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Abnormal phase transition in $BiNbO_4$ powders prepared by a citrate method

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ABSTRACT

Triclinic β-$BiNbO_4$ prepared below 750 °C and above 1040 °C (denoted as Low-β and High-β, respectively) and pure orthorhombic α-$BiNbO_4$ at 900 °C were successfully derived from a citrate method and the phase transition from β-$BiNbO_4$ to α-$BiNbO_4$ was first observed in $BiNbO_4$ powders. This phenomenon proves that the abnormal phase transition from β-$BiNbO_4$ to α-$BiNbO_4$ exists in $BiNbO_4$ powder system. The synthesis of Low-β powders can be attributed to the formation of the intermediate phase of $Bi_5Nb_3O_{15}$ by the citrate method. With increasing temperature, the Low-β phase gradually turns into α-$BiNbO_4$ 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 $BiNbO_4$ in comparison with powder samples. It brings us new understanding of the $BiNbO_4$ system and also provides a simple way to obtain $BiNbO_4$ for microwave and photocatalytic applications.

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 $BiNbO_4$, 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 $BiNbO_4$-based ceramics, phase transition is an important concern [4,5].

The triclinic $BiNbO_4$ (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 ($SbTaO_4$) structure [8], while β phase belongs to the $P\bar{1}$ (No. 2) space group [9]. As reported, the low-temperature orthorhombic $BiNbO_4$ 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-$BiNbO_4$ to α-$BiNbO_4$ in $BiNbO_4$ 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-$BiNbO_4$ powders convert into α-$BiNbO_4$ ones.

For the preparation of $BiNbO_4$, 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 $BiNbO_4$ 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-$BiNbO_4$ 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-$BiNbO_4$ to α-$BiNbO_4$ 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 $BiNbO_4$ powders was proposed.

2. Experimental procedures

The $BiNbO_4$ powders were prepared using a citrate method. The citrate method is an effective way to prepare $BiNbO_4$ at lower temperature [14]. The precursor materials of $BiNbO_4$ were bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$), 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. $Bi(NO_3)_3 \cdot 5H_2O$ 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

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influence of stress. The structure of the thermally treated powders was characterized by X-ray diffraction (XRD, Rigaku-D/Max 2000, Japan) with Cu Kα 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-scatting 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 $Bi_5Nb_3O_{15}$ is formed at 550 °C. For the sample thermally treated at 600 °C, Low-β as the major phase coexists with the $Bi_5Nb_3O_{15}$ 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.

