1)
O(1)	*48f*	0.3200(5)	0.1250	0.125	1	0.0208(1)
O(2)	*32e*	0.3911(4)	0.3911(4)	0.3911(4)	0.169	0.0257(18)
O(3)	*8a*	0.125	0.125	0.125	0.079	0.0074
	wRp XRD: 16.72		Rp: XRD: 13.78			
	ND: 5.05		ND: 6.72			Chi^2 = 8.43
	Combined: 5.64		Combined: 13.43			

* Occupancy of Zn(1) is obtained from the reduction of Zn(2).

Table 5
Bond distances for composition $Bi_{3.12}Zn_{1.84}Nb_{2.88}O_{13.72}$.

Cation site	Bond	Bond length (Å)
A′	Zn(1)–O(1)	2.18
		2.51 × 2
	Zn(1)–O(2)	2.28 × 2
		2.61 × 2
		2.20, 2.23,1.86, 2.68
A	Bi–O(1)	2.29
		2.48 × 2
		2.89 × 2
	Bi–O(2)	2.53 × 2
		2.34 × 2
		1.96, 2.10, 2.46, 2.41
B	Nb/Zn(2)–O(1)	2.01 × 6
	Nb/Zn(2)–O(3)	2.29 × 2

negative and was therefore given a default value. Unlike the case of $Bi_3Zn_2Ta_3O_{14}$, the composition of the Nb phase was oxygen-deficient and it was not possible to fix the occupancies of O(2) and O(3) to any simple value. Instead, during an earlier stage of refinement, the occupancies of O(2) and O(3) had been varied and the values obtained were used, fixed, in the final refinement. The total oxygen content in the final model, 13.52(6) per formula unit, is, within experimental error, close to that calculated from the cation stoichiometry of 13.72. The final refined atomic parameters are listed in Table 4, bond lengths in Table 5 and profile plots are shown in Fig. 3.

Many features of the structure refinements found here are similar to those reported for related Bi-based pyrochlore analogues. In particular, they are all based on the "ideal" stoichiometry $Bi_{1.5}ZnNb_{1.5}O_7$ in which Bi occupies A-sites, Nb occupies B-sites and Zn is distributed over both sets of sites. Of the three pyrochlores with X = Nb, Ta, Sb, only the Ta analogue appears to form with the ideal stoichiometry and, therefore, its structure, in principle, should be simpler than that of non-stoichiometric analogues. Nevertheless, for the Ta analogue, although both A- and B-sites appear to be fully occupied, the A-site contains off-centre displacement of both Bi and Zn to different *96g* general positions: a satisfactory refinement with combined displacement to a single set of sites was not obtained. This result is different to most of the reported refinements on related (mainly Nb) phases in which displacement to a single *96g* site is presumed. It is also different to the case of the two non-stoichiometric Sb analogues in which displacement of only Zn was found.

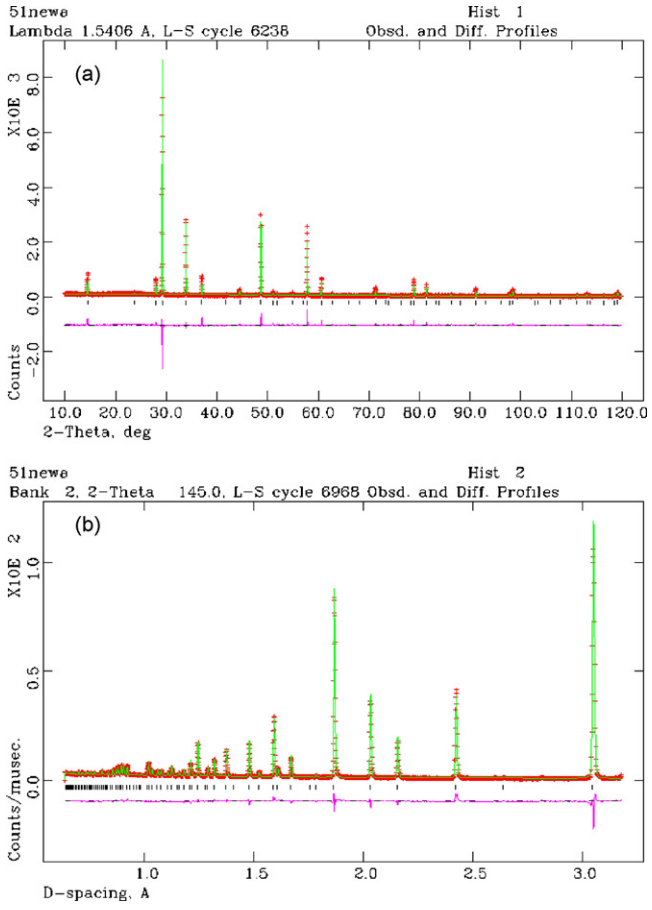

Fig. 3. Experimental, calculated and difference plots for (a) XRD data, and (b) ND data of composition $Bi_{3.12}Zn_{1.84}Nb_{2.88}O_{13.72}$.

For the Ta analogue, oxygen position O(1) is fully occupied but O(2) contains vacancies which are compensated by partial occupancy of site O(3). In addition, site O(2) appears to be split from its *8b* ideal special position to a *32e* site, consistent with most other structure reports on analogues, although O(2) is displaced to *96g* sites in the Mn analogue.

