



Abnormal phase transition in BiNbO₄ powders prepared by a citrate method

Hai-Fa Zhai^a, Xu Qian^a, Ji-Zhou Kong^a, Ai-Dong Li^{a,*}, You-Pin Gong^b, Hui Li^a, Di Wu^a

^a National Laboratory of Solid State Microstructures, Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

^b Nano Device and Material Division, Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO), Chinese Academy of Sciences, Suzhou 215123, People's Republic of China

ARTICLE INFO

Article history:

Received 7 April 2011

Received in revised form 21 August 2011

Accepted 22 August 2011

Available online 26 August 2011

Keywords:

BiNbO₄

Citrate method

Phase transition

ABSTRACT

Triclinic β -BiNbO₄ prepared below 750 °C and above 1040 °C (denoted as Low- β and High- β , respectively) and pure orthorhombic α -BiNbO₄ at 900 °C were successfully derived from a citrate method and the phase transition from β -BiNbO₄ to α -BiNbO₄ was first observed in BiNbO₄ powders. This phenomenon proves that the abnormal phase transition from β -BiNbO₄ to α -BiNbO₄ exists in BiNbO₄ powder system. The synthesis of Low- β powders can be attributed to the formation of the intermediate phase of Bi₅Nb₃O₁₅ by the citrate method. With increasing temperature, the Low- β phase gradually turns into α -BiNbO₄ due to the thermodynamically metastable state of Low- β . We also identified that the stress in pellet format can accelerate the phase transition from Low- β to α phase of BiNbO₄ in comparison with powder samples. It brings us new understanding of the BiNbO₄ system and also provides a simple way to obtain BiNbO₄ for microwave and photocatalytic applications.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Recently extensive studies have been carried out to develop low-temperature-cofired ceramics for microwave applications [1,2]. Bi-based dielectric ceramics, such as BiNbO₄, have been investigated for low-firing multilayer capacitors at the low sintering temperature (<1000 °C), making co-firing under reducing atmosphere compatible with silver or copper electrodes [3,4]. In the applications of BiNbO₄-based ceramics, phase transition is an important concern [4,5].

The triclinic BiNbO₄ (high temperature β phase) was first reported by Aurivellius [6]. Then Roth and Waring reported the existence of orthorhombic phase (low temperature α phase) [7]. X-ray diffraction (XRD) data showed that α phase is similar to that of stibotantalite-type (SbTaO₄) structure [8], while β phase belongs to the P $\bar{1}$ (No. 2) space group [9]. As reported, the low-temperature orthorhombic BiNbO₄ synthesized at 900 °C converts irreversibly to the high-temperature triclinic form at about 1020 °C. Subramanian and Calabrese thought that the structural difference between α and β phases could be the reason for the irreversible transition between them [10]. But in 2007, Zhou et al. first observed the phase transition from β -BiNbO₄ to α -BiNbO₄ in BiNbO₄ bulk samples [11]; they claimed that the transition from β to α phase is reversible in bulk ceramic samples which relates to associated activation of stress and heat energy in the heating course, whereas such a transition did not occur in powder samples and in the cooling course. Above

all, in knowledge of literature search, there has been no report that β -BiNbO₄ powders convert into α -BiNbO₄ ones.

For the preparation of BiNbO₄, conventional solid state reaction method may cause problems such as large grain growth, segregation of components and loss of stoichiometry owing to the volatilization of Bi element at high temperature. So, some wet-chemical methods have been developed to synthesize BiNbO₄ at lower temperature [12–14]. Among these routes, the citrate method is a simple way to obtain stable precursors and reactive and stoichiometric fine powders which has been widely used in the fabrication of various simple and complicated oxides [15–18].

In this work, β -BiNbO₄ powders were prepared below 750 °C and above 1040 °C (denoted as Low- β and High- β , respectively) by a citrate method and the abnormal phase transition from β -BiNbO₄ to α -BiNbO₄ in powder format was first observed. The possible mechanism of the formation of Low- β and the phase transition from Low- β to α phase of BiNbO₄ powders was proposed.

