

Thermal expansion and cation disorder in $\text{Bi}_2\text{InNbO}_7$

Qingdi Zhou^a, Brendan J. Kennedy^{a,*}, Valeska Ting^b, Ray L. Withers^b

^aSchool of Chemistry, The Centre for Heavy Metals Research, The University of Sydney, F11 Sydney, New South Wales 2006, Australia

^bResearch School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Received 1 November 2004; received in revised form 9 December 2004; accepted 10 December 2004

Available online 27 March 2005

Abstract

The structure of the pyrochlore-type oxide $\text{Bi}_2\text{InNbO}_7$ has been investigated between room temperature and 700 °C using electron and synchrotron X-ray powder diffraction and at room temperature and 10 K using neutron diffraction methods. $\text{Bi}_2\text{InNbO}_7$ exhibits an $A_2B_2O_7$ cubic pyrochlore-type average structure at all temperatures that is characterized by an apparently random mixing of the In^{3+} and Nb^{5+} cations on the octahedral *B* sites. The Bi cations on the eight-coordinate pyrochlore *A* sites are displacively disordered, presumably as a consequence of their lone pair electron configuration. Heating the sample does not alter this disorder.

Crown Copyright © 2004 Published by Elsevier Inc. All rights reserved.

Keywords: Bismuth pyrochlore; Cation disorder; Thermal expansion

1. Introduction

Bi(III) containing oxides have been extensively studied as a consequence of their interesting and potential technologically important properties including ferroelectricity [1], catalytic activity [2] and ionic conductivity [3]. The rich diversity of physical properties displayed by Bi(III) oxides is thought to be a consequence of their unusual structural and electronic features induced, at least in part, by the Bi 6s lone pair electrons. The pyrochlore phase in the $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5\text{--ZnO}$ system, $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ is one such example and as a consequence of its attractive dielectric properties it is under investigation for use in high-frequency multilayer capacitors [4–6]. Another Bi–Nb pyrochlore, $\text{Bi}_2\text{InNbO}_7$ acts as a photocatalyst under UV radiation and the large band gap in this material, 2.7 eV, can be tuned by partially replacing the In with Fe [7,8]. Other interesting examples include $\text{Bi}_2\text{Ru}_2\text{O}_{7-d}$ which shows promise both as an electrocatalysts and as a thin film

resistor [9,10], and $\text{Bi}_2\text{Sn}_2\text{O}_7$ [11–13]. The later is of particular interest since its structure at room temperature is strongly distorted away from the ideal cubic pyrochlore one, and it only adopts the ideal structure at elevated temperatures [14].

The rich variety of properties displayed by Bi containing pyrochlores is often tuned by doping with another cation. The ease of substitution is related to the stability of the pyrochlore structure. Pyrochlores are often written as $A_2B_2O(1)_6O(2)$ to highlight the two types of O anions present. The structure can be described as consisting of a rigid three-dimensional network of corner sharing BO_6 octahedra with the $A_2O(2)$ atoms occupying interstitial sites to form a Cu_2O -type linear network. The $B_2O(1)_6$ and $A_2O(2)$ networks weakly interact through the *A*–O(1) interaction and vacancies in the $A_2O(2)$ network are common place. The desirable physical properties of pyrochlores can be tuned either by doping the cation sites or by the introduction of anion vacancies.

The aim of the present work was to investigate the temperature dependent structural properties of the mixed metal bismuth pyrochlore $\text{Bi}_2\text{InNbO}_7$, in

*Corresponding author. Fax: +61 2 9351 3329.

E-mail address: kennedyb@chem.usyd.edu.au (B.J. Kennedy).

particular we wished to establish the possibility that the Bi 6s electrons have a similar stereochemical activity to the related $\text{Bi}_2\text{Sn}_2\text{O}_7$ system.

2. Experimental

The polycrystalline sample of $\text{Bi}_2\text{InNbO}_7$ was prepared by a conventional ceramic method from a stoichiometric mixture of Bi_2O_3 , Nb_2O_5 and In_2O_3 . The sample was heated at successively higher temperatures (750 °C for 24 h and then 1100 °C for 48 h) in order to avoid any loss of volatile material and then slowly cooled to room temperature.

