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Citation: *Appl. Phys. Lett.* **90**, 172910 (2007); doi: 10.1063/1.2732833

View online: <http://dx.doi.org/10.1063/1.2732833>

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## Phase transformation in BiNbO<sub>4</sub> ceramics

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(Received 7 February 2007; accepted 30 March 2007; published online 26 April 2007)

Phase transformation from  $\beta$ -BiNbO<sub>4</sub> to  $\alpha$ -BiNbO<sub>4</sub> in BiNbO<sub>4</sub> bulk samples was studied. From x-ray diffraction patterns, the transformation from  $\beta$  to  $\alpha$  phase of BiNbO<sub>4</sub> could be observed by heating the bulk samples of  $\beta$ -BiNbO<sub>4</sub> from low temperatures to 700–1030 °C. Such a transformation did not occur in powder samples and in the cooling course. This phenomenon might be related with associated activation of stress and heat energy in the heating course. Differential thermal analysis, shrinkage, and dielectric properties as a function of temperature were carried out, and all the results confirmed the transformation from  $\beta$  to  $\alpha$  phase of BiNbO<sub>4</sub>. © 2007 American Institute of Physics. [DOI: 10.1063/1.2732833]

The triclinic BiNbO<sub>4</sub> (high temperature  $\beta$  phase) and the isostructural BiTaO<sub>4</sub> were first reported by Aurivellius in 1951.<sup>1</sup> Subsequently Roth and Waring<sup>2,3</sup> reported the existence of the low temperature orthorhombic modification ( $\alpha$  phase), and powder x-ray diffraction data showed that the low temperature form is closely related to that of stibotantalite-type (SbTaO<sub>4</sub>) structure. They also reported that the low temperature form of BiNbO<sub>4</sub> transformed irreversibly to the triclinic form at about 1020 °C. As they reported, the transformation could not be reversed by cooling down to lower temperatures. Keve and Skapski<sup>4,5</sup> grew single crystals of  $\beta$ -BiNbO<sub>4</sub> in 1973 by reacting Bi<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> in a sealed Pt capsules at 1150 °C and concluded that the  $\beta$  structure is not related to stibotantalite-type SbTaO<sub>4</sub>. They also believed that once the  $\beta$  phase has been formed, it cannot be converted to  $\alpha$  phase by heating below lower temperatures. Subramanian and Calabrese<sup>6</sup> reported the growth of single crystal of  $\alpha$ -BiNbO<sub>4</sub> in 1993 from BiOF flux below 900 °C and gave the structure refinement. They claimed that the structural difference between  $\alpha$  and  $\beta$  phases could explain the irreversible nature of the transformation between the two phases.

From all the literatures above we could conclude that the  $\beta$ -BiNbO<sub>4</sub> has a smaller cell volume and a more stable structure than that of  $\alpha$ -BiNbO<sub>4</sub>. The  $\beta$  form cannot be transformed to  $\alpha$  form by cooling down to lower temperature under 1020 °C. But in this work, the different results have been gotten as follows. Being influenced seriously by the residual stress in samples, the transformation from  $\beta$  to  $\alpha$  phase is reversible in bulk ceramic samples caused by the stress while it is still irreversible in powder samples.

The pure BiNbO<sub>4</sub> samples were prepared using mixed oxide method. Proportionate amounts of reagent-grade starting materials of Bi<sub>2</sub>O<sub>3</sub> (>99%, Shu-Du Powders Co. Ltd, China) and Nb<sub>2</sub>O<sub>5</sub> (>99%, Zhu-Zhou Harden Alloys Co., Ltd., China) were prepared according to the composition of BiNbO<sub>4</sub>. Powders were mixed and milled using a planetary mill (Nanjing Machine Factory, China) by setting the running speed at 150 rpm with the zirconia balls (2 mm in diameter) as milling media. The mixed oxides were calcined at

