Cation disorder and structural studies on $Bi_{4-x}Nd_xTi_3O_{12}$ $(0.0 \leq x \leq 2.0)$

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Abstract. Here we report the results of combined powder X-ray and neutron diffraction studies of $Bi_{4-x}Nd_xTi_3O_{12}$ $(0.0 \leq x \leq 2.0)$ compositions. The parent $Bi_4Ti_3O_{12}$ has an orthorhombic lattice (space group: B2cb) with unit cell parameters $a = 5.4432(5)$ Å, $b = 5.4099(5)$ Å and $c = 32.821(2)$ Å, and $V = 966.5(1)$ Å^3. This orthorhombic lattice is retained in all the studied compositions. The unit cell parameters gradually decrease with Nd^{3+} ion concentration with a discontinuity at $x = 0.75$. Orthorhombicity of the lattice decreases with increase in Nd^{3+} content in the lattice. The orthorhombic unit cell parameters for a representative $Bi_2Nd_2Ti_3O_{12}$ composition are: $a = 5.3834(9)$, $b = 5.3846(9)$ and $c = 32.784(1)$ Å. The observed orthorhombic distortion at $x = 2.0$ is very small and thus the crystal structure apparently has a pseudo-tetragonal lattice. In addition, Nd^{3+} preferentially substitutes in the perovskite slab of the Aurivillius structure. The fraction of Nd^{3+} in the fluorite slab increases with increase in Nd^{3+} contents.

1. Introduction

Recently, lead-free ferroelectric materials have drawn a significant interest for environmental friendly storage and logic electronic devices. In this aspect, $Bi_4Ti_3O_{12}$ (BTO) and its related compounds of Aurivillius family have been considered as potential materials [1]. The Aurivillius compounds are intergrowth compounds of perovskite and fluorite lattices and the compositions can be written as $[M_2O_2]^{+2}[A_{m-1}B_mO_{3m+1}]^{2-}$, where $M = Bi^{3+}$ and m = thickness of perovskite slab. In the BTO structure, A and B cations are Bi^{3+} and Ti^{4+}, respectively, and have a three layer perovskite slab sandwiched between the Bi_2O_2 layers [2]. In the perovskite slab, both A and B sites are amenable for iso- or heterovalent cation substitutions. However, the Bi_2O_2 layers usually remain unsubstituted. Several

Table 1. Refined crystallographic parameters of BTO.

Atoms	Wyc.	x	y	z	B (Å)^2	Occ.
Bi1	8b	0.00000*	0.998(1)	0.0669(1)	0.69(7)	1
Bi2	8b	1.007(2)	0.019(1)	0.2111(1)	0.60(6)	1
Ti1	4a	0.044(3)	0	0.5	0.46*	1
Ti2	8b	0.048(2)	0.994(3)	0.3707(2)	0.46*	1
O1	8b	0.335(2)	0.267(2)	0.0068(3)	1.4(2)	1
O2	8b	0.276(2)	0.259(2)	0.2486(3)	0.4(1)	1
O3	8b	0.083(2)	1.072(2)	0.4403(2)	0.7(1)	1
O4	8b	1.048(3)	0.948(2)	0.3189(2)	1.0(2)	1
O5	8b	0.305(2)	0.257(2)	0.1114(2)	0.5(1)	1
O6	8b	0.224(2)	0.198(2)	0.8763(3)	1.5(2)	1

Space Group: B2cb; $a = 5.4461(4)$ Å, $b = 5.4091(4)$ Å, $c = 32.822(2)$ Å, $V = 966.9(1)$ Å^3; Bi1 (perovskite sublattice) and Bi2 (fluorite sublattice); R_{p}: 5.12 (7.99), $R_{\mathrm{wp}} = 6.55(10.6)$, $\chi^2 = 2.79(3.54)$, $R_{\mathrm{B}} = 5.12(5.67)$; $R_{\mathrm{F}} = 3.24(3.32)$ (numbers in parentheses are for X-ray diffraction data).
*Kept as invariants in refinements.