Powder neutron diffraction data were recorded on the high-resolution powder diffractometer at ANSTO's HIFAR reactor [15]. Data were collected in 0.05° steps over the angular range $10 \leq 2\theta \leq 150^\circ$ using 1.337 Å neutrons. The sample was held in a thin walled vanadium can. Temperature control was achieved using a closed cycle cryostat. Synchrotron X-ray powder diffraction data were recorded using the Debye–Scherrer diffractometer on beamline 20B, the Australian National Beamline Facility, at the Photon Factory, Tsukuba Japan [16]. Data were collected in 0.01° steps over the angular range $5 \leq 2\theta \leq 85^\circ$ using X-rays of wavelength 0.79628 Å. The sample was held in a 0.3 mm diameter quartz capillary and rotated throughout the measurements. Temperature control was achieved using a custom built furnace. Structures were refined using the Rietveld method as implemented in the program RIETICA [17].

3. Results and discussion

All the reflections observed in the powder X-ray diffraction pattern collected for $\text{Bi}_2\text{InNbO}_7$ at room temperature could be indexed to a cubic cell in $Fd\bar{3}m$ with $a = 10.79166(7)$ Å. The structure was first refined assuming the ideal pyrochlore structure type in which all the atoms, except for the O(1) anion, are on special positions, Table 1. The O(1) anions are located on 48f sites at $(x, \frac{1}{8}, \frac{1}{8})$ where the single variable positional parameter was refined to be 0.350(3) (see the refinement labeled “Ordered X-ray” in Table 1). Whilst the structural refinement was apparently satisfactory the refined displacement parameters for the various ions were each unusually large, allowing for the possibility of substantial displacive disorder. Moreover careful examination of the higher angle data revealed a number of reflections to be poorly modeled, Fig. 1. Since the Bi is by far the strongest scattering (for X-rays) it is most probable that the problem in the structural model is due to these cations.

The local environment of the Bi cation is a distorted scalenohedron and the possibility of anisotropic

Table 1

Representative results of the Rietveld refinements for $\text{Bi}_2\text{InNbO}_7$ at room temperature

Atom Site	x	y	z	B_{iso} (Å ²)
Ordered X-ray				
Bi 16d	0.5	0.5	0.5	2.74(6)
In/Nb 16c	0	0	0	3.00(8)
O(1) 48f	0.350(3)	0.125	0.125	7.6(7)
O(2) 8a	0.375	0.375	0.375	7.6(7)
Disordered 1 X-ray				
Bi 96h ^a	0	0.2249(1)	0.7751(1)	0.67(3)
In/Nb 16c	0	0	0	0.39(3)
O(1) 48f	0.322(1)	0.125	0.125	1.7(2)
O(2) 8a	0.375	0.375	0.375	1.7(2)
Disordered 2 X-ray				
Bi 96h ^a	0	0.2248(1)	0.7752(1)	0.69(4)
In/Nb 16c	0	0	0	0.38(3)
O(1) 48f	0.333(1)	0.125	0.125	1.5(2)
O(2) 32e ^a	0.360(2)	0.360(2)	0.360(2)	1.5(2)
Disordered 2 Neutron				
Bi 96h ^a	0	0.2249(1)	0.7751(1)	0.96(7)
In/Nb 16c	0	0	0	0.61(3)
O(1) 48f	0.3254(1)	0.125	0.125	2.3(3)
O(2) 32e ^a	0.3560(3)	0.3560(3)	0.3560(3)	1.4(2)

^aPartial occupancy of the site, as appropriate for the stoichiometry, occurs.