2. Experimental procedures

The BiNbO₄ powders were prepared using a citrate method. The citrate method is an effective way to prepare BiNbO₄ at lower temperature [14]. The precursor materials of BiNbO₄ were bismuth nitrate (Bi(NO₃)₃·5H₂O), citric acid (CA), ammonia and a Nb-citrate (Nb-CA) aqueous solution. The synthesis of water-soluble Nb-CA has been described in details in a previous work [19]. To compensate the loss of Bi, an excess of 5% bismuth nitrate was added. Bi(NO₃)₃·5H₂O was first dissolved in Nb-CA, followed by addition of citric acid. Then the solution was kept stirring at 60 °C, and ammonia was added to adjust the pH value to 7–8. Finally, a stable solution was obtained. The solution was dried at 180 °C for 4 h to evaporate the solvent and then received different heat treatments: (1) heating at 550–1150 °C for 3 h; (2) heating at 700 °C and 1050 °C for 3 h, respectively, then cooling down naturally, subsequently heating at 1000 °C for 3 h; (3) heating at 700 °C for 3 h, then the powders were pressed into pellets, and finally heating at 750 °C for 3 h to investigate the

* Corresponding author. Tel.: +86 25 83594689; fax: +86 25 83595535.
E-mail address: adli@nju.edu.cn (A.-D. Li).

influence of stress. The structure of the thermally treated powders was characterized by X-ray diffraction (XRD, Rigaku-D/Max 2000, Japan) with Cu K α radiation. The thermal decomposition and phase transition characteristics of the powder samples thermally treated at 500 °C were analyzed by a thermogravimetric and differential scanning calorimeter (TG/DSC, Netzsch STA 409 PC/PG, Germany). To check the structure consistency between Low- β and High- β , the Raman spectroscopy was measured using a JY HR800 Raman spectrometer under a back-scattering geometry. The 488 nm line of air-cooled Ar-ion laser was used as an excitation, and the output powder was set at 5 mW. The grain sizes of the powders were examined using scanning electron microscopy (SEM, Philips XL-30, the Netherlands) and transmission electron microscopy (TEM, Tecnai F20 S-Twin, FEI).

3. Results and discussion

Fig. 1(a) gives the XRD patterns of BiNbO $_4$ powders thermally treated at 550–1050 °C for 3 h. It can easily be seen that before the appearance of β -BiNbO $_4$ (Low- β), an intermediate phase of Bi $_5$ Nb $_3$ O $_{15}$ is formed at 550 °C. For the sample thermally treated at 600 °C, Low- β as the major phase coexists with the Bi $_5$ Nb $_3$ O $_{15}$ phase, consistent with other groups' results [14]. Almost pure Low- β powders are obtained between 700 and 750 °C. With increasing the thermal treatment temperature, the Low- β powders gradually turn into α -BiNbO $_4$ phase. There exists a temperature range (about 750–900 °C) where the Low- β and α -BiNbO $_4$ phases coexist. At about 900 °C, the Low- β completely transform into α -BiNbO $_4$. When thermally treated above 1040 °C, the α -BiNbO $_4$ transforms into β -BiNbO $_4$ (High- β) again. This result confirms that the abnormal phase transition from β -BiNbO $_4$ to α -BiNbO $_4$ exists in powder format. In order to check the reversibility of the phase transition, samples were first thermally treated at 700 °C and 1050 °C to synthesize Low- β and High- β phases, respectively, and then thermally treated at 1000 °C, as shown in Fig. 1(b) and (c). The abnormal phase transition from β -BiNbO $_4$ to α -BiNbO $_4$ is only observed in Low- β powders.

In addition, we also investigated the influence of stress on the phase transition from β -BiNbO $_4$ to α -BiNbO $_4$, as shown in Fig. 1(d). For the samples in pellet format, β -BiNbO $_4$ formed at 700 °C thoroughly turns into α -BiNbO $_4$ at 750 °C, while no phase transition happens for the powder samples. This result indicates that the transformation from β -BiNbO $_4$ to α -BiNbO $_4$ is accelerated, related to the associated activation of stress, as explained in [7].

In order to investigate the phase transition characteristics of BiNbO $_4$, TG/DSC curve was examined. Before the measurement, the sample was first thermally treated at 500 °C for 3 h. In Fig. 2, there are an exothermic peak at about 560 °C and an endothermic peak at about 1040 °C. The exothermic peak results from the thermal decomposition of metal-citrate and the formation of oxides, confirmed by the XRD patterns. Endothermic reaction occurs at about 1040 °C, corresponding to the phase transition from α -BiNbO $_4$ to High- β . Between 560 and 1040 °C, there is no abrupt change with an exothermic temperature range. Associated with the XRD results, we consider that the phase transition from Low- β to α -BiNbO $_4$ is exothermic with a gradual and diffuse phase transition process.

