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Single crystal growth and characterization of a new bismuth indium niobate compound, $Bi_5In_2Nb_3O_{18-x}$

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Abstract

Single crystals of a new bismuth indium niobate, $Bi_5In_2Nb_3O_{18-x}$, were grown by subsolidus reaction method. Differential thermal analysis measurements indicate that the compound has a melting point of 1224°C. Single crystal and powder X-ray diffraction methods show that the compound has the tetragonal system; *P4/mbm* space group, and lattice constants are $a = 12.6548(5)$, and $c = 3.9231(3)$ Å. The magnetic susceptibilities of compound $Bi_5In_2Nb_3O_{18-x}$ indicate Curie–Weiss behavior with an effective magnetic moment $\mu_{eff} = 0.72(1)\ \mu_B$

Keywords: $Bi_5In_2Nb_3O_{18-x}$; Single crystal; Magnetic moment; Crystal structure

1. Introduction

Up to now, several different compounds, $InNbO_4$ [1], $Bi_5Nb_3O_{15}$ [2], $Bi_{35}InO_{54}$ [3] and $Bi_{60}In_2O_{98}$ [4], have been reported for the In–Nb–O, Bi–Nb–O, and Bi– In–O systems, respectively. For the Bi–In–Nb–O system, however, only a ternary oxide compound, Bi_2InNbO_7 [5], was reported. The Bi_2InNbO_7 compound has a pyrochlore-type structure at room temperature, but the space group and lattice constants have not been reported [5]. It is known that numerous compounds with the pyrochlory structure exhibit antiferroelectric phases or dielectric anomalies, only a few compounds exhibit a ferroelectric behavior [6]. The detailed analysis shows that most niobate compounds consist of the three-dimensional network of NbO_6 and have interesting non-linear optical properties [7–9]. In order to gain a better understanding of the physical properties of niobate compounds such as magnetic and electrical properties, it is important to grow single crystals for structural studies of ternary niobate compounds.

In this paper, we report the growth of a new ternary bismuth indium niobate single crystal $Bi_5In_2Nb_3O_{18-x}$. To characterize the new single crystal, the compound was analyzed by the single crystal and powder X-ray diffraction methods. The magnetic and thermal properties for $Bi_5In_2Nb_3O_{18-x}$ compound were investigated by magnetic susceptibility and differential thermal analysis (DTA) measurements.

2. Experimental

$Bi_5In_2Nb_3O_{18-x}$ single crystals were grown by a subsolidus reaction method using high purity Bi_2O_3 (99.9%), ln_2O_3 (99.9%), and Nb_2O_5 (99.9%) under ambient pressure. Fig. 1 shows a schematic procedure of single crystal growth in this work. First of all, Bi_2O_3, In_2O_3, and Nb_2O_5 were converted into $Bi(NO_3)_3$, $In(NO_3)_3$, and $Nb(NO_3)_5$, respectively, using HNO_3(16N) at 60°C. The solutions were mixed and stirred well, then NH_4OH (7.5 N) was added to the mixed solution. A precipitate was obtained from the mixed solution. The precipitate was dried at about 200°C in air, and calcined in a furnace at 900°C for 10 h. Then the calicined material was pressed into a pellet, placed in a Pt crucible and inserted into the vertical furnace. The furnace was heated from room temperature to 1300°C over 20 h held at 1300°C for 10 h and slowly cooled to 650°C at a cooling rate 1°C/h, then rapidly cooled to room temperature. The single crystals of light yellow color were obtained.

The chemical composition of the crystals was determined by scanning electron microscope– X-ray energy