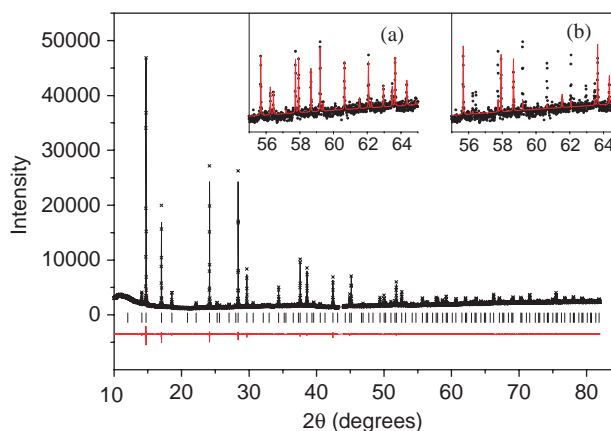


Fig. 1. The observed, calculated and difference synchrotron X-ray diffraction pattern of $\text{Bi}_2\text{InNbO}_7$ at room temperature. The inserts show the detail of the fit between 55° and 65° for (a) the disordered model described in the text and (b) the ideal ordered structure.

displacement of the Bi cations was then considered. Although this led to an improvement in the quality of the refinements a number of reflections, however, still remained poorly fitted. The introduction of vacancies onto the Bi site was tried next but did not significantly improve the quality of the fit. The compound thus appears to be stoichiometric with respect to Bi. In this respect $\text{Bi}_2\text{InNbO}_7$ is different to other Bi pyrochlores

such as $\text{Bi}_{1.89}\text{Ru}_2\text{O}_{6.92}$ [18], $\text{Bi}_{1.89}\text{GaSbO}_{6.84}$ [19] and $\text{Bi}_{1.95}\text{Rh}_2\text{O}_{6.83}$ [20] studied recently.

Recent studies of $\text{Bi}_{2-x}\text{Yb}_x\text{Ru}_2\text{O}_{7-d}$ [21] and $\text{Bi}_2\text{CrTaO}_7$ [22] have demonstrated that static displacive disorder of the Bi cations from the $16d$ ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) site to a $96h$ ($0\ y\ -y$) site occurs in Bi pyrochlores. Such a model was therefore tested for $\text{Bi}_2\text{InNbO}_7$. This lead to a significant improvement in the fit, a large change in the unknown x parameter of O(1) (from 0.350 to 0.322) and a significant reduction in the magnitudes of the refined displacement parameters for all sites (see the refinement labeled “Disordered 1 X-ray” in Table 1). The effect of this Bi displacive disorder is very clear in Fig. 1. As noted by Avdeev et al. [23], displacement of the Bi away from the $16d$ sites is expected to force the O(2) atoms away from the $8b$ ($\frac{3}{8}\frac{3}{8}\frac{3}{8}$) sites to a disordered $32e$ (xxx) site. Attempts to verify this using the synchrotron diffraction data (see the refinement labeled “Disordered 2 X-ray” in Table 1) were inconclusive.

High-resolution powder neutron diffraction data were then collected for the sample of $\text{Bi}_2\text{InNbO}_7$ using 1.33 \AA neutrons. Using this wavelength is expected to improve the precision in the determination of the displacement parameters of the various atoms due to the increased d -range to 0.68 \AA , compared to 0.96 \AA if 1.88 \AA neutrons had been employed. In order to further augment the results a second diffraction pattern was collected with the sample cooled to 10 K . A satisfactory fit to the neutron diffraction data at both temperatures was obtained where the O(2) anions occupied the $32e$ sites (see the refinement labeled “Disordered 2 Neutron” in Table 1). The refinement R -factors for the 10 K neutron diffraction data show a significant improvement once the Bi is allowed to disorder from the $16d$ site. $R_p = 5.98$ and $R_{wp} = 8.74\%$ in the ordered model decrease to 4.6 , 6.02% in disordered model 1 and 4.46 and 5.73% in disordered model 2. The small improvement in the R -factors on allowing disorder of the O(2) anions is accompanied by a significant decrease in the displacement parameter for this anion from $6.4(2)\text{ \AA}^2$ in disordered model 1 to $1.3(2)\text{ \AA}^2$ in disordered model 2.