reports also indicate that lone pair containing cations as well as highly polarizable cations can be substituted in place of Bi^{3+} of Bi_2O_2 layer [3,4]. Extensive studies on the $Bi_4Ti_3O_{12}$ and Ln^{3+} (lanthanide)-substituted BTO suggest that optimum Ln^{3+}-substituted compositions are more useful than the parent BTO. The lanthanide-substituted BTO has been of interest for the fatigue-free ferroelectric performance. In general, ferroelectricity is a crystal structure related property of materials. Thus, accurate crystal structure information is essential to explain such properties. The variation of structures of perovskite and related compounds originating from tilting of the rigid octahedral units can be confirmed from the accurate location of the oxygen atoms. The location of oxygen atoms in the presence of heavy scatterer like Bi^{3+}, can be unequivocally determined from neutron diffraction studies. However, accurate unit cell parameters and symmetry can be more conveniently determined from X-ray diffraction studies. In addition, the problem of negative scattering length and large incoherent scattering cross-section of Ti can be compensated by the simultaneous refinement of neutron and X-ray diffraction data. The variations in crystal structure as well as the cation distribution in the two possible sites of Bi^{3+}, namely, fluorite and perovskite sites, are obtained by combined XRD and ND studies and the results are explained in this manuscript.

2. Experimental

Polycrystalline samples of $Bi_{4-x}Nd_xTi_3O_{12}$, for $x = 0.00, 0.75, 1.00$ and 2.00, were prepared by conventional solid state reaction of pre-heated Bi_2O_3, Nd_2O_3 and TiO_2. Crystalline phase pure products were obtained by heating pellets of homogeneous mixture of reactants at 1200°C. The powder XRD data were collected on Philips X'pert-pro diffractometer in the angle range of 10–110° with step width of 0.02°, using Ni filtered CuKα radiation. The powder neutron diffraction data

of the samples were collected at Dhruva research reactor in the angle range of 3–140° using monochromatized neutron wavelength of 1.249 Å. The observed X-ray and neutron diffraction data were analysed by Rietveld method using the Fullprof software package [5]. The details of the structural refinements and analysis are explained later.

3. Results and discussion

The crystal structure of BTO is well-known as an intergrowth structure of fluorite and three-layer perovskite lattices. However, the symmetry of the BTO is still under debate. The crystal structure and polarization of BTO have been explained with an orthorhombic (space group B2cb) [3] and a monoclinic (space group P1a1) lattice [6]. The present observed XRD pattern shows no characteristic monoclinic distortion. The accurate unit cell parameters of the orthorhombic lattice were
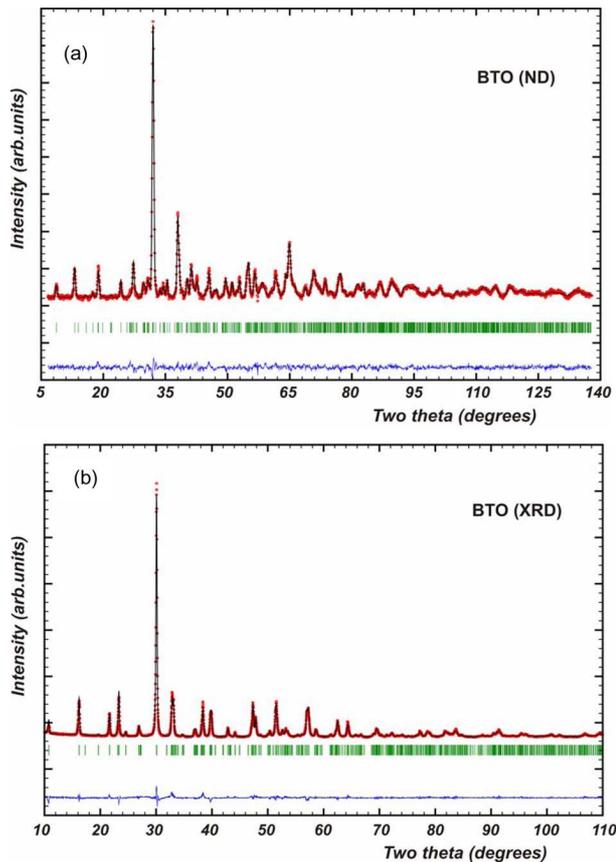