700 °C first. After being crushed and milled for 5 h, the powders were sintered at 1000 °C for 4 h to form pure  $\alpha$ -BiNbO<sub>4</sub>. At last the samples were sintered at 1100 °C for 4 h to obtain pure  $\beta$ -BiNbO<sub>4</sub>. Then the samples were crushed and remilled again for 5 h using ZrO<sub>2</sub> balls and de-ionized water. After being dried, some powders were pressed into cylinders in a steel die under monoaxial pressure of 20 kN/cm<sup>2</sup> with polyvinyl alcohol binder addition. Both the powder and cylindrical samples received the following different heat treatments: (1) heating at 400–1500 °C for 100 min then cooling down naturally, (2) heating at 1100 °C for 100 min then cooling down to 900 °C with different rates and incubation times, and (3) heating at 700 °C for 100 and 1000 min. Then the crystalline structures of the samples (crushed powders) were investigated using an x-ray diffractometry with Cu K $\alpha$  radiation (Rigaku D/MAX-2400 x-ray diffractometry, Japan). Differential thermal analyses (DTA) of powder and bulk samples of  $\beta$ -BiNbO<sub>4</sub> were studied using a thermoanalyzer system (DELTA-7, PE). Thermal expansion parameters were measured using a dilatometer (DIL 402C, NETZSCH, Germany). Dielectric behavior as a function of temperature was measured using a LCR meter (HP4284, Agilent) with a self-made high temperature system.

After different heat treatments mentioned above, x-ray diffraction (XRD) patterns of powder samples only show the pure  $\beta$ -BiNbO<sub>4</sub> phase and it corresponded well with the previous literatures. XRD results of crushed bulk samples (crushing has no influence on phase transformation here) show interesting results, as shown in Fig. 1. After being heated at 700 °C for 100 min, the  $\beta$ -BiNbO<sub>4</sub> started to transform to  $\alpha$  phase, as shown in Fig. 1(a). Almost only  $\alpha$  phase could be observed from XRD pattern of sample sintered at 750 °C for 100 min. This is very different from the results of powder samples and literatures. This result indicates that the transformation from  $\beta$ -BiNbO<sub>4</sub> to  $\alpha$ -BiNbO<sub>4</sub> is possible. Between sintering at temperature of 750–1030 °C, only  $\alpha$  phase exists. When sintered at 1050 °C/100 min,  $\alpha$ -BiNbO<sub>4</sub> transformed to  $\beta$ -BiNbO<sub>4</sub> again. Figure 1(b) shows the influence on the transformation from different cooling courses. Natural cooling rate of our furnace used here was about 10 °C/min when temperature is above 800 °C. It is seen that different cooling rates and incubation times at 900 °C have no influence on the phase transformation, and

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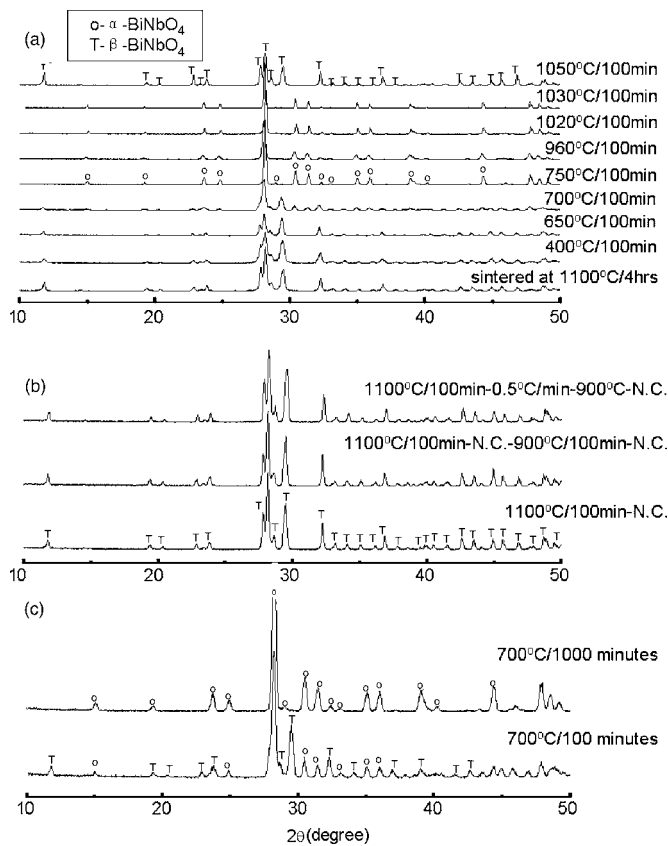