In the ideal pyrochlore structure type, Fig. 2, the Bi sites lie in the center of a puckered hexagon of O(1) atoms (see Fig. 3), with the Bi–O(1) distance being $2.707(1)\text{ \AA}$. The eightfold co-ordination geometry of the Bi ion is completed by the two, much closer, apical O(2) atoms at $2.337(1)\text{ \AA}$. The $0.0251\ \langle 1\bar{1}0 \rangle$ ($= 0.3831\text{ \AA}$) displacive shifts of the Bi ions occur in the plane of the puckered hexagon so that it now has three distinct Bi–O(1) bonds distances at $2.361(1)$, $2.706(2)$ and $3.011(1)\text{ \AA}$ with the two apical O(2) atoms remaining around $2.366(2)\text{ \AA}$ away. In both geometries the Bi is noticeably underbonded, bond valence calculations giving BVS of 2.2 and 2.4 , respectively. Displacement of the O(2) anions onto the $32e$ sites does not alter the effective bond valence of the Bi cations since moving the

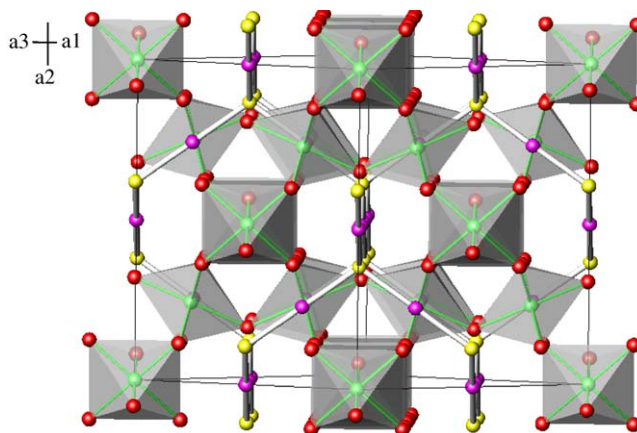


Fig. 2. View of the ideal $A_2B_2O_6O'$ pyrochlore structure, highlighting the interpenetration of the networks of B_2O_6 corner sharing octahedra and the A_2O' chain.

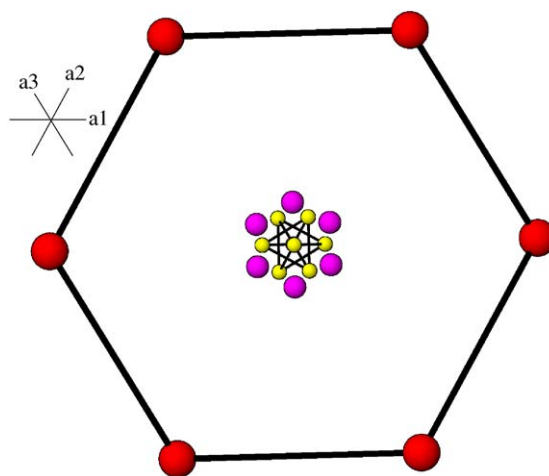


Fig. 3. View of the local disorder in $\text{Bi}_2\text{InNbO}_7$ looking along the Bi_2O chains. The large outer spheres represent the O(1) atoms that form the $(\text{InNb})_2\text{O}_6$ pyrochlore framework. The medium size spheres represent the Bi atoms showing 6-fold disorder as a result of the 011 displacement of the Bi atoms away from the edge of the $(\text{In/Nb})\text{O}_6$ octahedra. The smallest spheres illustrate the 4-fold disorder of the O(2) atoms.

O(2) off-center in its tetrahedron of surrounding Bi ions will reduce one Bi–O(2) distance but simultaneously increase three others.

Structured diffuse scattering (in the form of sheets of diffuse intensity perpendicular to the six $\langle 110 \rangle$ directions of the average structure) observed in electron diffraction patterns (see Fig. 4) is identical in form to that characteristic of β -cristobalite implying the existence of β -cristobalite-type orientational disorder of essentially rigid, O(2) Bi_4 tetrahedra within the pyrochlore average structure type [24,25]. It is thus believed that the O(2) Bi_4 tetrahedra rotate as essentially rigid bodies with the O(2) remaining in the center of the tetrahedra. The In and Nb are apparently statistically distributed at the center of octahedra in the B_2O_6