Figure 1. Typical Rietveld refinement plots for $Bi_4Ti_3O_{12}$ (**a**) ND and (**b**) XRD.

obtained by profile refinement of powder XRD data. Subsequently, Rietveld refinements of the powder XRD and neutron diffraction data were carried out together. Pseudo-Voigt profile function was used to refine the peak profile. The backgrounds of the powder X-ray and neutron diffraction patterns were modelled with a fifth-order polynomial function and linear interpolation of selected background points, respectively. Preferred orientation parameters were refined for the X-ray data only. Subsequently the position coordinates and thermal parameters were refined. The refined structural parameters of BTO are given in table 1. The final Rietveld refinement XRD and ND plots for BTO are shown in figure 1.

The observed diffraction data of the Nd^{3+}-substituted samples were similarly refined with a starting model based on the structure of parent BTO. In the initial model, the available Nd^{3+} atoms of the nominal compositions were distributed equally in two crystallographic sites of Bi, namely 8b (fluorite site) and 8b (perovskite site). The X-ray diffraction pattern was used to constrain the unit cell parameters of the neutron diffraction data. In the refinement of the position coordinates and thermal parameters more weights were given to the neutron data. Further, the occupancies of Nd^{3+} in the two sites were refined with a constraint limited by the initial nominal compositions. The refined unit cell parameters and the residuals of the refinements are given in table 2. The final Rietveld refinement plot of ND data of $Bi_2Nd_2Ti_3O_{12}$ is shown in figure 2a. It is observed that both a and b-parameters decrease with Nd^{3+} contents in all the nominal compositions. However, the c-parameter increases up to the nominal composition with $x = 0.75$ and then decreases. Also, the orthorhombic distortion gradually decreases with the increase in Nd^{3+} concentration. The distribution of Nd^{3+} in the fluorite and perovskite sublattices shows that Nd^{3+} preferentially substitutes the perovskite than fluorite sublattice. But the fraction of Nd^{3+} in the fluorite sublattice increases

Table 2. Comparison of crystallographic data of various nominal compositions.

	$Bi_4Ti_3O_{12}$	$Bi_{3.25}Nd_{0.75}Ti_3O_{12}$	$Bi_{3.00}Nd_{1.00}Ti_3O_{12}$	$Bi_2Nd_2Ti_3O_{12}^*$
Sym.	B2cb (No. 41)	B2cb (No. 41)	B2cb (No. 41)	B2cb (No. 41)
a (Å)	5.4461(4)	5.4117(4)	5.4055(6)	5.3834(9)
b (Å)	5.4091(4)	5.4003(5)	5.3959(6)	5.3846(9)
c (Å)	32.822(2)	32.834(1)	32.827(2)	32.784(1)
V (Å)^3	966.9(1)	959.6(2)	957.5(2)	950.3(2)
R_p, R_{wp}, χ^2	5.12, 6.55, 2.79	3.06, 4.35, 1.88	3.31, 4.99, 2.41	4.24, 5.4, 2.36
R_B	5.67	5.74	6.00	4.73
D	3.4×10^{-3}	1.05×10^{-3}	0.8×10^{-3}	0.1×10^{-3}
N_{Nd1}	0	0.092	0.160	0.378
% of Nd	0	12	16	19
N_{Nd2}	0	0.658	0.840	1.622
% of Nd	0	88	84	81

