

Structure of Bi₂Nd₄O₉ Monoclinic Phase

Y. C. Lan,* X. L. Chen,*¹ and J. Q. Li†

*Institute of Physics and Centre for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China; and

†National Laboratory of Superconductivity, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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A new phase, Bi₂Nd₄O₉, was synthesized in the binary system Bi₂O₃–Nd₂O₃ and structurally characterized from powder X-ray diffraction data. It crystallizes in monoclinic symmetry with lattice parameters $a = 6.7037(2)$ Å, $b = 3.9062(1)$ Å, $c = 3.9542(1)$ Å, $\beta = 125.258(1)^\circ$, $Z = 2$, and a subcell space group of $C2/m$. Its average structure had been determined by X-ray powder diffraction and refined by the Rietveld method. The average structure can be described as an oxygen-deficient fluorite structure of the δ -Bi₂O₃ type with Nd and Bi randomly distributed on the cation site, similar to Bi₂La₄O₉, reported by Chen *et al.* (*J. Solid State Chem.* 124, 300 (1996)). In addition, a strong superstructure had been observed by transmission electron microscopy. © 2000 Academic Press

Key Words: Rietveld refinement; superstructure; Bi₂Nd₄O₉.

I. INTRODUCTION

The binary systems Bi₂O₃–Ln₂O₃ ($Ln = Y, La-Lu$) have been widely investigated over the Bi-rich region (1–7) because δ -Bi₂O₃ and doped Bi₂O₃ with fluorite-like structures exhibit high ionic conductivity. On the other hand, the Ln-rich side of the binary systems has also been explored (1,2,5–10) as the phases with high concentrations of Ln were expected to exhibit various types of magnetic ordering at low temperature (8). A large group of rhombohedral phases (Bi₃Ln₅O₁₂) (8, 9) and orthorhombic compounds (Bi₈La₁₀O₂₇) (11) has been characterized. Recently, Chen *et al.* (1) observed a new monoclinic phase, Bi₂La₄O₉, with the lattice parameters $a = 6.8290(3)$ Å, $b = 3.9887(1)$ Å, $c = 4.0524(1)$ Å, $\beta = 125.094(3)^\circ$, and space group $C2/m$.

In the present work, a monoclinic compound Bi₂Nd₄O₉ was synthesized in the Nd-rich Bi₂O₃–Nd₂O₃ system. Here we report X-ray diffraction data and the average structure of the monoclinic phase.

II. EXPERIMENTAL

The compound was prepared by solid-state reaction of mixtures of Nd₂O₃ (purity 99.99%) and Bi₂O₃ (purity

¹To whom correspondence should be addressed. E-mail: xlchen@aphy.iphy.ac.cn.

99.99%). Before weighing, Nd₂O₃ was preheated at 900°C for 12 h to remove the carbon dioxide and water it absorbs in air. The mixture was ground, preheated at 800°C for 12 h in air, and then fired at 1100°C for 5–7 days with intermediate grindings. The sample was finally quenched at room temperature in air. The weight loss, presumably due to Bi₂O₃ vaporization during heating, was always less than 0.8% of the total sample weight (1).

Phase identification, determination of lattice parameters, and Rietveld refinement were performed on a Rigaku diffractometer using CuK α radiation at room temperature. For phase identification, the data were collected in the normal scanning mode from 10° to 80°. The lattice parameters were calculated with the program DICVOL91 (12). For Rietveld refinement, the data were collected in the step scanning mode with steps of 0.02° (2θ). An angular range from $2\theta = 25^\circ$ to 130° and a measuring time of 1 s per step were applied. The divergence, scattering, and receiving slits were set at 1°, 1°, and 0.1 mm, respectively. A total of 5251 points with a maximum count of 17,193 and 83 independent reflections were measured.

The observed powder diffraction data of Bi₂Nd₄O₉ are given in Table 1. The main peaks can be indexed using a monoclinic subcell with lattice parameters $a = 6.7037(2)$ Å, $b = 3.9062(1)$ Å, $c = 3.9542(1)$ Å, and $\beta = 125.258(1)^\circ$ ($F(25) = 52.2$). The observed condition for diffraction allows for the space group $C2/m$, $C2$, or Cm . The cell can be transformed to another setting with $a = 5.474(1)$ Å, $b = 3.906(5)$ Å, $c = 3.954(1)$ Å, and $\beta = 90.91(2)^\circ$ ($F(25) = 50.6$), corresponding to the space groups $I2/m$, $I2$, or Im . It is evident that the cell parameters of its body-centered cell are closely related to those of fluorite type δ -Bi₂O₃ (fcc) by the relations $b \approx c \approx a\sqrt{2}/2$. Since the unindexed diffraction peaks are weak, the approximate crystal structure could be refined with the subcell.