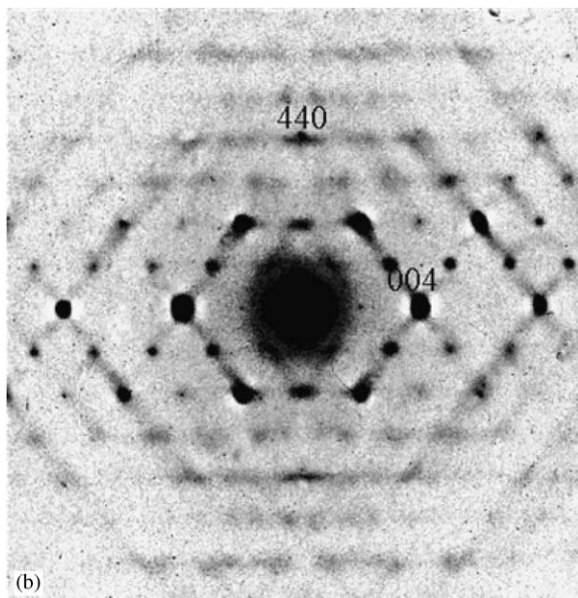
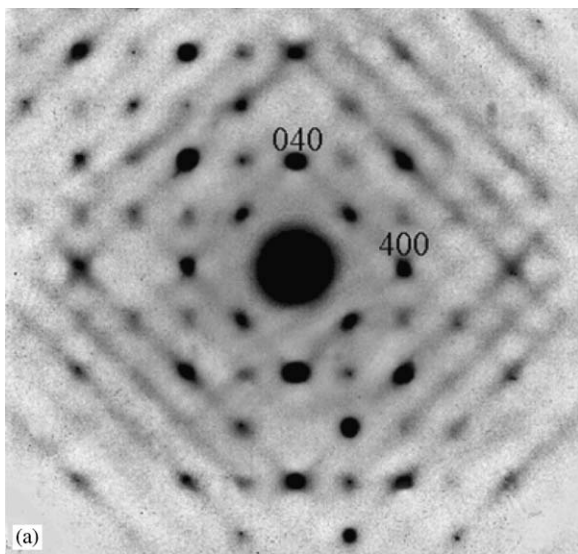


Fig. 4. Electron diffraction pattern of $\text{Bi}_2\text{InNbO}_7$ showing the characteristic polarized $\{110\}$ sheets of diffuse intensity.

network. The observed (In/Nb)–O(1) bond distance is 2.0740(6), being smaller than expected for a In(III)–O bond and longer than a typical Nb(V)–O distance. The bond valence for both sites is approximately 4, however we do not believe this indicates the stabilization of unusual oxidation states for In or Nb. The fact that $\text{Bi}_2\text{InNbO}_7$ is pale yellow is consistent with the nominal oxidation states. It is likely that there is some disorder of the O(1) anions on a local scale depending upon whether it is bonded to two In's, two Nb's or one In and one Nb. This is not observed, however, since the diffuse scattering is dominated by the heavier Bi cations.

The disorder of the Bi cations suggests little if any Bi actually occupies the average $16d$ positions. The observed displacive disorder of the Bi cations (in the plane of the puckered hexagon of surrounding O(1)

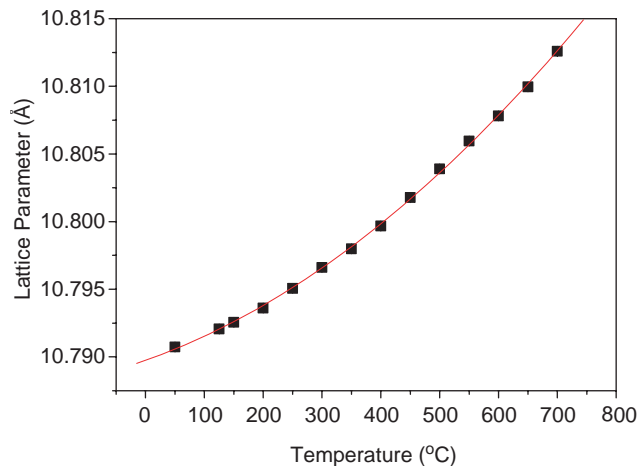


Fig. 5. Temperature dependence of the lattice parameter of $\text{Bi}_2\text{InNbO}_7$ obtained from powder synchrotron X-ray diffraction data.

