

Synthesis and crystal growth of sillenite phases in the $\text{Bi}_2\text{O}_3 - \text{TiO}_2 - \text{Nb}_2\text{O}_5$ system

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The synthesis of $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$ sillenite phase (BNbO) and the solubility of this phase with $\text{Bi}_{12}\text{TiO}_{20}$ was investigated by solid-state reaction synthesis and niobium doped $\text{Bi}_{12}\text{TiO}_{20}$ (BTO:Nb) crystals were grown by the Top Seeded Solution Growth (TSSG) technique. The structures of polycrystalline compounds were checked by X-ray powder diffraction method at room temperature. The correct composition of the sillenite phase stabilized with niobium was determined as $\text{Bi}_{12}[\text{Nb}_{0.17}\text{Bi}_{0.83}]\text{O}_{19.7}$ (BNbO) with unit cell parameter $a = 10.261(2)$ Å. The system BTO-BNbO is poorly soluble, but niobium doped BTO crystals were grown from the liquid composition $10\text{Bi}_2\text{O}_3 : x\text{TiO}_2 : (1-x)/2 \text{Nb}_2\text{O}_5$, with $x = 0.95$ and 0.90 . A niobium concentration limit in the liquid phase is established in order to grow BTO:Nb with good crystalline quality.

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1 Introduction

Bismuth oxide (Bi_2O_3) is an interesting dielectric material with four main crystalline phases, usually indicated by the letters α , β , γ and δ . The γ -phase bismuth oxide is metastable but can be stabilized at room temperature by the addition of some metal ions [1]. The resulting structure, known as sillenite, has a body centered cubic unit cell with space group I23 [2]. Depending on the metal ion used, the general formulae of the sillenite compounds can be written as $\text{Bi}_{12}\text{MO}_{20}$, with the cation $M = \text{Ge}, \text{Si}, \text{Ti}$, and others, or with the cation in the form of isomorphous mixtures $M = (\text{Bi}, \text{Ga}), (\text{Bi}, \text{V}), (\text{Bi}, \text{Zn}), (\text{Bi}, \text{Fe}), (\text{Fe}, \text{P})$, and others [3].

Sillenite crystals exhibit a number of interesting properties, including: piezoelectric, electro-optical, elasto-optical, optical activity and photoconductive properties. Of particular interest is the combination of the electro-optical and photoconductivity properties from which results the so-called photorefractive effect, consisting of a reversible light-induced change in the refractive index [4]. Due to these properties, sillenite crystals are useful for many advanced and promising applications, such as reversible recording medium for real-time holography or image processing [5]. The $\text{Bi}_{12}\text{TiO}_{20}$ (BTO) crystals have been considered as the most adequate sillenite material because of its practical advantages for photorefractive applications, such as lower optical activity, higher electro-optic coefficient and increased sensitivity to red light [6].

In recent years, many articles have been published about the influence of impurities on growth conditions and on optical, electrical and spectroscopic properties of BTO crystals [7-14]. These studies remain valid and it is very important to understand the effect of these impurities on physical properties. New compositions with better properties can be obtained by adding some impurities in the crystal. There are few studies about the γ -

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phase Bi_2O_3 stabilized with niobium and there is some controversy about its correct composition. According to Levin and Roth [1] the compositions $6\text{Bi}_2\text{O}_3:\text{Nb}_2\text{O}_5$ and $24\text{Bi}_2\text{O}_3:\text{Nb}_2\text{O}_5$ yielded a metastable bcc phase. A compound with sillenite structure and composition $\text{Bi}_{12}\text{Nb}_{0.29}\text{O}_{18.7}$ is reported in ref. [15]. Ling et al. [16] report a partial temperature-composition phase diagram of the system $\text{Bi}_2\text{O}_3 - \text{Nb}_2\text{O}_5$ for temperatures above 800 °C which includes a sillenite phase whose composition, obtained by graphic inspection, can be written as $\text{Bi}_{12}[\text{Nb}_{0.20}\text{Bi}_{0.80}]\text{O}_{19.7}$.

This paper discusses the results of our investigations on synthesis of $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$ sillenite phase, the solubility with $\text{Bi}_{12}\text{TiO}_{20}$ and the growth of niobium doped $\text{Bi}_{12}\text{TiO}_{20}$ (BTO:Nb) crystals. It is the first time, to our knowledge, that the sillenite structure in the system $\text{Bi}_2\text{O}_3\text{-TiO}_2\text{-Nb}_2\text{O}_5$ will be reported. The polycrystalline compounds were obtained by solid-state reaction synthesis and their crystalline structures were checked by X-ray powder diffraction method at room temperature. The BTO:Nb single crystals were grown by the Top Seeded Solution Growth (TSSG) technique.

