

A RIETVELD REFINEMENT APPROACH IN STRUCTURAL STUDY OF BISMUTH ZINC NIOBATE CUBIC PYROCHLORES

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ABSTRACT

A brief introduction of Rietveld structural refinement and detailed procedure was discussed in this paper. High accuracy data is a prerequisite in structural study and therefore data are rendered from the state-of-art instruments, e.g. high resolution X-ray diffraction (XRD) and neutron diffraction (ND). The structural study of non-stoichiometric bismuth zinc niobate (BZN) pyrochlores was performed using General Structure Analysis System (GSAS); a comprehensive system for the refinement of structural models to both x-ray and neutron diffraction data. The stoichiometry calculated from the refinement was in excellence agreement to the phase diagram-determined stoichiometry. Powder neutron data were used to study oxygen sites as XRD data are insensitive to oxygen positions in the presence of heavy atoms such as Bi and Nb in the pyrochlore structure. The high R values and relatively long bond distance in A-O(1) indicated that displacement of A site cations were required in order to stable the structure, however, only preliminary steps and results were discussed at this stage; whilst, a more comprehensive displacement model would be addressed later.

INTRODUCTION

Rietveld refinement is a useful tool for the investigation of crystal structures. It is commonly used to probe compositional differences between phases in terms of oxygen content, atomic co-ordinates and cation occupancy on non-equivalent sites. In a Rietveld refinement, a calculated powder pattern, based on a proposed structure model, is varied in a least squares refinement procedure until it provides a good match to the observed pattern. It should be noted that each data point in the pattern is treated as an "observation" which can arise from any number of *hkl* reflections [1]. During the Rietveld refinement procedure, a series of profile parameters such as background, scale factor, lattice parameter, peak shapes and structural parameters, such as atomic coordinates and site occupancies are varied in order to provide a calculated profile of best fit with the experimental data.

The refinement progress is monitored by difference profile, R factors, χ^2 and thermal parameter, Uiso. A series of R-values (residual values) are used to measure the

difference between the observed and calculated intensities and thereby judge the quality of the fit in Rietveld refinement. These criteria can be described as follows:

$$R_p = \frac{\sum |y_{io} - y_{ic}|}{\sum y_{io}} \quad (1) \quad R_{\text{exp}} = \left[\frac{(N-P)}{\sum w_i y_{io}^2} \right]^{1/2} \quad (2)$$

$$R_{wp} = \left[\frac{\sum w_i (y_{io} - y_{ic})^2}{\sum w_i y_{io}^2} \right]^{1/2} \quad (3) \quad R_I = \frac{\sum |I_{ko} - I_{kc}|}{\sum I_{ko}} \quad (4)$$

$$\text{Goodness-of-Fit} = \chi^2 = \frac{\sum w_i (y_{io} - y_{ic})^2}{N-P} = \left(\frac{R_{wp}}{R_{\text{exp}}} \right)^2 \quad (5)$$

I_{ko} = Observed intensity of the Bragg Reflection, k

I_{kc} = Calculated intensity of the Bragg Reflection, k

N = number of data points in pattern

P = number of refined parameters

y_{io} = observed intensity, y_{ic} = calculated intensity and w_i = weight at step i

The weighted R-value, wRp , and χ^2 are calculated by minimising the square of the difference between the observed and calculated data, including the background data points, with the peak positions, shapes and heights. The refinement is considered reliable if wRp and $\chi^2 < 10\%$. Values $> 20\%$ usually infer that the structure model is only partially correct. However, R-values should not be considered alone when assessing the accuracy of a structural model; a low R-value is not necessarily indicative of structural accuracy and a high R value does not automatically represent something that is incorrect [1-2]. On the other hand, evaluation of the thermal parameters is also a good way of monitoring the refinement process. Uiso values are associated with atomic vibrations. A larger Uiso than the average of the other thermal parameters i.e., $> \sim 0.05 \text{ \AA}^2$, can suggest, particularly with X-ray diffraction (XRD) data, that less electron scattering is required on that site. This can be overcome by reducing the occupancy or by replacing the atom with one that has a smaller electron scattering factor. Conversely, negative or very small Uisos suggest that more electron scattering may be needed on that site.

It should be noted that the value of each refined parameter is given with an indication of error, or e.s.d, estimated standard deviation. The scale of the e.s.d. reflects the precision of the refined parameters and not their accuracy. However this is not always the case when there are systematic errors in the data. For instance, e.s.d's found in XRD data may be influenced by diffraction profiles that suffer from anisotropic line broadening due to the effects of micro-strain and stacking faults or preferred orientation [1].

In XRD, the profile shapes are more complicated. They are best described by both Gaussian and Lorentzian character.

The peak width is modelled by the following

$$FWHM^2 = U \tan^2 \theta + V \tan \theta + W \quad (6)$$

Gaussian component of the peak shape and

$$FWHM^2 = X \tan \theta + Y/\cos \theta \quad (7) \text{ Lorentzian component.}$$

where parameters U , V , W describe the variation of the peak width at FWHM as a function of the diffraction angle, θ . A more detailed discussion about Rietveld refinement procedures can be found elsewhere [1-2].