ions) is in fact strongly reminiscent of the displacive disorder seen in a range of rare earth zirconate and titanate pyrochlores (see, e.g. Tabira et al. [24]). The characteristic signature of the displacive disorder in these cases was the existence of an extremely characteristic diffuse intensity distribution (in the form of transverse polarized sheets of diffuse intensity perpendicular to the six $\langle 110 \rangle$ directions) identical in form to that shown by the high-temperature β polymorph of SiO_2 cristobalite [25]. The existence of this characteristic diffuse intensity distribution was shown to imply the existence of β -cristobalite like orientational disorder of essentially rigid, $\text{O}(2)(\text{A})_4$ tetrahedra within the average pyrochlore structure type. The existence of an essentially identical diffuse intensity distribution in the current case (see Fig. 4) thus implies the displacive disorder of the Bi ions arises from correlated tetrahedral rotation $\text{O}(2)\text{Bi}_4$ tetrahedra.

Displacive disorder of Bi cations has also been observed in $\text{Bi}_2\text{Sn}_2\text{O}_7$ at elevated temperatures, and further heating of this oxide results in a transition to an ordered structure [14]. To investigate the possibility of this occurring in $\text{Bi}_2\text{InNbO}_7$ a number of synchrotron X-ray diffraction data sets were collected at successively higher temperatures. Analysis of the data showed no evidence for a transition to an ordered Bi distribution, to 700 °C, the highest temperature studied, Fig. 5 and Table 2. As expected the cubic structure shows a systematic increase in size as the temperature is increased, Fig. 5. The refined Bi positional parameter showed an almost linear dependence on temperature resulting in the systematic reduction in the magnitude of the displacement illustrated in Fig. 6. It is evident from this figure that considerably higher temperatures would be required if the Bi was to become localized at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ assuming a continuous transition from the disordered to ordered structures.

Table 2
Representative results of the Rietveld refinements for $\text{Bi}_2\text{InNbO}_7$ at 700°C

Atom	Site	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$
	Ordered	X-ray	R_p 3.02	R_{wp} 3.78	$a = 10.81386(7) \text{\AA}$
Bi	16d	0.5	0.5	0.5	4.96(8)
In/Nb	16c	0	0	0	0.41(4)
O(1)	48f	0.331(1)	0.125	0.125	0.5(2)
O(2)	8a	0.375	0.375	0.375	0.5(2)
	Disordered 1	X-ray	R_p 2.70	R_{wp} 3.32	
Bi	96h*	0	0.2269(1)	0.7731(1)	0.78(5)
In/Nb	16c	0	0	0	0.08(4)
O(1)	48f	0.329(1)	0.125	0.125	0.6(2)
O(2)	8a	0.375	0.375	0.375	0.6(2)

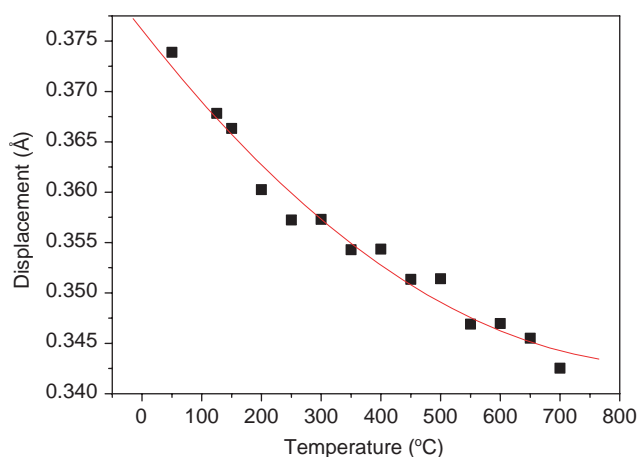


Fig. 6. Temperature dependence of the magnitude of the Bi cation displacement in $\text{Bi}_2\text{InNbO}_7$.