To check the structure consistency between Low- β and High- β , furthermore, to understand the process of phase transition, the Raman spectroscopy was measured, as seen in Fig. 3. From the Raman spectra, the Low- β and High- β powders have the same curve shape, which means that the vibrational modes are identical for both samples. So we can conclude that the Low- β and High- β have the same structure, in accordance with the XRD results. The sample thermally treated at 850 °C has the sharp peaks at 104.7 cm $^{-1}$ and 144 cm $^{-1}$ from the vibration modes of β -BiNbO $_4$ and α -BiNbO $_4$, respectively, which also proves that the phase transition from Low- β to α -BiNbO $_4$ is a gradual and diffuse phase transition process. In Fig. 3, the Raman spectra of the triclinic oxides are noticeably more complex than that of orthorhombic oxides,

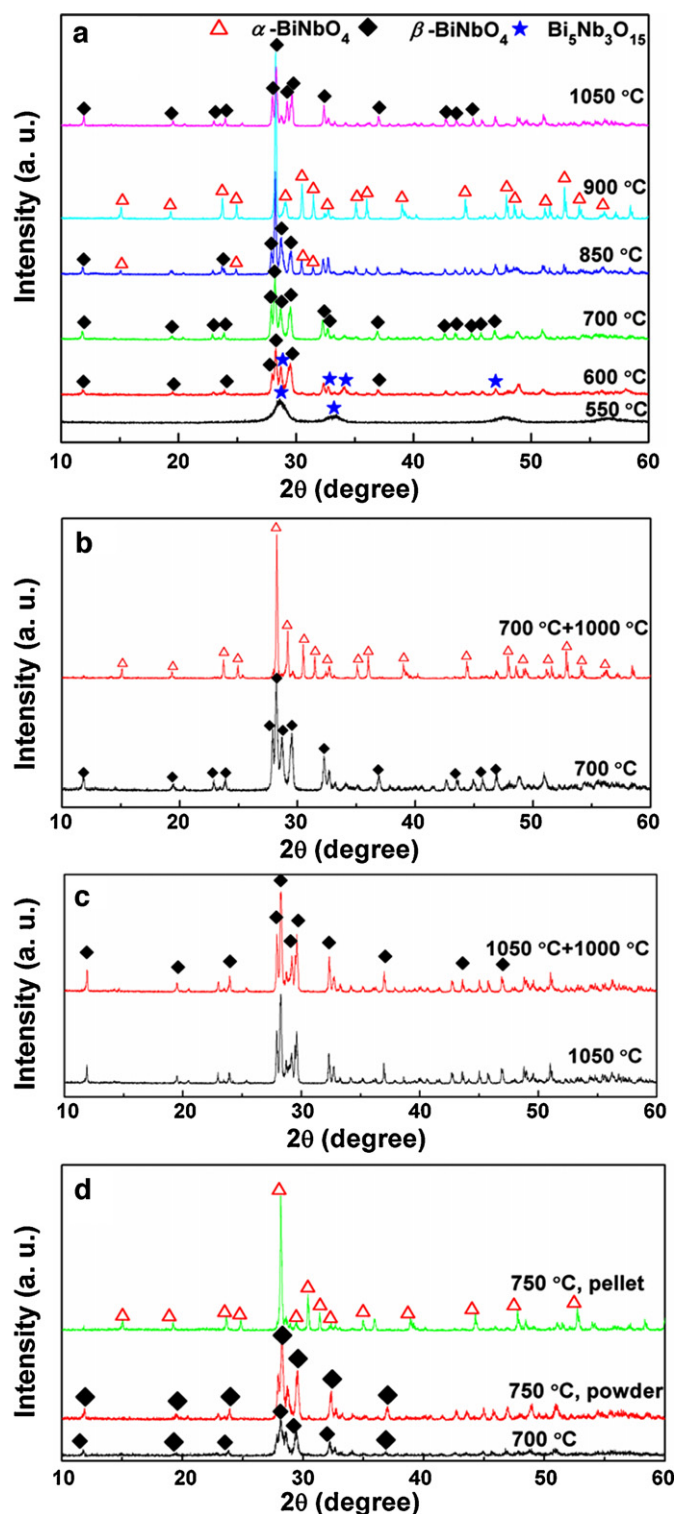


Fig. 1. XRD patterns of BiNbO $_4$ powders thermally treated (a) at different temperatures for 3 h, (b) at 700 °C and sequentially at 1000 °C for 3 h, (c) at 1050 °C and sequentially at 1000 °C for 3 h, and (d) at 700 °C for 3 h, then the powders were pressed into pellets, and finally both the powder and pellet were thermally treated at 750 °C for 3 h.

because the lowered symmetry of triclinic phase produces more Raman active modes.

Fig. 4 shows the crystal structures of Bi $_5$ Nb $_3$ O $_{15}$, β -BiNbO $_4$ and α -BiNbO $_4$, respectively. The structure of Bi $_5$ Nb $_3$ O $_{15}$ is a mixed-layer Aurivillius-related phase, consisting of a

Download English Version:

<https://daneshyari.com/en/article/1616777>

Download Persian Version:

<https://daneshyari.com/article/1616777>

[Daneshyari.com](https://daneshyari.com)