2 Experimental

Synthesis of the compounds was carried out according to the solid-state reaction from conventional mixture of the starting oxides. Bismuth oxide (Bi_2O_3 , Aldrich, 99,9%), titanium oxide (TiO_2 , Johnson Matthey, 99,995%) and niobium oxide (Nb_2O_5 , Aldrich, 99,99%) were used as starting materials. The compositions tested were prepared by thoroughly mixing appropriate amounts of oxides, grinding the mixture in an alumina mortar and heating the product in a platinum crucible at temperatures up to between 700 and 800 °C. The grinding procedure was repeated three times a day and isopropyl alcohol was used as a liquid medium to improve the mixing. The entire process ranged from 60 to 110 hours.

Crystals were grown by the Top Seeded Solution Growth (TSSG) technique using excess of Bi_2O_3 as solvent. A resistance heating furnace equipped with a 2416 Eurotherm microprocessor-based digital temperature controller unit attached to a Pt-Pt10%Rh thermocouple was used. Temperature fluctuations were typically lower than 0.2K and the axial temperature gradient above the melt was of about 30K/cm. BTO seeds oriented along the [001] direction, held in a pure platinum seed holder, were used to initiate crystal growth. All runs were carried out in air. Pulling rate of 0.20 mm/h and rotation rate of 30 rpm were used. The pulling and the rotation rates were kept constant in each experiment during the entire process and crystal diameter was visually controlled changing the furnace temperature. After growth the crystals were annealed in temperatures between 700 and 750°C during about 72 hours to eliminate thermal stress.

X-ray powder diffraction was used to check the crystalline structures. The diffraction data were collected using $\text{Cu-K}\alpha$ radiation from an automatic SHIMADZU XRD-6000 diffractometer in the step scan mode with 0.02° step-interval and 2.5 sec step-time. All measurements were made at room temperature.

3 Results and discussion

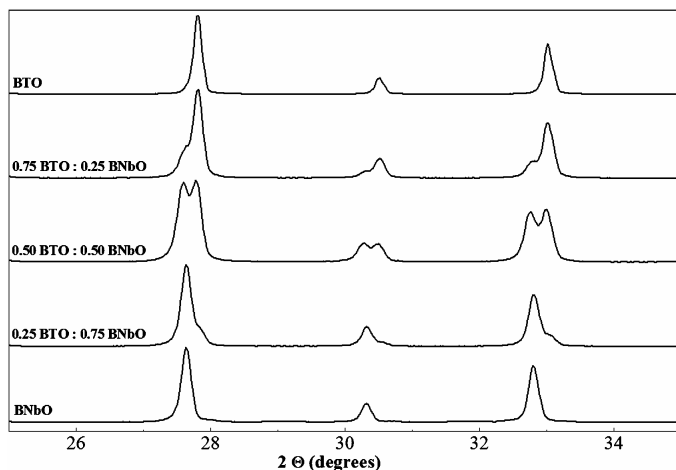
3.1 Solid-state reaction synthesis

We synthesized the composition $\text{Bi}_{12}\text{Nb}_{0.29}\text{O}_{18.7}$, as suggested in ref. [15] using the conditions shown in table 1, and the result was not a single sillenite phase, but a mixture of tetragonal [17] and sillenite phases. We tested the composition $\text{Bi}_{12}[\text{Nb}_{0.29}\text{Bi}_{0.71}]\text{O}_{19.8}$, where the occupation of the tetrahedral *M* site in the structure is complete, and the same mixture of those two phases was obtained. It is well known that the occurrence of tetragonal and bcc phases in pure Bi_2O_3 is dependent on the thermal history of the sample [18]. Maybe a difference in the route synthesis could explain the discrepancy between our results and those of ref. [15]. As shown in table 1, we investigated the synthesis of many compositions around the composition referred by Ling et al. [16] and our result is very close to that. The composition of the sillenite phase stabilized with niobium obtained by us is $\text{Bi}_{12}[\text{Nb}_{0.17}\text{Bi}_{0.83}]\text{O}_{19.7}$, hereafter named BNbO, with unit cell parameter $a = 10.261(2)$ Å, as calculated from the powder diffraction data.

Table 1 Summary of synthesis carried out in the system Bi_2O_3 - Nb_2O_5 . 'T' and 'S' indicate the tetragonal [17] and sillenite phases, respectively. Bracketed phases have a minor presence.