FIG. 1. XRD patterns of crushed bulk  $\text{BiNbO}_4$  ceramics (a) calcined at different temperatures for 100 min, (b) cooled down with different rates and incubation times, and (c) heated with different incubation times at 700 °C.

$\beta$ - $\text{BiNbO}_4$  could not transformed to  $\alpha$ - $\text{BiNbO}_4$  during the cooling course. Figure 1(c) shows the influence of different incubation times during the heating course on the phase transformation. Both  $\alpha$  and  $\beta$  phases were revealed in XRD patterns of sample sintered at 700 °C/100 min. After sintered for 1000 min, only pure  $\alpha$  phase was observed. This indicates that longer incubation time could accelerate the transformation from  $\beta$  to  $\alpha$  phase.

Figure 2 shows the crystal structures of  $\alpha$ - and  $\beta$ - $\text{BiNbO}_4$ . There are four formula units in the unit cell in both structures. The  $\alpha$  structure, being orthorhombic with a space group  $Pnna$  (No. 52),<sup>6</sup> typically consists of layers of vertex-sharing  $\text{NbO}_6$  octahedra which is normal to the  $c$  plane, and the  $\text{Bi}^{3+}$  are located on the sites between these layers. The  $\beta$  phase was found to have a triclinic structure with sheets of formula  $[\text{NbO}_4]_n$  along the  $bc$  plane, in which the  $\text{NbO}_6$  octahedra are joined at four vertices so that the two free oxygen atoms are in  $c$  axis, as shown in Fig. 2. The Bi atoms hold these sheets together and are coordinated to eight oxygen atoms in the form of a much more distorted square antiprism. In general, the structure of  $\alpha$  phase could be thought to be consisted of two bismuth layers and two separated octahedral layers having different distortions.  $\beta$ - $\text{BiNbO}_4$  is made up of two bismuth layers and two joined octahedron layers. As we discussed above,  $\beta$ - $\text{BiNbO}_4$  started to transform to  $\alpha$ - $\text{BiNbO}_4$  when heating temperature reached about 700 °C, which means that the two joined octahedron layers were opened up and separated by a layer of bismuth. When sintering temperature reached above 1020 °C, the two neighboring layers of octahedrons joined together again and  $\alpha$ - $\text{BiNbO}_4$  transformed to  $\beta$ - $\text{BiNbO}_4$ . The joining and open-