In this Study, XRD and neutron diffraction (ND) are applied; the collected data serve different purposes in structure determination and refinement. XRD is sensitive to heavy atoms with strong diffracted radiation scattered by electrons. Therefore scattering strength increases with atomic number, Z . XRD data give valuable information about the cation thermal parameters and occupancies. However, interpretation of oxygen parameters via X-ray analysis alone can be difficult as oxygen is a relatively light element and a poor scatterer of X-rays. For example, oxygen's position within a bismuth zinc niobate (BZN) pyrochlore structure is dominated by much heavier elements such as Bi and Nb and is therefore difficult to refine accurately. Unlike X-rays, neutrons in most cases are scattered by the nuclei and the scattering amplitude (expressed as scattering length) varies in an irregular way with Z . Hence, ND, is particularly efficient when refining structure parameters of lighter elements, for example oxygen and hydrogen with relatively strong scattering length if compared to heavy metal atoms surrounding them [3]. In addition, ND is capable of distinguishing atoms with similar Z that cannot be discerned using XRD alone, for example Zn and Ni with Z of 30 and 28 and neutron scattering lengths of 5.6 and 10.3, respectively [4]. Conversely, monitoring structural features of heavy cations using ND data alone is sometimes inadequate. Problems may also arise using neutrons if two or more cations have similar scattering length. For instance, difficulty in refining Sb/ Zn cation occupancies has been reported by [5] due to the similar bound coherent scattering lengths, b_c of Zn and Sb with values, 5.680(3) and 5.570(3) fm, respectively. In this case, refinement was insensitive to Zn / Sb ratio on the B site. Therefore, structural refinement combining these two diffraction techniques would be most beneficial.

EXPERIMENTAL PROCEDURE

High purity oxides: Bi₂O₃ (Aldrich, 99.9 %), ZnO (Alfa Aesar, 99.95 %), and Nb₂O₅ (Alfa Aesar, 99.95 %) were used as starting materials. Stoichiometric quantities totalling 2–3 g were weighed out, mixed with acetone in an agate mortar, dried, transferred into gold foil boats and pre-fired at 700 °C for 24 h. Subsequently, the mixtures were fired at 800 °C and 950 °C for 24 h each with intermediate regrinding. In cases where products were phase mixtures, samples were reheated at 950 °C for an additional 24 to 48 h to ensure completion of reaction. Samples were analysed using a Stoe STADI P high resolution X-ray powder diffractometer with a small linear position sensitive detector, CuK α radiation, scan rate 0.1° min⁻¹; the data were used for cell parameter refinement using the WinXpow software. Powder ND 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 μ s [6]. The Rietveld refinement was performed based on the collected XRD and ND data using the

GSAS package.

RESULTS AND DISCUSSION

As described, the pyrochlore consists of two structurally distinctive sites, a A_2O' tetrahedral and a B_2O_6 octahedral, forming a interpenetrating framework with general formula $A_2B_2O_7$ [7-9]. These sites are commonly occupied by a combination of A^{3+} and B^{4+} cations, A^{2+} and B^{5+} cations or other combinations with required average mixed valency [10-11]. The ideal cubic pyrochlore, $Bi_3Zn_2Nb_3O_{14}$, has been reported to contain minute amounts of secondary phase, ZnO; phase pure pyrochlores are in fact, Zn deficient. The crystallography of the P solid solutions is undoubtedly complex. Structural studies using ND data suggest that this is mainly due to short-range order involving the A-site cations and surrounding oxygens. Complexities arise because (a) the A-site contains two cations of rather different size/bonding requirements, (b) the A-site may not be fully occupied but contains Zn vacancies, (c) the A-site cations appear to be displaced off-centre, together with displacement of bonded oxygens; since the multiplicity of the off-centre sites is much higher than that of the ideal sites, this gives considerable possibility for correlated short-range order. In addition to these structural complexities that have already been addressed in the literature, the phase diagram results indicate further complexities associated with (d) a variable amount of Zn vacancies, (e) a variable Bi/Nb ratio and (f) a variable oxygen content [12].

Refinement of XRD data alone is presented in detail for composition 37. The starting model for the refinement of this composition was based on the ideal pyrochlore structure, space group $Fd3m$ (227). The Bi: Zn: Nb cation ratio and distribution over the A and B sites were assumed as $(ZnBi_3)(ZnNb_3)O_{14}$. It was further assumed at the outset that the cation sites were fully occupied; the Zn deficiency was ignored since Zn is a light atom relative to Bi; tests on compositions with different Zn contents showed that the XRD data were insensitive to the possibility of a small concentration of Zn vacancies. In the ideal pyrochlore structure, atomic co-ordinates on the cation A, $16d$ site and cation B, $16c$ site and the O(2), $8b$ site are fixed and located on special positions (i.e., co-ordinates are multiples of $1/8$, i.e. 0.5, 0, 0.375). There is only one positional variable x for O(1), $48f$ [10]. In the starting model, the O(1) x value obtained by [5] was inserted.