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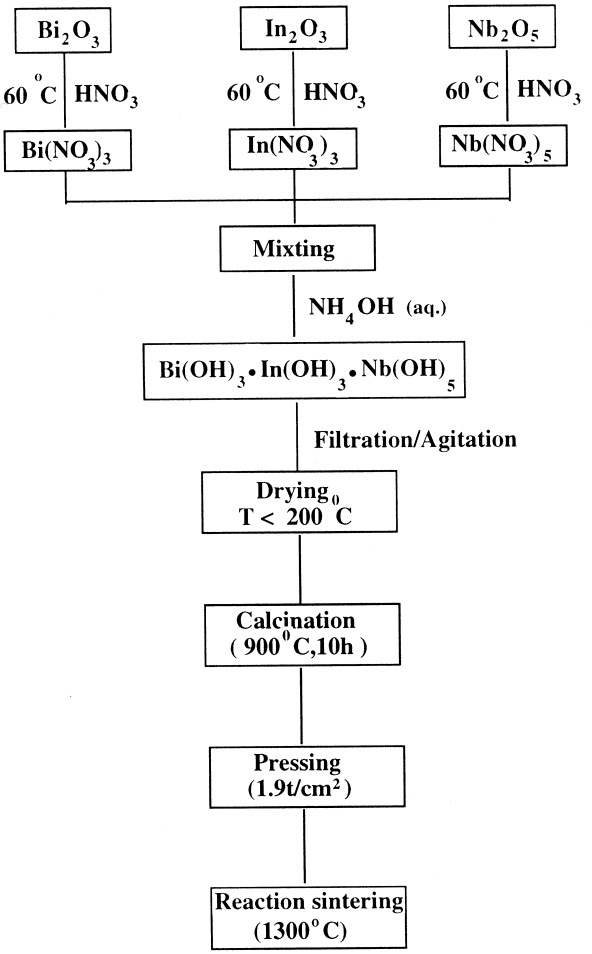

Fig. 1. Schematic diagram of the synthetic procedure for $Bi_5In_2Nb_3O_{18-x}$.

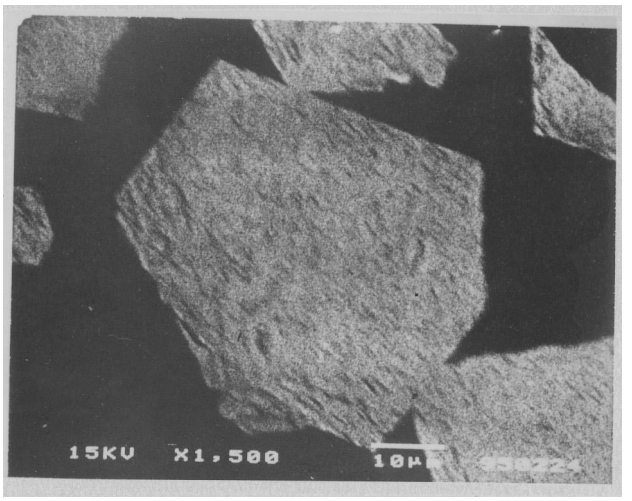

Fig. 2. SEM photograph of $Bi_5In_2Nb_3O_{18-x}$ single crystals.

dispersion spectrum (SEM–EDS) with an accelerating voltage of 25 kV. Thermal measurements of the $Bi_5In_2Nb_3O_{18-x}$ were performed by differential thermal and thermogravimetry analysis (DT–TGA). Single crystal X-ray diffraction using a precession camera and an AFC-5R four-circle diffractometer (MoKα radiation, λ= 0.71073 Å) were performed to determine the crystal structure and lattice constants. Powder X-ray diffraction was carried out by an X-ray diffractometer with CuKα radiation (λ=l.5418 Å). Magnetic susceptibility was measured using a Superconducting Quantum Interference Device (SQUID) magnetometer.