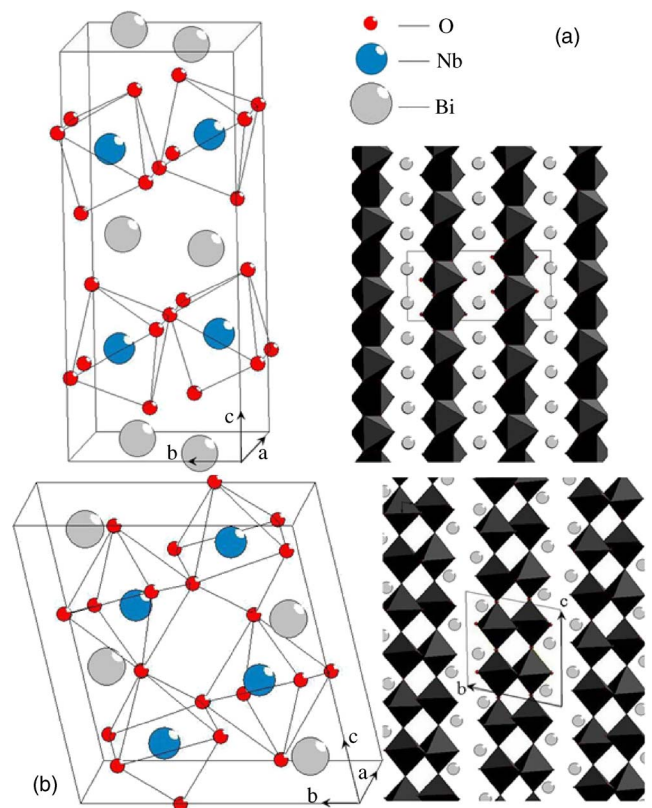


FIG. 2. (Color online) Schematic illustrations of crystal structure of  $\alpha$ - and  $\beta$ - $\text{BiNbO}_4$ .

ing up of the two neighboring layers of octahedrons dominate the transformation between  $\alpha$ - and  $\beta$ - $\text{BiNbO}_4$ . Considering the XRD results, it is concluded that the two joined octahedron layers could be opened up by high temperature (between 700 and 1020 °C) and long incubation time in the heating course and joined together again when the sintering temperature is above 1020 °C. It is notable that the two joined octahedron layers could not be opened up in the cooling course or in powder samples. Generally speaking, this novel transformation from  $\beta$ - to  $\alpha$ - $\text{BiNbO}_4$  might be caused by the associated activation of stress and heat energy in the heating course and the specific transformation theory needs to be studied further.

Figure 3 plots the temperature difference as a function of temperature of both powder and bulk samples. For powder

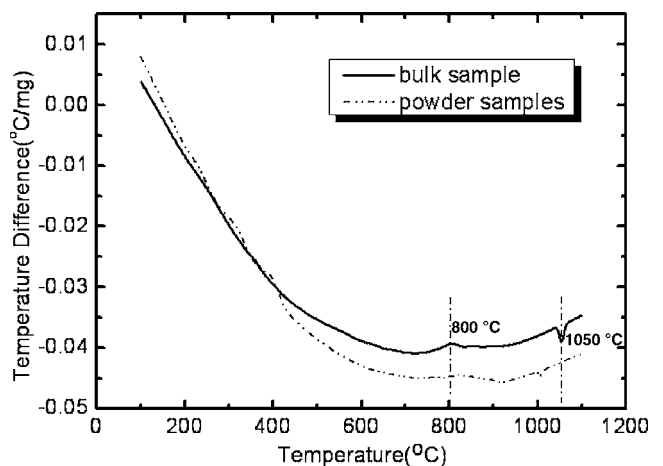


FIG. 3. DTA curves of both bulk and powder  $\text{BiNbO}_4$  samples of  $\beta$  phase.

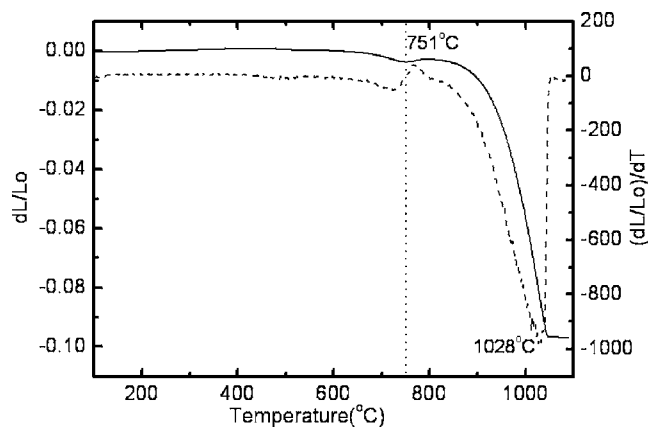


FIG. 4. Shrinkage (solid line) and its differential (dashed line) of green  $\beta$ - $\text{BiNbO}_4$  ceramic as a function of temperature.

samples, there is no abrupt change between the temperature range from 100 to 1100 °C. The powder keeps the  $\beta$  phase always. But for bulk samples, there is an exothermic and endothermic peaks in DTA curves at about 800 and 1050 °C, respectively. This indicates that in the bulk sample of  $\beta$  phase transforms to  $\alpha$  phase at 800 °C with exothermic reaction and then transform to  $\beta$  phase again at about 1050 °C with endothermic reaction. This evidence corresponds well with the results of XRD study.