Rietveld refinement results for composition 37, $Bi_3Zn_{1.76}Nb_3O_{13.76}$ are summarised in Table 1 with experimental/observed (red crosses), calculated (green line) and difference (purple line) plots of XRD data shown in Figure 1. The observed pattern is denoted in green, calculated pattern in maroon and the plots difference is indicated in purple, respectively. At the outset, the O(1) positional parameter was varied and fixed. The occupancies of the two cation sites were then allowed to vary within an overall occupancy of unity for both sites. The refined occupancies were then fixed and the temperature factors, Uiso's, allowed to vary, with the results shown in Table 1.

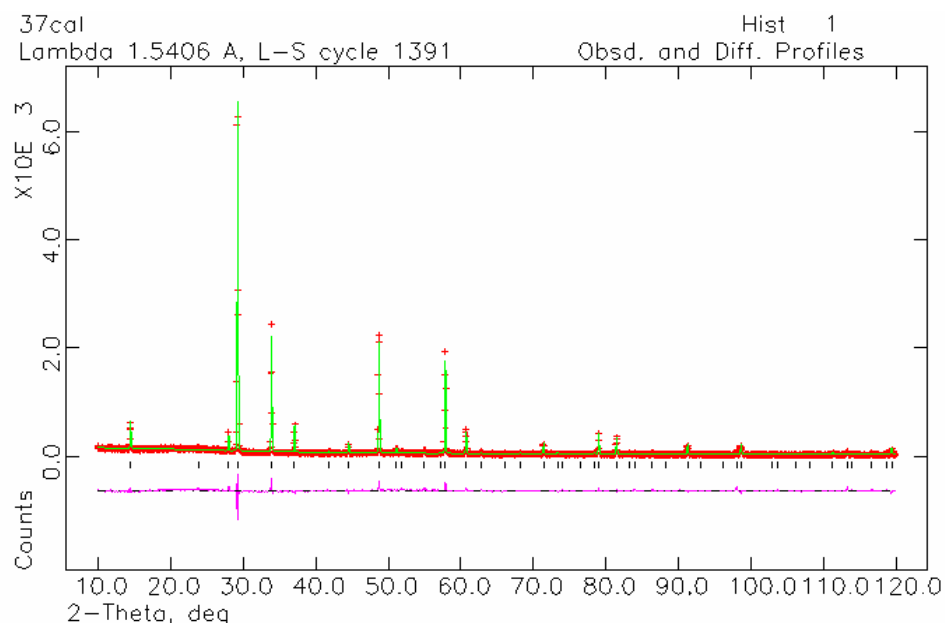


Figure 1: Observed, calculated and difference plots obtained from Rietveld refinement of XRD data for the composition 37, $\text{Bi}_3\text{Zn}_{1.76}\text{Nb}_3\text{O}_{13.76}$

Table 1: Structural parameters obtained from Rietveld refinement of powder XRD data for composition 37

Atom	Wyckoff	x	y/z	Occupancy	Uiso ($\text{\AA}^2$)
Zn(1)	16d	0.500	0.500	0.218	0.0425(4)
Bi		0.500	0.500	0.782	0.0425(4)
Zn(2)	16c	0.000	0.000	0.238	0.0303(5)
Nb		0.000	0.000	0.762	0.0303(5)
O(1)	48f	0.3185(1)	0.125	1.0	0.025
O(2)	8b	0.375	0.375	1.0	0.025
wRp = 12.33		Rp = 10.31		Chi ² = 1.62	

The refined Bi, Nb contents are similar to those expected from the experimental composition. The thermal parameters of the cation sites in composition 37 are small and positive suggesting that these sites are stable. The x parameter of O(1) has a value of 0.3185 which is within the range observed for other pyrochlore phases (where $x = 0.315 - 0.375$) [5, 10]. This x value indicates that for this composition, the B site cation has an undistorted octahedral coordination while the A site is centered within a distorted scalenohedron with A- O'- A linkages perpendicular to the puckered six-membered octahedral rings, resulting in eight-fold coordination of the A-cation. However, at this stage, no attempt was made to consider displacement of either A site cations or oxygens from their ideal positions, as has been observed in refinement of neutron diffraction data [8-9].