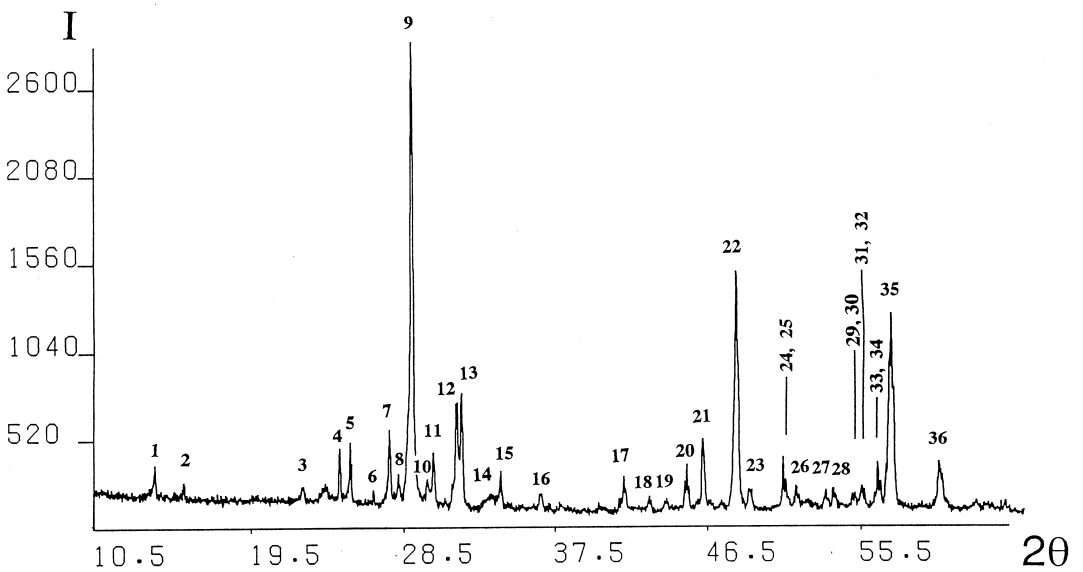

Fig. 3. Powder X-ray diffraction pattern of 2θ=10.0~60.0 for $Bi_5In_2Nb_3O_{18-x}$. The reflection index peak is given with the attached number in Table 1.

3. Results and discussion

A typical SEM photograph of $Bi_5In_2O_{18-x}$ single crystals grown by the subsolidus reaction method is shown in Fig. 2. The crystals with the maximum size of ~1.5×1.0×0.6 mm^3 were obtained from crystalline pieces of the crushed subsolidus product. The chemical component of $Bi_5In_2Nb_3O_{18-x}$ single crystal was determined using characteristic X-rays of Nb$L\alpha$, In$L\alpha$, and Bi$M\alpha$. The composition content was decided using the ZAF quantification method. The SEM–EDS analysis showed that the crystal has a homogenous atomic distribution with no other additional elements. As a result, the atomic ratio of Bi:In:Nb=4.95(3):2.11(2):3:00(1) was obtained as an average of measurements made at several different points. Oxygen content was calculated from the EDS results [5].

Single crystal and powder X-ray diffraction measurements were used to determine the crystal structure and lattice constants of these single crystals. Precession photos of $Bi_5In_2Nb_3O_{18-x}$ single crystal showed *4/mmm* Laue symmetry. Single crystal intensity data were collected on a four-circle AFC-SR diffractometer. Automatic peak search and indexing procedures yielded a primitive tetragonal cell which was used for all further work. The lattice constants, $a=12.6548(5)$ and $c=3.9231(3)$ Å, were refined by the least-squares method using 25 reflections with $2\theta>40°$. Systematic absences for the reflections of *okl*, $k=2n+1$; *hol*, $h=2n+1$ were observed and no other special absences exist. As a result, the structure is revealed to be a tetragonal system with space group *P4/mbm*. The detailed crystal structure will be published elsewhere [10].

Powder X-ray diffraction patterns were also analyzed using the obtained bulk specimen. The indexed powder X-ray diffraction pattern of the $Bi_5In_2Nb_3O_{18-x}$ sample is shown in Fig. 3. It can be seen that almost all of the diffraction peaks were successfully indexed based on the lattice constants and the space group determined by single crystal measurements. Only three reflections of $I<1$ could not be indexed. These very weak peaks may be contributed to the very small impurity phases. The observed and calculated *dhkll* values are given in Table 1. The refined lattice constants with the data of Table 1 are $a=12.657(3)$, $c=3.924(1)$ Å. The result is in a good agreement with those of single crystal X-ray diffraction.

Fig. 4 shows DTA curves of $Bi_5In_2Nb_3O_{18-x}$ single crystal. DTA analysis of $Bi_5In_2Nb_3O_{18-x}$ was carried out from 25°C to 1300°C with heating rate 5°C/min in air. The α-Al_2O_3 was used as a standard. The DTA curve exhibits a clear endothermic peak at 1224°C and an exothermic peak at 1223.6°C. Thus it is concluded that the congruent melting point of $Bi_5In_2Nb_3O_{18-x}$ crystals is 1224°C and

Table 1
Comparison of observed and calculated *dhkl* values of $Bi_5In_2Nb_3O_{18-x}$ based on the powder X-ray diffraction pattern shown in Fig. 3[a]