The structure refinement of the Nb analogue reported here is intrinsically more complex than that of the Ta analogue since this composition is both Zn-deficient and has an increased Bi:Nb ratio compared to that of the ideal stoichiometry. The refined structure has many similarities to the Ta analogue. In particular, off-centre displacement of the A-site cations occurs to different sites for Bi and Zn. Partial occupancy of site O(3) is found to essentially compensate the vacancies in site O(2). The composition studied is, overall, cation-deficient compared with the ideal stoichiometry and the evidence is that the cation deficiency is accommodated by Zn vacancies on the B-site. This is not conclusive but is the best indicator from the Rietveld refinement results. It is, however, in contrast to all other refinements of non-stoichiometric compositions which assume or prefer vacancies on the A-sites with full occupancy of the B-site.

In summary, the main differences between the results reported here and those elsewhere concern (a) the cation distribution in the A-site and (b) partial occupancy of both O(2) and O(3) sites. Our conclusion that the A-site cations occupy different sites is, perhaps, more logical from a crystal chemical point of view given the very different sizes of Bi^{3+} and divalent transition metal cations.

Although the broad features of these pyrochlore structures are now clear, these represent average features and undoubtedly the local structure is considerably more complex and may vary from one composition to the next. The structure may be regarded as two interpenetrating networks of general formula A_2O and B_2O_6. The B_2O_6 network appears to be without major controversy since the O(1) sites are fully occupied and the B-sites constitute a random mixture of divalent and pentavalent cations, with the possibility of cation vacancies in non-stoichiometric compositions.

The A_2O network, however, is much more complex; most models for this network consider similar, off-centre displacement of the A cations, whereas we find, in examples from all three systems with, X = Nb, Ta, Sb, that the A cations are not displaced to a common set of *96g* positions, that the O(2) sites are only partially occupied and these are essentially compensated by partial occupancy of the O(3) sites. It should be pointed out that the Rietveld refinement results of ourselves and others are close to the limits of what is achievable with confidence using powder diffraction data. Thus, for the A-sites, there are simply too many variables to permit complete refinement with a high level of confidence. This is because the *96g* site has two positional variables, *x* and *z*, occupancy and U_{iso} value; with the likelihood that Bi and Zn occupy different *96g* sites, there are eight refinable variables to fully specify the A-site distribution. Inevitably, therefore, different authors

use different strategies and simplifications in order to achieve a stable refinement. Our approach has been to make no assumptions at the outset and to test various structural models before selecting the most appropriate. With high multiplicity sites, such as *96g*, individual occupancies become very small, e.g. ~0.04 for Zn and the reliability of, and errors in, such small occupancies are then questionable, especially given the close link between occupancy and U_{iso} parameters. Similar questions arise concerning the oxygen positions O(2) and O(3). Most authors do not consider partial occupancy of the O(2) site, whereas we find clear evidence for a refined partial occupancy. However, again, there is considerable uncertainty since there is a strong and self-compensating correlation between site multiplicity/atomic coordinates, occupancy and U_{iso} which makes it difficult to achieve a unique refinement with a high level of confidence. Some authors include anisotropic thermal parameters in their refinements, which introduce several more variables; this is not a strategy that we have adopted.

Given these discrepancies and uncertainties over the average structures of this particular family of complex pyrochlore phases, detailed modeling of the local structures, which inevitably are more complex than indicated by an averaged model are subject to even more uncertainty. Further structural studies on this complex family of materials are certainly required.

4. Conclusions

With careful attention to the Rietveld refinement procedure, and by testing the validity of possible models containing different site multiplicities, parameters and occupancies, satisfactory models for the average structures of the present pyrochlore phases are obtained. It is clear that the different-sized Zn^{2+} and Bi^{3+} ions occupy different positions within the A-sites. This is linked to off-centre displacement of surrounding O(2) ions, allowing a local structure (presently undefined) that gives reasonable Zn–O and Bi–O bond lengths. Oxygen non-stoichiometry, associated with variable cation contents in the pyrochlore solid solutions, is readily accommodated by partial occupancy of O(2) and O(3) sites, which occurs even in the case of the stoichiometric composition, $Bi_{1.5}ZnTa_{1.5}O_7$. Variable cation stoichiometry is accommodated by varying the X:Zn occupancies of the B-sites together with the Bi:Zn occupancies of the A-sites, but without any evidence for spill-over of either excess Bi onto the B-sites or excess X onto the A-sites. There is some evidence that Zn deficiency is accommodated by B-site vacancies. Off-centre displacement of both A-site ions (to different off-centre sites for X = Nb, Ta) and O(2) ions provides a mechanism for satisfying the bonding requirements of the different-sized Bi^{3+} and Zn^{2+} ions. The flexibility in cation and oxygen (O(2) and O(3)) site distributions and occupancies provides a basis to rationalize the unusual solid solution ranges that are found and that are significantly different for X = Nb, Ta and Sb.

Acknowledgements

We thank MOSTI, Malaysia for financial support and Rutherford Appleton Laboratory, ISIS facility, UK for neutron diffraction data collection. Special thanks are extended to Prof. A.R. West for his constructive suggestions and discussion.

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