Similar refinement procedures were adopted for composition 73, $\text{Bi}_{2.93}\text{Zn}_{1.96}\text{Nb}_{3.07}\text{O}_{14.03}$, composition 47, $\text{Bi}_{2.92}\text{Zn}_{1.84}\text{Nb}_{3.08}\text{O}_{13.92}$ and composition 51, $\text{Bi}_{3.12}\text{Zn}_{1.84}\text{Nb}_{3.12}\text{O}_{13.72}$ and the results are shown in Table 2, 3 and 4; Figure 2, 3 and 4, respectively. Generally, the thermal parameters are higher on the A site than the B site. This is probably due to the incompatibility of Bi and Zn sharing the same site. In addition, Bi dominates the A site as there is three times the amount of Zn. It has a considerably larger ionic radius, 1.17 Å when octahedrally co-ordinated, than that of Zn^{2+} , 0.60 Å when tetrahedral and 0.74 Å when octahedral. Though Zn is able to exist in an 8-fold environment, it prefers to be coordinated tetrahedrally or octahedrally and is almost certainly considered unstable when in a larger space [13]. Therefore, Zn may be displaced in order to achieve a smaller co-ordination environment, e.g. 5-fold, and shorter bond distance as suggested by [5]. Zn-rich composition 73 (Table 2) shows a high Uiso on the A site, 0.0689 Å². This suggests further that there may be significant Zn displacement at the A site in accordance with results reported by [8]. R factors for the four refinements are > 10 % but these are considered reasonable as no attempt had been made to refine oxygen parameters at this stage.

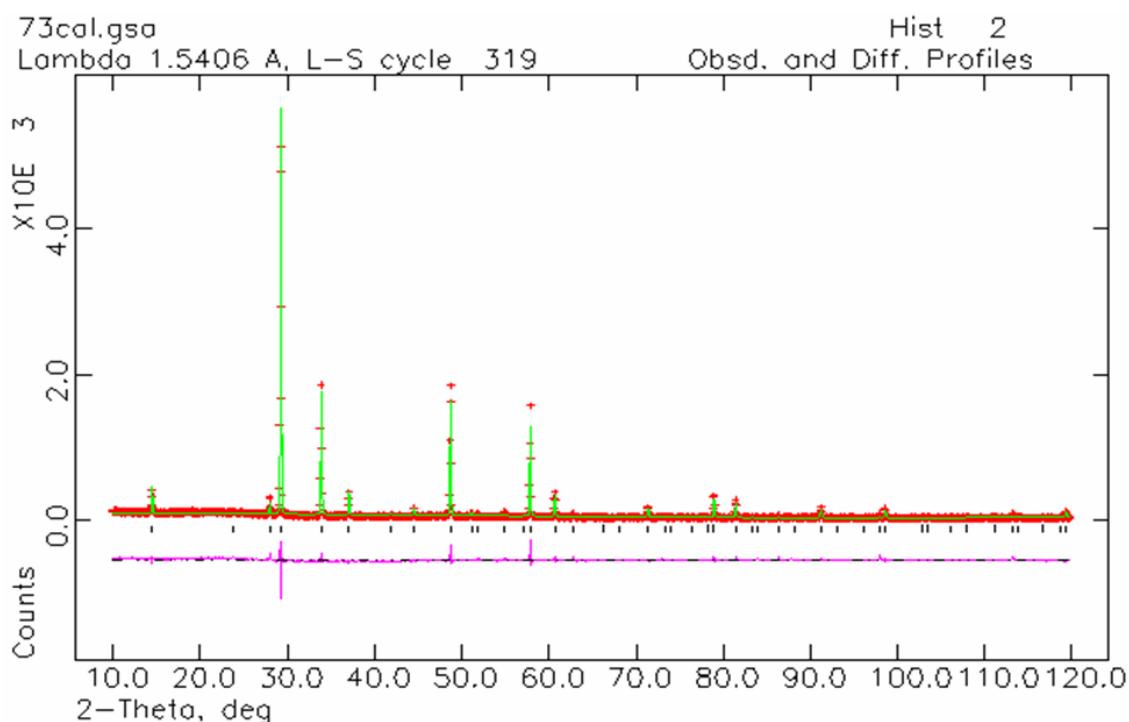


Figure 2: Observed, calculated and difference plots obtained from Rietveld refinement of data for the composition 73, $\text{Bi}_{2.93}\text{Zn}_{1.96}\text{Nb}_{3.07}\text{O}_{14.03}$