No.	*h*	*k*	*l*	$2\theta_{obs}$	d_{obs}	d_{calc}	*I*
1	2	0	0	13.98	6.3293	6.3286	6
2	2	1	0	15.64	5.6611	5.6604	3
3	0	0	1	22.54	3.9413	3.9246	3
4	1	1	1	24.72	3.5984	3.5940	9
5	3	2	0	25.36	3.5090	3.5 105	11
6	2	0	1	26.70	3.3359	3.3351	3
7	2	1	1	27.64	3.2245	3.2250	14
8	4	0	0	28.18	3.1640	3.1643	2
9	4	1	0	28.96	3.0805	3.0698	100
10	3	3	0	29.98	2.9780	2.9833	2
11	2	2	1	30.24	2.9530	2.9505	9
12	4	2	0	31.60	2.8289	2.8302	17
13	3	1	1	31.88	2.8047	2.8021	22
14		–		33.56	2.6680		<1
15	3	2	1	34.24	2.6166	2.6164	5
16	4	0	1	36.70	2.4466	2.4633	3
17	5	3	0	41.58	2.1701	2.1707	7
18	5	1	1	43.06	2.0989	2.0978	2
19	6	1	0	44.00	2.0562		2
20	6	2	0	45.28	2.0010	2.0013	8
21	0	0	2	46.20	1.9632	1.9621	15
22	6	3	0	48.20	1.8864	1.8868	51
23	6	0	1	48.98	1.8581	1.8581	4
	7	1	0			1.7900	
24	5	5	0	50.98	1.7898	1.7900	9
25	6	2	1	51.12	1.7852	1.7828	6
26	5	4	1	51.74	1.7653	1.7654	3
27	3	2	2	53.46	1.7125	1.7128	1
28	6	3	1	53.86	1.7007	1.7005	3
29	4	0	2	55.00	1.6681	1.6676	2
30		–		55.16	1.6637		<1
31	4	1	2	55.54	1.6532	1.6533	3
32	3	3	2	55.70	1.6488	1.6394	2
33	7	1	1	56.46	1.6284	1.6286	9
	5	5	1			1.6286	
34		–		56.64	1.6237		<1
35	4	2	2			1.6125	
	6	4	1	57.22	1.6086	1.6023	40
36	5	1	2	60.00	1.5405	1.5393	9

[a] The intensities I_{obs} are normalized by the strongest reflection. Calculation was performed on the basis of a tetragonal unit cell with space group *P4/mbm*, $a=12.657(3)$ and $c=3.924(1)$ Å which were obtained by least-squares refinements [8] using powder X-ray diffraction data with $\lambda=1.54050$ Å.

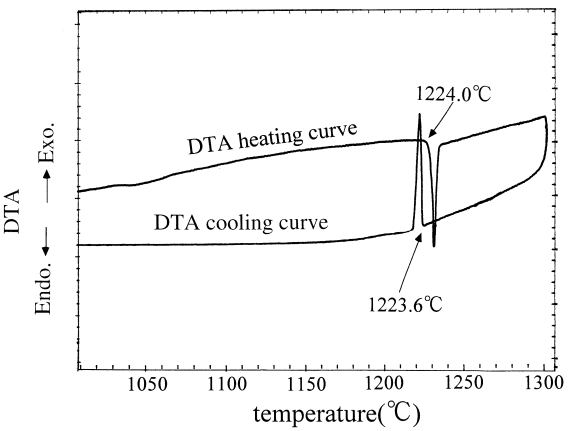

Fig. 4. The results of DTA for $Bi_5In_2Nb_3O_{18-x}$. Initial weight of sample is 10.00 mg, heating and cooling rates of the temperature are 5.0°C/min, and a thermocouple of Pt–PtRh13% was used.

the congruent crystallizing point is 1223.6°C. It is noted that a slight difference between the melting and crystallizing points is obtained from endothermic and exothermic peaks. This difference may be contributed to the instrumental error of DTA measurement. The result suggests that $Bi_5In_2Nb_3O_{18-x}$ crystal is a concordant fused compound, and has identical melting and crystallizing points.