III. RIETVELD REFINEMENT

Because of the apparent close relationship with the fluorite structure, calculations were performed with starting

TABLE 1
X-Ray Powder Diffraction Data of Bi₂Nd₄O₉, for Cu Radiation, $\lambda = 1.5406 \text{ \AA}$

h	k	l	Observed		Calculated		h	k	l	Observed		Calculated	
			d	I/I ₀	d	I/I ₀				d	I/I ₀	d	I/I ₀
	*		4.605	2			4	0	-2	1.591	11	1.591	9
	*		3.714	3			2	2	0			1.590	
	*		3.573	5			2	2	-2	1.389	5	1.389	4
	*		3.412	1			4	0	0	1.368	2	1.369	2
0	0	1	3.232	31	3.229	31	2	0	-3	1.285	1	1.286	1
2	0	-1	3.184	100	3.182	100	1	1	2	1.277	4	1.277	
1	1	0			3.180		4	0	-3			1.277	4
	*		3.044	2			2	2	1	1.267	3	1.268	3
	*		2.904	2			1	3	0	1.266	3	1.267	3
1	1	-1	2.780	32	2.779	32	5	1	-2			1.260	5
2	0	0	2.738	14	2.737	15	4	2	-1	1.259	6	1.259	
	*		2.011	2			3	1	-3	1.248	2	1.249	2
2	0	-2	1.977	9	1.977	7	0	2	2	1.244	2	1.244	1
1	1	1	1.961	19	1.961	19	1	3	-1	1.236	2	1.237	2
0	2	0	1.953	10	1.953	10	4	2	-2			1.234	4
3	1	-1	1.939	21	1.940	19	3	1	1	1.233	4	1.233	
1	1	-2	1.685	8	1.686	7	5	1	-1	1.222	2	1.222	2
3	1	-2			1.672		1	1	-3	1.142	2	1.142	1
0	2	1	1.671	17	1.671	17	2	0	2	1.133	1	1.133	1
2	0	1	1.666	4	1.667	4	5	1	-3	1.130	2	1.130	2
2	2	-1	1.664	9	1.665	9	1	3	1	1.129	2	1.129	2
3	1	0	1.653	8	1.653	9	3	3	-1	1.125	2	1.125	2
4	0	-1	1.647	4	1.647	4	4	2	0	1.120	2	1.121	2
0	0	2	1.614	3	1.614	3	6	0	-2	1.117	1	1.117	1

Note. For the indexed subcell, the Smith-Snyder figure of merit $F(25) = 52.2$ (0.0082, 58). Reflections marked by * are due to the superstructure.

positional parameters according to those of the classical fluorite. The subcell then should contain one (Bi, Nd)₂O₃. Starting with $C2/m$, the Bi and Nd atoms were located statistically on the site $2a(0,0,0)$ with the initial ratio Nd/Bi = 2.0. The oxygen atoms were set on the site $4i(x, 0, z)$ with $x = 0.25$ and $z = 0.75$. The occupancy factor for oxygen was set to 0.75, corresponding to three oxygen atoms in the cell.

Using the computer program DBWS-9411 (13), the Rietveld refinement was carried out. The pseudo-Voigt function was used for the simulation of the peak shapes (14). Intensities within 16 times of the full width at half-maximum were considered to contribute to the reflection. Peaks below 75° (2θ) were corrected for asymmetry effects after Rietveld (15). The preferred orientation was refined using the March-Dollase function. The background was refined by use of a third-order polynomial in 2θ . In the first step, the scattering factor, zero point, background, profile parameters, lattice constant, and atomic coordinates were fitted.

Under these conditions, successive refinements of the positional parameters of oxygen and the isotropic thermal parameters lead to $R_{wp} = 18.72\%$, $R_{exp} = 6.70\%$, and $R_{Bragg} = 7.73$. At this stage, refinement of the ratio Bi/Nd

while keeping their isotropic thermal parameters fixed confirmed the ratio Bi/Nd = 1:2.

Attempts with space groups $C2$ and Cm only yielded larger agreement factors. Hence, the most probable space group is $C2/m$. The results of the refinement are plotted in Figure 1. Table 2 gives the structure parameters of the final refinement. Figure 2 shows the average crystal structure of Bi₂Nd₄O₉.