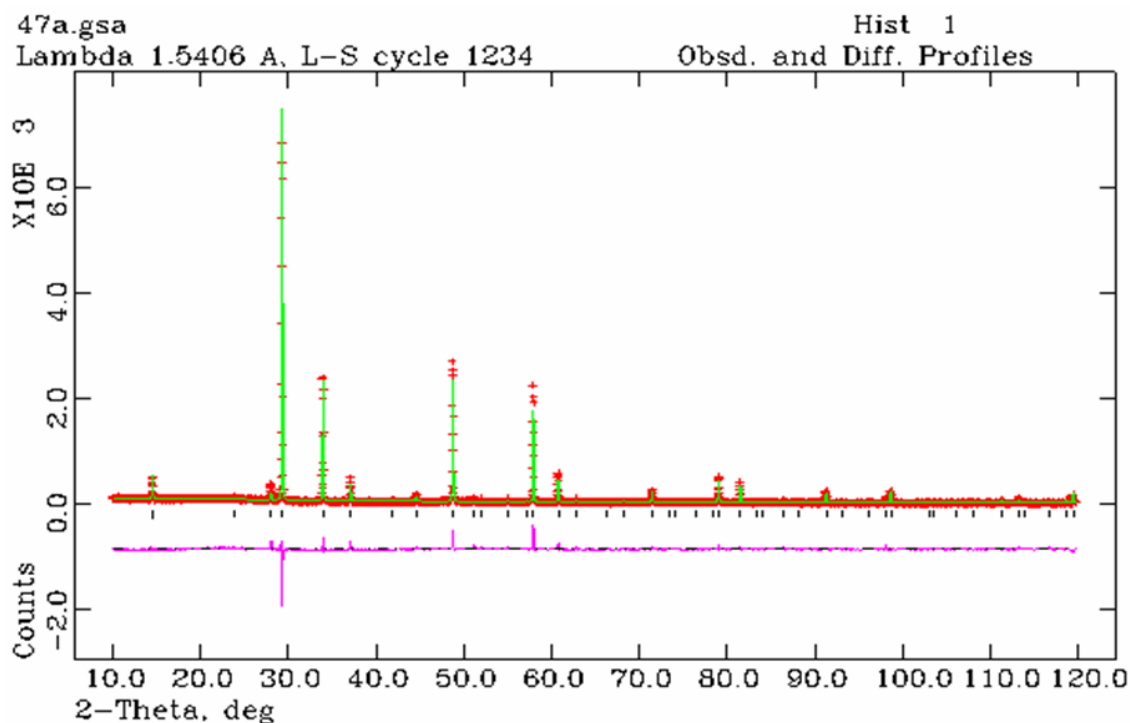


Figure 3: Observed, calculated and difference plots obtained from Rietveld refinement of XRD data for the composition 47, $\text{Bi}_{2.92}\text{Zn}_{1.84}\text{Nb}_{3.08}\text{O}_{13.92}$

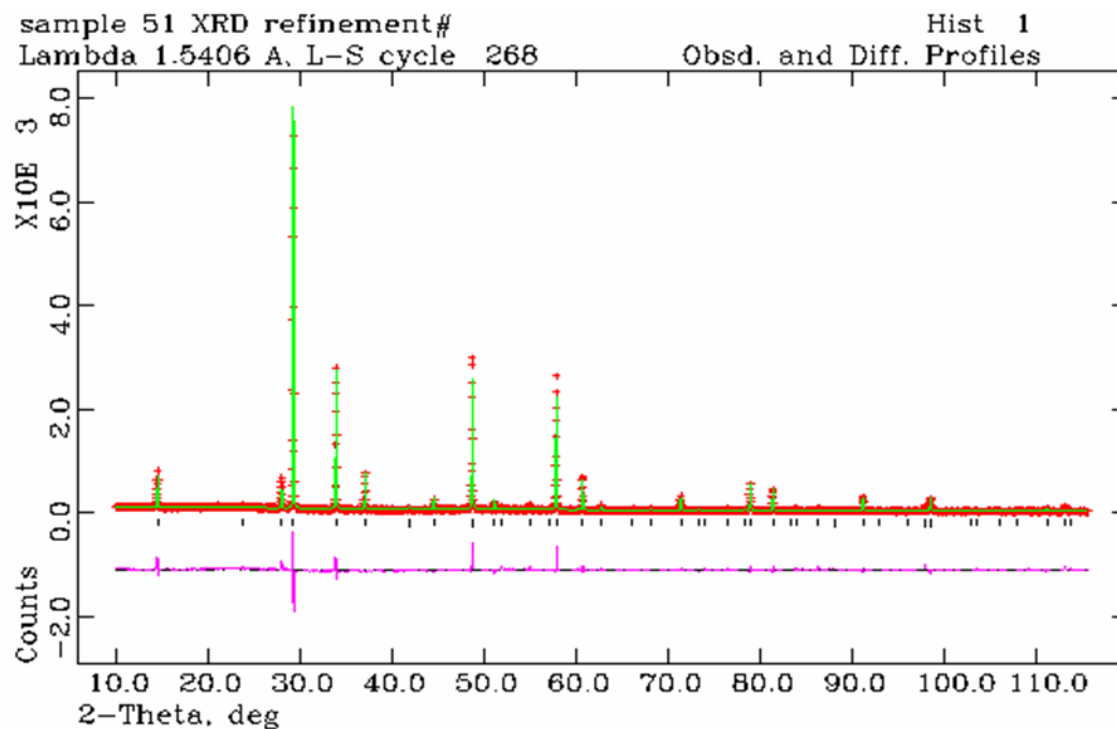


Figure 4: Observed, calculated and difference plots obtained from Rietveld refinement of XRD data for the composition 51, $\text{Bi}_{3.12}\text{Zn}_{1.84}\text{Nb}_{3.12}\text{O}_{13.72}$