The shrinkage of a green cylinder sample of  $\beta$ - $\text{BiNbO}_4$  was measured from 100 to 1090 °C, as shown in Fig. 4. As the measuring temperature increases first, the sample kept on shrinking slowly. At about 751 °C, an unusual change could be observed on the shrinkage curve. The shrinkage suddenly stopped increasing and decreased a little. Then it goes on increasing slowly. This means that the sample suddenly expanded a little in the shrinkage course at about 751 °C. Considering the acceptable errors of temperature measurement, this phenomenon could be related with the phase transformation between  $\alpha$ - and  $\beta$ - $\text{BiNbO}_4$ . At about 751 °C, the sample changed from  $\beta$  to  $\alpha$  phase with the cell volume increasing from 325.44 to 330.66 Å<sup>3</sup> which resulted in the abrupt increase in the length of sample. When temperature is above 900 °C, the sample began to shrink acutely and the grain growth and elimination of pores occurred during this temperature range. At about 1020 °C, sample began to transform to  $\beta$  phase again. Because of the sharp shrinkage of sample in this temperature region, the small unusual change caused by phase transformation ( $\alpha$  to  $\beta$ ) could not be observed clearly, as shown in Fig. 4. After 1040 °C, there was no clear change on the shrinkage curve.

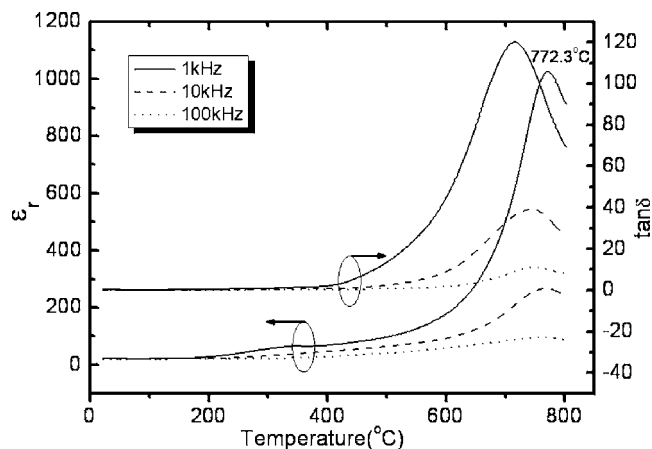


FIG. 5. Temperature dependence of dielectric properties of  $\beta$ - $\text{BiNbO}_4$  ceramic.

The dielectric properties of  $\beta$ - $\text{BiNbO}_4$  as a function of temperature between 25 and 80 °C were shown in Fig. 5. As the temperature increases, both the permittivity and dielectric loss increase. At about 768.5 °C, permittivity reached a maximum of about 1100 and the peak was sharp at frequency of 1 kHz. After this temperature, permittivity decreased dramatically. Subsequently, the dielectric loss also showed a little difference in peak before this temperature at 680 °C. According to the XRD analysis above, these phenomena were caused by the transformation from  $\beta$  to  $\alpha$  phase. The peaks of permittivity and dielectric loss could be observed at 1, 10, and 100 Hz with just a little difference in peak values.

In summary, the phase transformation from  $\beta$ - $\text{BiNbO}_4$  to  $\alpha$ - $\text{BiNbO}_4$  in bulk samples was studied in this work and was confirmed by several kinds of measurements. This conclusion overset the traditional viewpoint of that phase transformation from  $\alpha$ - to  $\beta$ - $\text{BiNbO}_4$  was irreversible. Both  $\alpha$  and  $\beta$  phases of  $\text{BiNbO}_4$  could be stable in different temperature regions. This interesting phenomenon needs to be studied theoretically further in the future work and it may provide more basic understanding to the  $\text{BiNbO}_4$  ceramics.

This work was supported by the National 973-project of China under Grant No. 2002CB613302, National 863-project of China under Grant No. 2006AA03Z0429, and NSFC project of China under Grant No. 50572085.

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