IV. DISCUSSION

Figure 2 gives the monoclinic unit cell of Bi₂Nd₄O₉ that has been shown to be isostructural with Bi₂La₄O₉ (1). However, a -, b -, and c -axes shrank from 6.8290 Å, 3.9887 Å, and 4.0524 Å for Bi₂La₄O₉ (1) to 6.703 Å, 3.906 Å, and 3.954 Å for Bi₂Nd₄O₉. The unit cell volume of Bi₂Nd₄O₉ was found to be smaller than that of Bi₂La₄O₉. The bond length between Nd and O atoms is also shorter than that between La and O atoms in Bi₂La₄O₉. All these verities can be attributed to the smaller ionic radius of Nd³⁺ (1.08 Å) in comparison with that of La³⁺ (1.15 Å).

From Table 2, it is obvious that the oxygen atom site in Bi₂Nd₄O₉ tends to occupy the ideal site, (0.25, 0, 0.75), of the

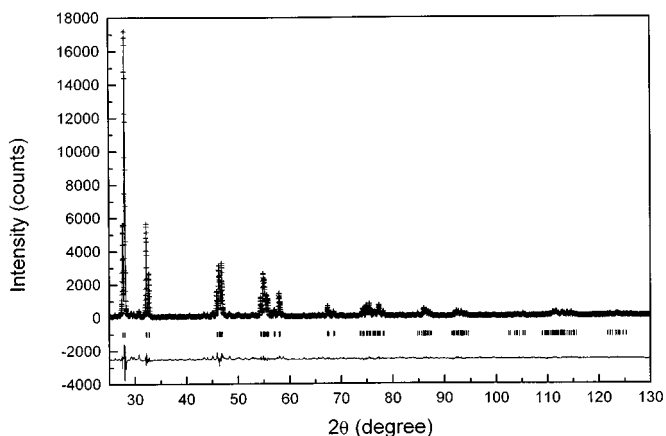


FIG. 1. Final Rietveld refinement pattern of $\text{Bi}_2\text{Nd}_4\text{O}_9$. Small crosses represent the experimental values and solid lines the calculated pattern. The solid line at the bottom is the difference between the experimental and calculated values. The vertical markers show positions calculated for Bragg reflections.

fluorite structure compared with the case in $\text{Bi}_2\text{La}_4\text{O}_9$. At the same time, in the body-centered cell, $\beta = 91.30^\circ$ (1) in $\text{Bi}_2\text{La}_4\text{O}_9$ and $\beta = 90.91^\circ$ in $\text{Bi}_2\text{Nd}_4\text{O}_9$. The decrease of β indicates that the monoclinic structure is inclined to orthorhombic structure with the decrease of the ionic radius of Ln . Therefore, it is reasonable to presume that the smaller ionic radius of Ln is favorable for the oxygen site being at the ideal site and stable non-monoclinic compounds. Maybe this is why there are no other monoclinic isostructural compounds with further lanthanide ions. The monoclinic structure is no longer stable with the smaller cations.

The isothermal temperature factors B for $(\text{Bi}, 2\text{Nd})$ and O are $1.8(3) \text{ \AA}^2$ and $5.6(4) \text{ \AA}^2$, respectively. The values are rather large. Comparably large B values were also observed for $\text{Bi}_{0.7}\text{La}_{0.3}\text{O}_{1.5}$ [$B(\text{La}, \text{Bi}) = 0.91\text{--}1.35 \text{ \AA}^2$, $B(\text{O}) = 1.40\text{--}4.93 \text{ \AA}^2$] (16), $\text{Bi}_8\text{La}_{10}\text{O}_{27}$ [$B(\text{La}, \text{Bi}) = 1.6\text{--}2.5 \text{ \AA}^2$, $B(\text{O}) = 1.9\text{--}6.3 \text{ \AA}^2$] (11), and $\text{Bi}_2\text{La}_4\text{O}_9$ [$B(\text{La}, \text{Bi}) = 1.8 \text{ \AA}^2$, $B(\text{O}) = 1.5 \text{ \AA}^2$] (1). The large B values are usually attributed to the ordering phenomena which will result in the superstructure in the compounds. Because of the better ordering of atoms in $\text{Bi}_2\text{Nd}_4\text{O}_9$, B values are larger than those in

TABLE 2
Final Rietveld Refinement Parameters of $\text{Bi}_2\text{Nd}_4\text{O}_9$, from X-Ray Powder Diffraction Data

Atom	Site	x/a	y/b	z/c	$B (\text{Å}^2)$	Occupancy
Nd } Bi }	2a	0	0	0	1.8(1)	0.667
						0.333
O	4i	0.264(6)	0	0.774(5)	5.6(4)	0.75

Note. $R_{\text{wp}} = 18.72\%$, $R_{\text{exp}} = 6.70\%$, $R_{\text{Bragg}} = 7.73$.