Table 2: Structural parameters obtained from Rietveld refinement of powder XRD data for composition 73

Atom	Wyckoff	x	y/z	Occupancy	Uiso ($\text{\AA}^2$)
Zn(1)	16d	0.500	0.500	0.266	0.0689(9)
Bi		0.500	0.500	0.733	0.0689(9)
Zn(2)	16c	0.000	0.000	0.254	0.0260(8)
Nb		0.000	0.000	0.754	0.0260(8)
O(1)	48f	0.316(1)	0.125	1.0	0.025
O(2)	8b	0.375	0.375	1.0	0.025
wRp = 15.32 Rp = 11.32 Chi ² = 2.32					

Table 3: Structural parameters obtained from Rietveld refinement of powder XRD data for composition 47

Atom	Wyckoff	x	y/z	Occupancy	Uiso ($\text{\AA}^2$)
Zn(1)	16d	0.500	0.500	0.262	0.0497(5)
Bi		0.500	0.500	0.738	0.0497(5)
Zn(2)	16c	0.000	0.000	0.188	0.0330(6)
Nb		0.000	0.000	0.812	0.0330(6)
O(1)	48f	0.319	0.125	1.0	0.025
O(2)	8b	0.375	0.375	1.0	0.025
wRp = 14.2 Rp = 10.82 Chi ² = 1.64					

Table 4: Structural parameters obtained from Rietveld refinement of powder XRD data for composition 51

Atom	Wyckoff	x	y/z	Occupancy	Uiso ($\text{\AA}^2$)
Zn(1)	16d	0.500	0.500	0.1930	0.0432(6)
Bi		0.500	0.500	0.8070	0.0432(6)
Zn(2)	16c	0.000	0.000	0.2860	0.0308(8)
Nb		0.000	0.000	0.7140	0.0308(8)
O(1)	48f	0.315	0.125	1.0	0.025
O(2)	8b	0.375	0.375	1.0	0.025
wRp = 13.8 Rp = 11.43 Chi ² = 2.82					

The refinement results of these four compositions are used to supplement the phase diagram results of the cubic pyrochlore solid solutions. XRD data are sensitive to the change in Bi: Nb ratio and give confirmatory evidence for the existence of solid solutions with variable y parameter, mechanism 5, i.e. $\text{Bi}_{3+y}\text{Zn}_{2-x}\text{Nb}_{3-y}\text{O}_{14-x-y}$ [12]. In order to estimate the agreement between the cation compositions determined by Rietveld refinement and those expected from the experimental syntheses, the estimated

standard deviations (e.s.d.s) obtained from refinement of the cation occupancies of each of the four compositions are shown in Figure 5. In all cases, the compositional data of the four compositions agree with those expected within 2-3 e.s.d's. In particular, they confirm a significant difference in Bi / Nb ratio for the three compositions 47, 37 and 51 and in addition, demonstrate that composition 73 has a lower (Bi + Nb) content than the other three compositions.