Composition	Final annealing temperature (°C)	Final annealing time (h)	Phases identified by XRD
$\text{Bi}_{12}\text{Nb}_{0.29}\text{O}_{18.7}$	850	67	T + (S)
$\text{Bi}_{12}[\text{Nb}_{0.29}\text{Bi}_{0.71}]\text{O}_{19.8}$	850	113	T + (S)
$\text{Bi}_{12}[\text{Nb}_{0.20}\text{Bi}_{0.80}]\text{O}_{19.7}$	820	60	T + S
$\text{Bi}_{12}[\text{Nb}_{0.19}\text{Bi}_{0.81}]\text{O}_{19.7}$	800	74	T + S
$\text{Bi}_{12}[\text{Nb}_{0.18}\text{Bi}_{0.82}]\text{O}_{19.7}$	800	90	(T) + S
$\text{Bi}_{12}[\text{Nb}_{0.17}\text{Bi}_{0.83}]\text{O}_{19.7}$	800	89	S

For the purpose of investigating the solubility of BTO-BNbO, samples with nominal composition $x \text{Bi}_{12}\text{TiO}_{20} : (1-x) \text{Bi}_{12}[\text{Nb}_{0.17}\text{Bi}_{0.83}]\text{O}_{19.7}$, with $x = 0.25, 0.50$ and 0.75 , were prepared by solid-state reaction synthesis, using experimental conditions similar to those shown in table 1. Powders were analyzed by X-ray diffraction and the results are shown in figure 1 for $25^\circ \leq 2\theta \leq 35^\circ$, pure BTO and BNbO are also shown for comparison. The results clearly indicate that there are only insoluble BTO-BNbO mixtures, i. e. solids solutions are not formed in this composition range. Although they have isomorphic structures, the non-solubility in this range can be due to the large differences among the unit cell parameters of BTO ($a = 10.178(8) \text{ \AA}$ [19]) and BNbO ($a = 10.261(2) \text{ \AA}$).

**Fig. 1** Partial X-Ray power diffraction patterns of $x\text{Bi}_{12}\text{TiO}_{20} : (1-x)\text{Bi}_{12}[\text{Nb}_{0.17}\text{Bi}_{0.83}]\text{O}_{19.7}$, with $x = 0.25, 0.50$ and 0.75 . The diffraction patterns of pure BTO and BNbO are also shown for comparison.

Direct substitution of titanium by niobium in the compositions $\text{Bi}_{12}\text{Ti}_x\text{Nb}_{(1-x)}\text{O}_{20}$ with $x = 0.95$ and 0.90 was also tried. For the first composition ($\text{Bi}_{12}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_{20}$) we have obtained a homogeneous phase with sillenite structure and for the other ($\text{Bi}_{12}\text{Ti}_{0.90}\text{Nb}_{0.10}\text{O}_{20}$), a mixture of two sillenite phases, as verified by X-ray powder diffraction. This suggests that - for lower concentrations of niobium - the BTO structure can accommodate niobium ions in tetrahedral positions, partially substituting the titanium ions. However higher concentrations of niobium cannot be accommodated because of the high lattice deformation required and therefore a new phase is formed. Although niobium has poor solubility in BTO it is indeed possible to grow Nb-doped BTO crystals.

3.2 Crystal growth

BTO:Nb single crystals were grown from the liquid phase with the nominal composition $10\text{Bi}_2\text{O}_3 : x\text{TiO}_2 : (1-x)/2\text{Nb}_2\text{O}_5$, with $x = 0.95$ and 0.90 . Starting solutions were thoroughly mixed and melted in high purity cylindrical crucibles. A Pt5%Au alloy was used to minimize the wetting effect. In all growth experiments only around one third of the starting charges were crystallized.

From the starting composition $10\text{Bi}_2\text{O}_3 : 0.95\text{TiO}_2 : 0.025\text{Nb}_2\text{O}_5$ a good crystal, named BTO:Nb-03.01, was grown (Figure 2a). The BTO:Nb-03.02 crystal, shown in Figure 3a, was grown from the $10\text{Bi}_2\text{O}_3 : 0.90\text{TiO}_2 : 0.05\text{Nb}_2\text{O}_5$ starting composition. In this latter case the growth process presented different characteristics from those observed for the first crystal. The initial and middle-part of the crystal is highly

stressed, with cracks and some inclusions, as we can see in the slice shown in Figure 3c; the end-part is just a polycrystalline opaque mass, Figure 3b.

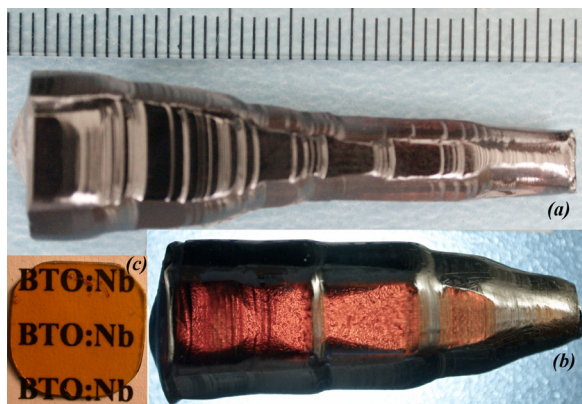


Fig. 2 As-grown BTO:Nb single crystals: (a) BTO:Nb-03.01, (b) BTO:Nb-03.03, (c) polished sample.