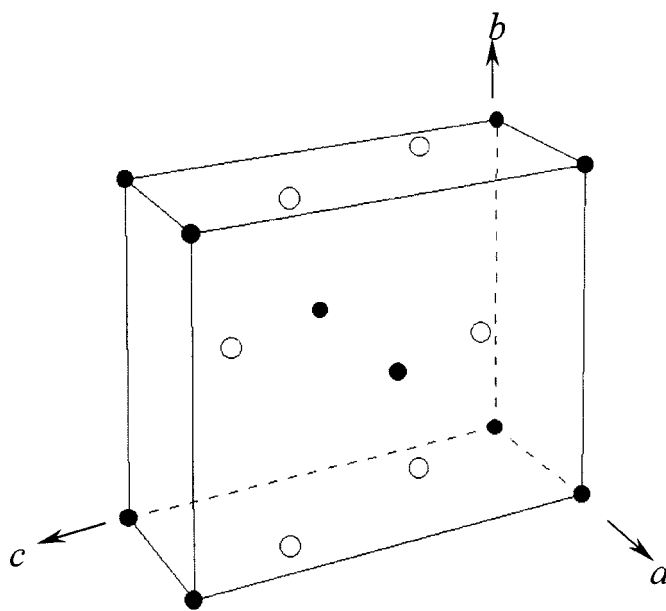


FIG. 2. Monoclinic subcell of $\text{Bi}_2\text{Nd}_4\text{O}_9$. The open circles stand for Nd or Bi atoms and the filled circles for oxygen.

other compounds. Correspondingly, transmission electron microscopy investigation revealed the existence of a strong superstructure in $\text{Bi}_2\text{Nd}_4\text{O}_9$.

Figure 3 shows the electron diffraction pattern along $[100]$ of the body-centered cell. Strong spots originate from

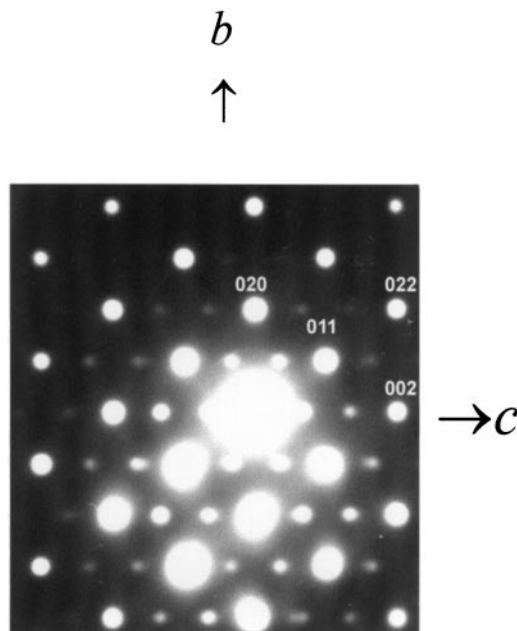


FIG. 3. Electron diffraction pattern of $\text{Bi}_2\text{Nd}_4\text{O}_9$. The electron beam is parallel to $[100]$. The superstructure is along $[001]$ with a period $3c$ (horizontal direction).

the average structure, while weak spots indicate a possible triple superstructure along [001] of the body-centered cell. The weak spots are more noticeable comparing the reported data. Thus TEM indicates a strong superstructure in the compound.

A weak superstructure has also been observed in Bi₃Nd₅O₁₂ (8), BiLa₂O_{4.5} (9), Bi₂La₄O₉ (1), Bi₃Pr₇O_x (6), Bi₂Gd₃O_{7.5} (5), etc. The superstructure generally originates from atomic ordering in compounds. In the above-mentioned compounds the superstructural spots were usually very weak and *B* values were smaller than 2.0. However, in the Bi₂Nd₄O₉ compound, the superstructural spots were very noticeable. The strong superstructure should originate from the better order of the Bi/Nd atoms in Bi₂Nd₄O₉ and results in the larger *B*(Bi,Nd) and *B*(O). At the same time, the superstructural lines which cannot be indexed by *C2/m* resulted in the larger *R*_{wp} refined by the Rietveld method.

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