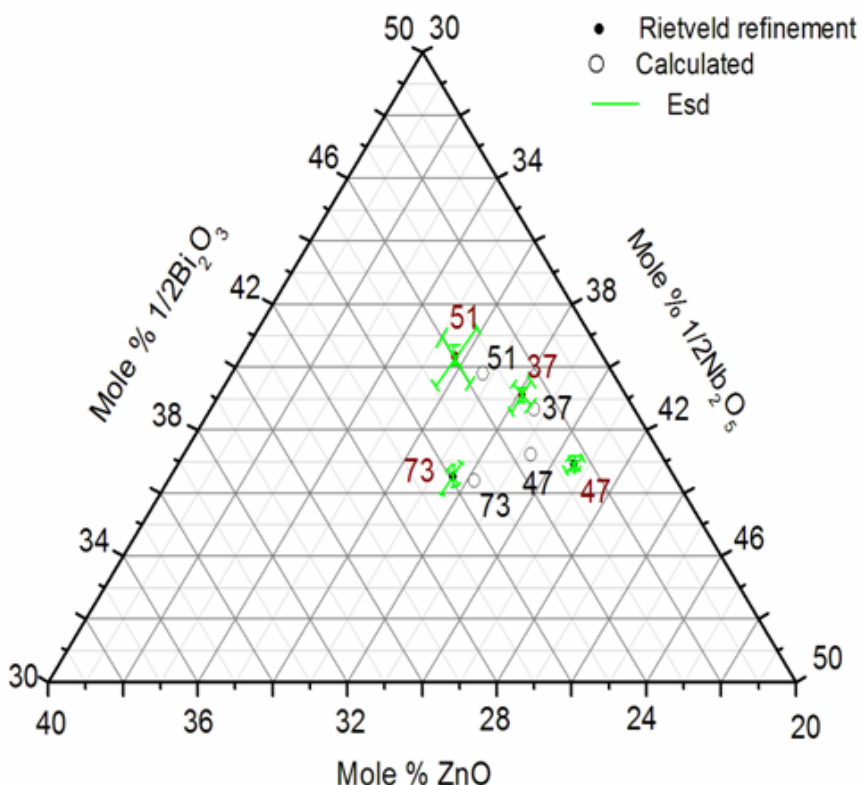


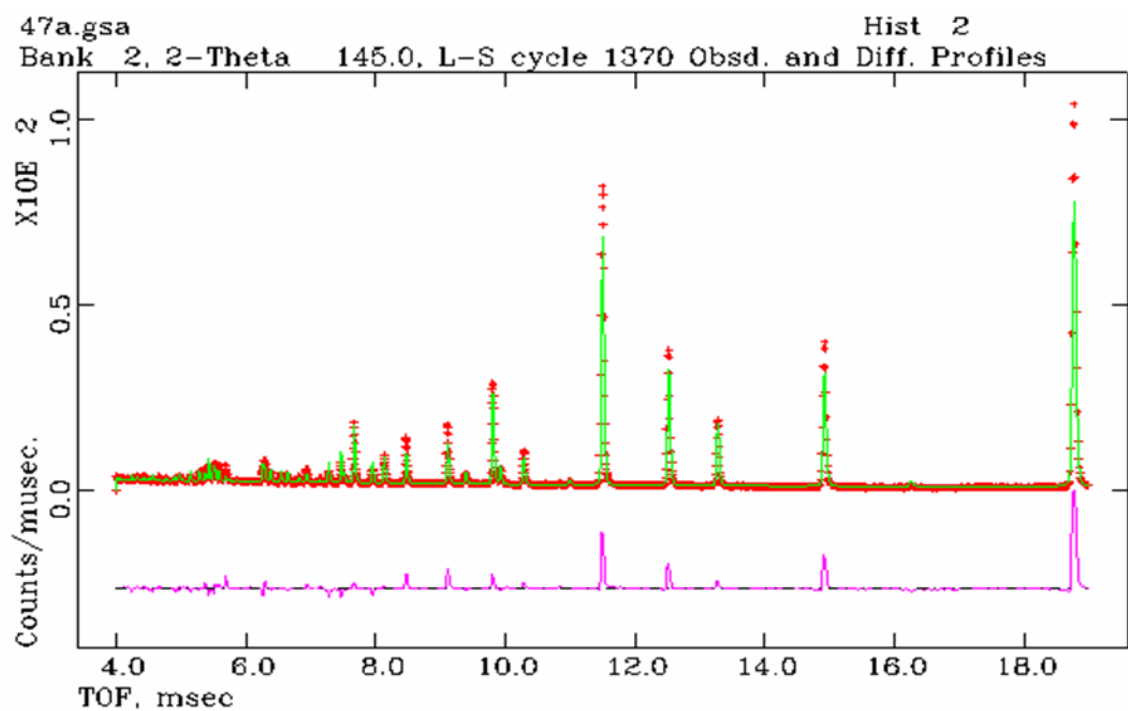
Figure 5: Refinement results of selected samples showing starting compositions (open circles) and compositions based on refined cation site occupancies

For a more complete structural analysis, in particular to study oxygen sites, powder ND data are required since XRD data are insensitive to oxygen positions in the presence of heavy atoms such as Bi and Nb. Composition 47, $\text{Bi}_{2.92}\text{Zn}_{1.84}\text{Nb}_{3.08}\text{O}_{13.52}$, was selected for further investigation of this nature; oxygen parameters and cation displacement were investigated using combined XRD and ND data. The starting model was identical to that of the X-ray refinement although the refined cation occupancies were inserted. No attempt was made to refine the cation occupancies further using combined XRD and ND as addition of ND data would serve no extra benefit here. Thermal parameters and occupancies of the cation sites were constrained and oxygen sites were fixed with occupancies of 1.0. The occupancies of O(1) and O(2) were then refined separately with fixed x parameter. Following this, the Uiso and O(1) x parameter were varied by the same procedure. The oxygen occupancies of both O(1) and O(2) were refined to 0.997 and 1.0, respectively. This was unexpected as oxygen vacancies are expected in