Acknowledgments

The authors gratefully acknowledge the support of this work from the Australia Research Council. Synchrotron diffraction measurements were performed at the Australian National Beamline Facility with support from the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program. Neutron diffraction measurements were supported by the Australian Institute of Nuclear Science and Engineering. The authors also gratefully acknowledge Dr. Margaret Elcombe for help with the

neutron data collection, and Dr. James Hester for assistance at ANBF.

References

- [1] E.C. Subbarao, *J. Phys. Chem. Solids* 23 (1962) 665.
- [2] D.J. Buttrey, T. Vogt, U. Wildgruber, W.R. Robinson, *J. Solid State Chem.* 111 (1994) 118.
- [3] N. Yasuda, M. Miyayama, T. Kudo, *Solid State Ion.* 133 (2000) 273.
- [4] A. Mergen, W.E. Lee, *Mater. Res. Bull.* 32 (1997) 175.
- [5] R.L. Withers, T.R. Welberry, A.-K. Larsson, Y. Liu, L. Norén, H. Rundlöf, F.J. Brink, *J. Solid State Chem.* 177 (2004) 231.
- [6] I. Levin, T.G. Amos, J.C. Nino, T.A. Vanderah, C.A. Randall, M.T. Lanagan, *J. Solid State Chem.* 168 (2002) 69.
- [7] Z. Zou, J. Ye, H. Arakawa, *Solid State Commun.* 116 (2000) 259.
- [8] Z.G. Zou, J.H. Ye, R. Abe, H. Arakawa, *Catal. Lett.* 68 (2000) 235.
- [9] G. Facer, M.M. Elcombe, B.J. Kennedy, *Aust. J. Chem.* 46 (1993) 1987.
- [10] R.A. Beyerlein, H.S. Horowitz, J.M. Longo, M.E. Leonowicz, J.D. Jorgensen, F.J. Rotella, *J. Solid State Chem.* 51 (1984) 253.
- [11] I. Radosavljevic, J.S.O. Evans, A.W. Sleight, *J. Solid State Chem.* 136 (1998) 63.
- [12] R.H. Jones, K.S. Knight, *J. Chem. Soc. Dalton Trans.* 15 (1997) 2551.
- [13] I. Radosavljevic Evans, J.A.K. Howard, J.S.O. Evans, *J. Mater. Chem.* 13 (2003) 2098.
- [14] B.J. Kennedy, Ismunandar, M.M. Elcombe, *Mater. Sci. Forum* 278–281 (1008) 762.
- [15] C.J. Howard, C.J. Ball, R.L. Davis, M.M. Elcombe, *Aust. J. Phys.* 36 (1983) 507.
- [16] T.M. Sabine, B.J. Kennedy, R.F. Garrett, G.J. Foran, D.J. Cookson, *J. Appl. Crystallogr.* 28 (1995) 513.
- [17] C.J. Howard, B.A. Hunter, *A Computer Program for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns*, Lucas Heights Research Laboratories, NSW, Australia, 1998, pp. 1–27.
- [18] R.E. Carbonio, J.A. Alonso, J.L. Martinez, *J. Phys.: Condens. Matter* 11 (1999) 361.
- [19] Ismunandar, B.J. Kennedy, B.A. Hunter, *J. Solid State Chem.* 130 (1996) 81.
- [20] B.J. Kennedy, *Mater. Res. Bull.* 32 (1997) 479.
- [21] L. Li, B.J. Kennedy, *Chem. Mater.* 15 (2003) 4060.
- [22] Ismunandar, T. Kamiyama, K. Oikawa, A. Hoshikawa, B.J. Kennedy, Y. Kubota, K. Kato, *Mater. Res. Bull.* 39 (2004) 553.
- [23] M. Avdeev, M.K. Haas, J.D. Jorgensen, R.J. Cava, *J. Solid State Chem.* 169 (2002) 24.
- [24] Y. Tabira, R.L. Withers, T. Yamada, N. Ishizawa, *Z. Krist.* 216 (2001) 92.
- [25] R.L. Withers, J.G. Thompson, T.R. Welberry, *Phys. Chem. Min.* 16 (1989) 517.