The temperature-dependent molar magnetic susceptibility of a batch of randomly oriented $Bi_5In_2Nb_3O_{18-x}$ single crystals is shown in Fig. 5. Magnetic susceptibility data were measured up to 0.5 Tesla in the temperature range between 5 K and 300 K. The magnetic susceptibility in the temperature range could be fit to a modified Curie–Weiss relation according to the equation, $\chi = \chi_0 + C/(T + \Theta)$, where χ_0 is temperature-independent contributions such as Van Vleck and Pauli magnetism, C is the Curie constant, and Θ is the Curie–Weiss temperature. A nonlinear least-squares fitting of the observed data yielded $\Theta = -0.4(1)$ K and $\chi_0 = -2.55\times10^{-3}$ emu/mol. A plot of $1/(\chi - \chi_0)$ as a function of temperature is nearly linear in the temperature range (see Fig. 5). We obtained an effective magnetic moment of $\mu_{eff} = 0.72(1)\ \mu_B/Nb^{4+}$ (assuming spin-only contribution). The effective magnetic moment is much smaller than the theoretical value of 1.73 for a spin-only one electron system [11]. This means that only a little fraction of the charge carriers are localized, while the major fraction might be delocalized. In fact, the deviations from the expected effective magnetic moment in other niobate compounds were also reported by Xu et al. and Matsuura et al. [11,12]. The effective magnetic moments of $K_7Nb_{14,13}P_{8.87}O_{60}$ and $K_{6.10}Ba_{0.63}Nb_{14}P_9O_{60}$ are 0.98 and 1.30, which are smaller than that of theoretical value [11]. In order to make clear the origin of the unusual magnetic properties, further magnetic structure analysis seems to be necessary. The study of the electrical properties of $Bi_5In_2Nb_3O_{18-x}$ is also in progress, which is believed to supply more concrete information of localized/delocalized electrons in the compound.

In conclusion, we prepared single crystal samples of a new bismuth indium niobate, $Bi_5In_2Nb_3O_{18-x}$, by subsolidus reaction method, and investigated its structural, magnetic and thermal properties. Single crystal and powder X-ray diffractions showed that the compound has the tetragonal system; *P4/mbm* space group, and lattice constants are $a = 12.6548(5)$, and $c = 3.9231(3)$ Å. The temperature dependence of the magnetic susceptibility shows Curie–Weiss behavior, with considerably smaller effective magnetic moment than the theoretical value. These results are consistent with the presence of localized/delocalized electrons. The thermal analysis suggests that $Bi_5In_2Nb_3O_{18-x}$ crystal is a concordant fused compound, and has identical melting and crystallizing points. Because the compound can be grown easily as a single crystal or single phase and without the need for other special conditions, we believe that the compound will be useful as a standard in research of the chemical state of niobium in niobate compounds.

The authors would like to thank Professor Y. Nishihara for his valuable discussion.

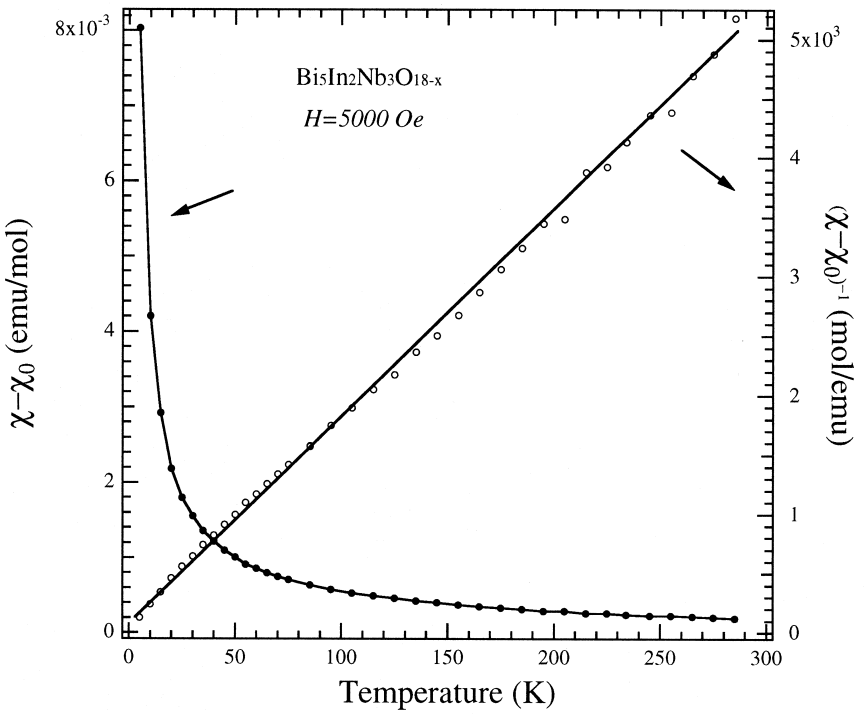

Fig. 5. Temperature dependence of the magnetic susceptibility of the $Bi_5In_2Nb_3O_{18-x}$ compound. The solid lines represent fits of the data to the Curie–Weiss law.

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