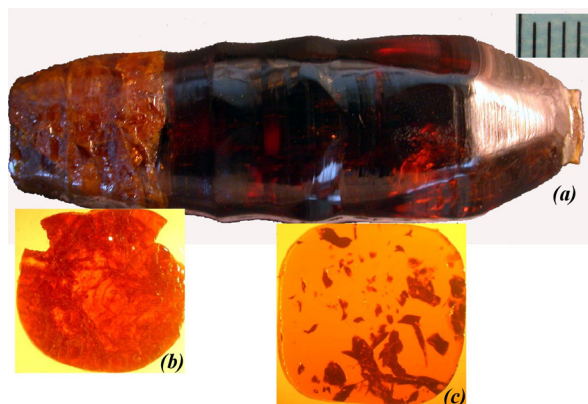


Fig. 3 (a) As-grown BTO:Nb-03.02 crystal. Slices in the bottom were cut perpendicular to the growth direction: (b) end-part and (c) middle-part.

X-ray diffraction measurements from the powdered pieces of the middle and of the end-part of BTO:Nb-03.02 crystal were made. To emphasize the results the 2θ values were limited to the range from 25 to 35 degrees, as shown in Figure 4. The X-ray diffraction profile of the crystal end-part shows that it is formed by two distinct sillenite phases, corresponding to BTO:Nb and BNbO, on the other hand the middle-part shows a single sillenite phase (BTO:Nb). We can understand these results considering that during crystal growth segregated niobium in the growth interface progressively increases its concentration in the liquid phase until reaching a composition - possibly an eutectic composition - where not just one but two distinct phases crystallize. This imposes a niobium concentration limit in the liquid phase in order to grow good BTO:Nb crystals.

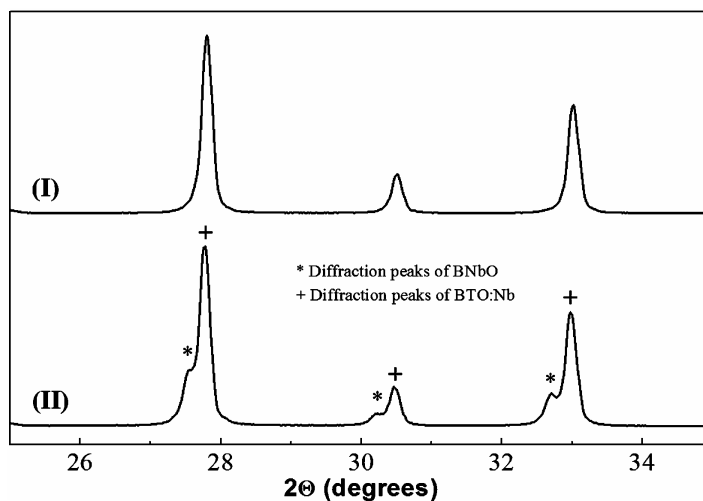


Fig. 4 Partial X-Ray power diffraction patterns of (I) middle-part of BTO:Nb-03.02 crystal and (II) end-part displaying the occurrence of two crystalline phases.

After BTO:Nb-03.02 crystal growth, the remaining crucible charge was completed with the composition $6\text{Bi}_2\text{O}_3:\text{TiO}_2$ and, from this solution with lower niobium concentration, the BTO:Nb-03.03 crystal, shown in figure 2b, was grown with good crystalline quality.

The intrinsic defect features in BTO:Nb were the same as pure BTO, as determined by us previously [20]. A dark core was visible in the crystal shoulder, where the solid/liquid interface was convex. In the region corresponding to the growth interface shape inversion from convex to planar we have verified the presence of

some inclusions; growth striations, characteristically present in pure BTO crystals, were also observed. In spite of the proper difficulties involved in the growth of these crystals, good optical quality samples were obtained from the major body parts of BTO:Nb crystals, as the polished slice shown in Figure 2c.

3 Conclusion

We have investigated the experimental conditions required to obtain the Bi₂O₃-Nb₂O₅ sillenite phase and we have determined its correct composition as Bi₁₂[Nb_{0.17}Bi_{0.83}]O_{19.7}. The system BTO-BNbO do not form a solid solution and niobium can directly replace titanium in the composition Bi₁₂Ti_xNb_(1-x)O₂₀, for x = 0.95. Although poor solubility of niobium in BTO matrix and the characteristic difficulties involved in the growth of sillenite crystals, we have grown niobium doped BTO crystals with good crystalline quality, and a niobium concentration limit in the liquid phase was established.

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