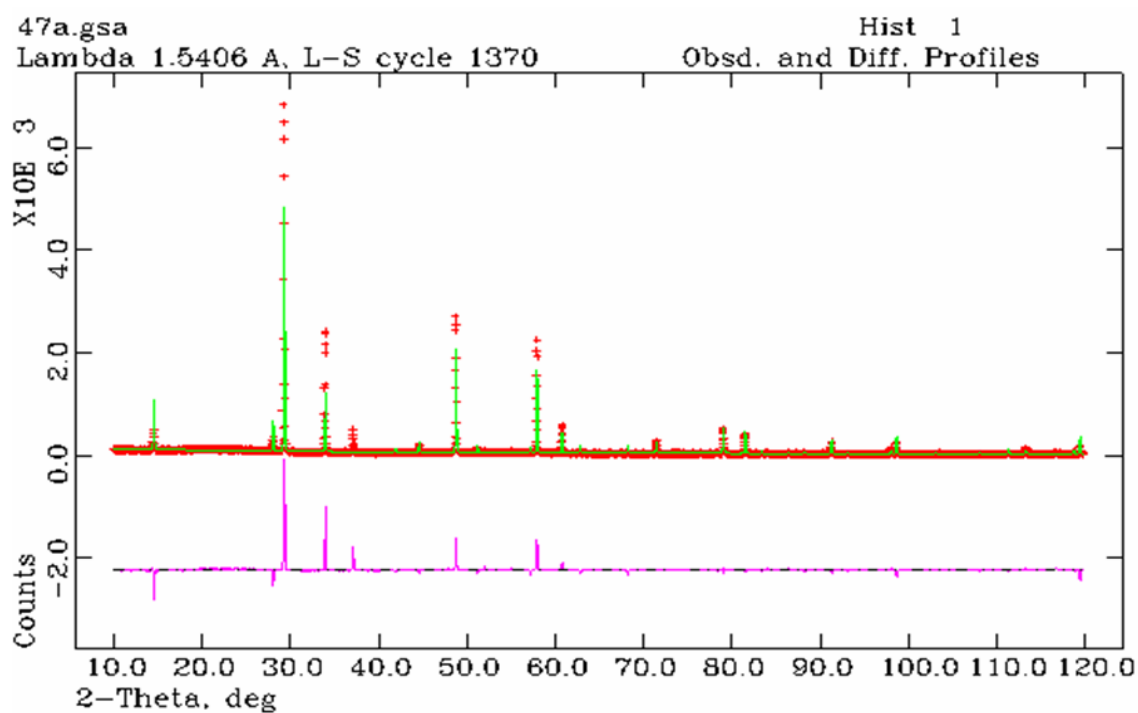
composition 47 in order to compensate for Zn deficiency and to maintain the charge neutrality as suggested by phase diagram analysis. When fully occupied, the thermal parameter for O(2) was very high, $0.099 \text{ \AA}^2$. However, when the oxygen occupancy was fixed at 0.75 in order to give the required number of oxygen vacancies for charge neutrality, the thermal parameter decreased to 0.0743. This suggests that O(2) is more stable with the presence of oxygen vacancies, hence, the model has been fixed in this way. The structural parameters and R factors are given in Table 5. The difference profiles for both XRD and ND data, Figures 6a and b, are relatively poor, however, and suggest that further structural probing is required.

Table 5: Refined structural parameter and R factors of composition 47 using XRD and ND data

Site	Atom	Wyckoff	x	y	Uiso (Å²)	Occupancy
A	Zn(1)	16d	0.5	0.5	0.0923(5)	0.262
	Bi		0.5	0.5		0.738
B	Zn(2)	16c	0.0	0.0	0.0103(6)	0.188
	Nb		0.0	0.0		0.812
O(1)	O(1)	48f	0.317(13)	0.125	0.0188	1.0
O(2)	O(2)	8b	0.375	0.375	0.0750	0.75
wRp	X = 14.9		Rp X = 11.79		Chi² = 14.44	
N = 7.79			N = 7.78			
Combined = 8.08			Combined = 11.58			



(a)



(b)

Figure 6: Refined difference profile for composition 47 (a) ND (b)

The O(1) positional parameter has a value, 0.317 which is at the lower end of the allowed x parameter range. This suggests that the B cation is in a stable undistorted octahedron, similar to composition 37 as discussed earlier. The thermal parameter on the B site was stable, 0.0103(6) Å², but that of the A site was unstable, 0.0923(5). This may be attributed, again, to difficulties with Bi and Zn sharing the same site. Also, ND may somehow dilute the XRD data in this case to give higher R values than those obtained for refinement of XRD data alone. The R values for XRD are higher than the R values for ND due to the high thermal parameter on the A site. The typical M-O oxide bond lengths within the pyrochlore structure are shown in Table 6 and a comparison is made between calculated bond lengths and those observed [10, 13] As discussed previously, A-O(1) bond distance, 2.60 Å, is too long for Zn. In accordance with research carried out by [5, 8], it was decided that a displacement model should be investigated. However, only preliminary refinement steps and results are discussed at this stage; whilst, a more comprehensive displacement model would be addressed later [14].

CONCLUSION

The structural properties of BZN cubic pyrochlores are successfully investigated by high resolution XRD and ND data using GSAS software. This study elucidates the use of Rietveld refinement to correlate the structural property with the compositions studied. In addition, this provides further insight into the pyrochlore structure and also confirmatory evidence for the existence of solid solutions with the mechanisms proposed. The refinement results of these four compositions are used to supplement the phase diagram results of the cubic pyrochlore solid solutions. The stoichiometry calculated from the refinement is in excellent agreement to the phase diagram-determined stoichiometry. On the other hand, a displacement model is required to address the high thermal parameters and relatively long bond distance for Zn(1) in order to stabilise the pyrochlore structure.

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