*Residuals for I4/mmm model: $R_p = 4.25$, $R_{wp} = 5.62$, $\chi^2 = 2.42$ and $R_B = 5.47$; D: orthorhombicity defined as $(|b - a|)/(b + a)$; N_{Nd1} and N_{Nd2}: Total atoms per formula unit (occ. number) in fluorite and perovskite sublattice; % of Nd: percent of total Nd occupied in fluorite sub-lattice and perovskite sublattice.
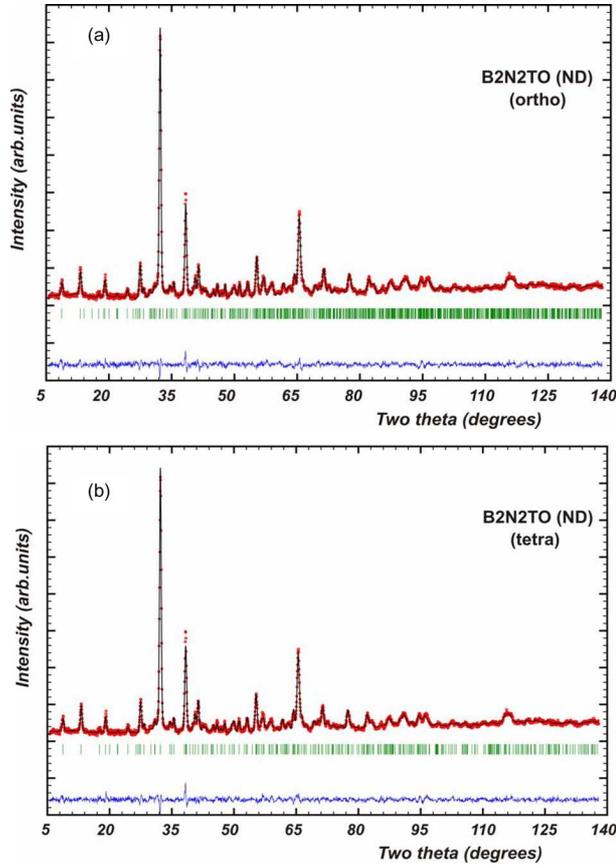
Figure 2. Typical Rietveld refinement plots for $Bi_2Nd_2Ti_3O_{12}$ (**a**) B2cb and (**b**) I4/mmm.

with Nd^{3+} concentration of the nominal composition. The refined unit cell parameters of $Bi_2Nd_2Ti_3O_{12}$ (i.e., $x = 2.0$) indicate an insignificant orthorhombic distortion, and thus can be expected to have a tetragonal or pseudo-tetragonal lattice. The diffraction data observed for $Bi_2Nd_2Ti_3O_{12}$ has also been refined with a model based on the prototype tetragonal (I4/mmm) lattice of BTO. The refined unit cell parameters of the tetragonal lattice are: $a = b = 3.8072(1)$ Å and $c = 32.783(1)$ Å. The final Rietveld plot of the ND data is shown in figure 2b. This tetragonal unit cell can be related to the earlier mentioned orthorhombic unit cell as: $a_o = a_T - b_T, b_o = a_T + b_T, c_o = c_T$. The residuals of the refinements (in particular R_B) are higher in the tetragonal symmetry compared to those in orthorhombic symmetry (table 2). In addition, the observed ferroelectric behaviour of $Bi_2Nd_2Ti_3O_{12}$ supports the non-centrosymmetry in the unit cell. Thus a polar subgroup of I4/mmm, namely, Fmmm, Fmm2 and B2cb are the possible space groups for $Bi_2Nd_2Ti_3O_{12}$. Based on the lower residuals of refinements we conclude that structure of $Bi_2Nd_2Ti_3O_{12}$ is orthorhombic.

The tilting of the TiO_6 octahedra as well as off-centre displacement of Ti^{4+} and Bi^{3+} transform the prototype tetragonal phase of BTO to orthorhombic ferroic phase. The tilts of the octahedral units are usually resulted from the cooperative displacement of oxygen atoms which may either be due to temperature/pressure or ionic size of the stuffed cation. The smaller ionic radius of the stuffed cation shows higher tilting and hence lower symmetry. A cation with a lone pair can also cause a tilting of octahedra due to the asymmetric charge cloud. Thus, the presence of Bi^{3+} in the perovskite of all the studied compositions may be a plausible reason for the distortion.

4. Conclusions

Crystal structure and unit cell parameters of $Bi_{4-x}Nd_xTi_3O_{12}$ ($0.0 \leq x \leq 2.0$) are obtained from combined ND and XRD studies. The orthorhombic structure of parent $Bi_4Ti_3O_{12}$ is retained in all the compositions. However, the orthorhombicity decreases with the increase in Nd^{3+} substitution. The orthorhombic distortions in all the compositions are related to the Bi^{3+} ions of the perovskite sub-lattice. Besides, it is also concluded that non-lone pair cation like Nd^{3+} can partially substitute the Bi^{3+} of the fluorite slab of Aurivillius compounds, but they preferentially occupy only the perovskite sub-lattice.

References

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