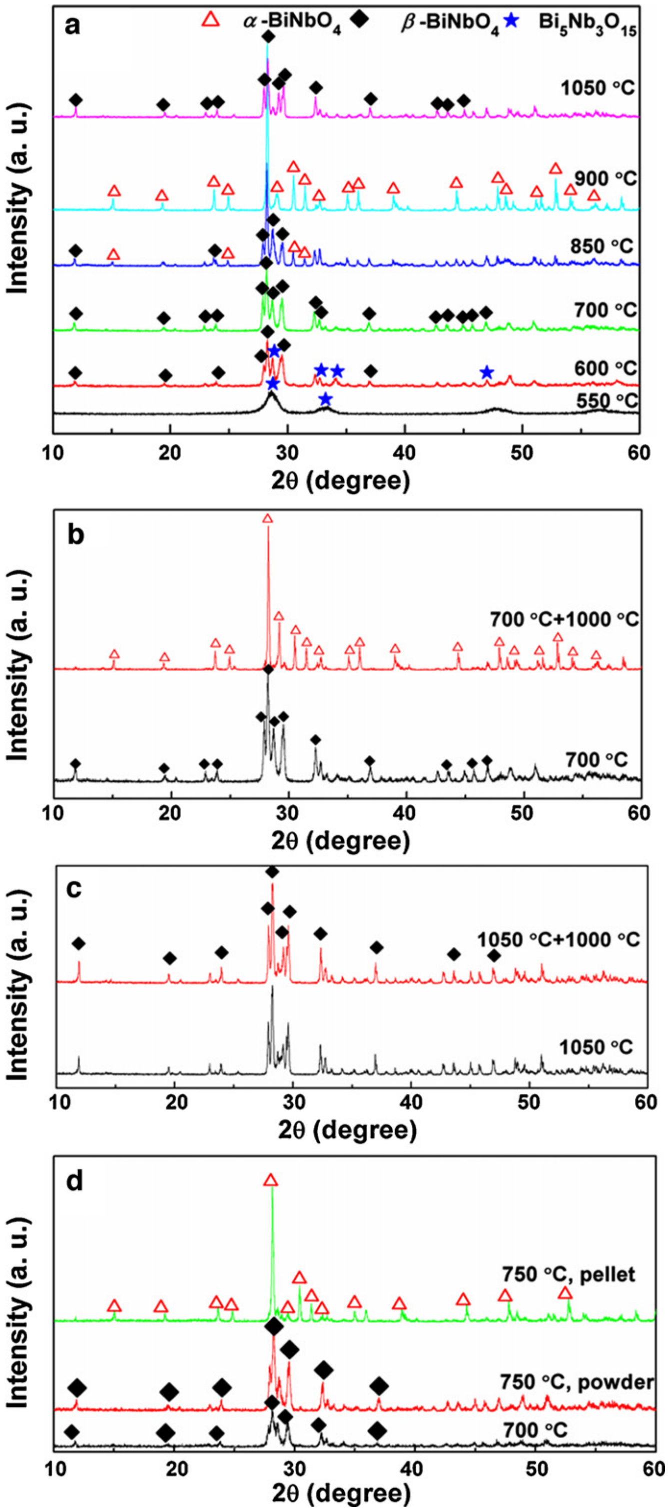

Fig. 1. XRD patterns of $BiNbO_4$ powders thermally treated (a) at different temperatures for 3 h, (b) at 700 °C and sequentially at 1000 °C for 3 h, (c) at 1050 °C and sequentially at 1000 °C for 3 h, and (d) at 700 °C for 3 h, then the powders were pressed into pellets, and finally both the powder and pellet thermally treated at 750 °C for 3 h.

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

Fig. 4 shows the crystal structures of $Bi_5Nb_3O_{15}$, β-$BiNbO_4$ and α-$BiNbO_4$, respectively. The structure of $Bi_5Nb_3O_{15}$ is a mixed-layer Aurivillius-related phase, consisting of a

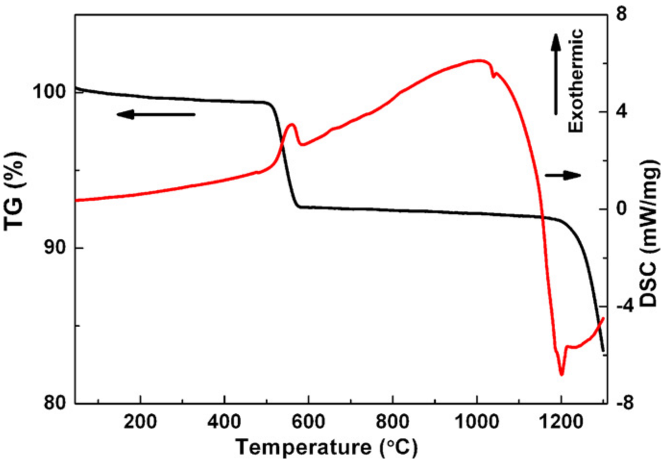

Fig. 2. TG/DSC curves of $BiNbO_4$ powders obtained at 500 °C for 3 h.

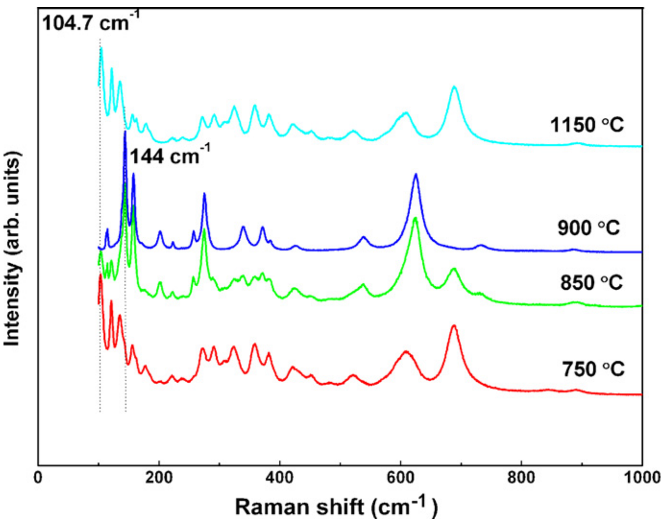

Fig. 3. Raman spectra of the $BiNbO_4$ powders thermally treated at different temperatures in air.

$[Bi_2O_2]+[NbO_4]+[Bi_2O_2]+[BiNb_2O_7]$ stacking sequence [20], as illustrated in Fig. 4(a). The NbO_6 octahedra are joined at four vertices to form the sheets of formula $[NbO_4]_n$ with some distortion. The triclinic β-$BiNbO_4$ (Fig. 4(b)) consists of pseudo layers of $[Bi_2O_2]$ units connected with each other and surrounded by sheets of formula $[NbO_4]_n$ along the *bc* plane. Also, the $[Bi_2O_2]$ units tilt each other not in a linear arrangement. It can also be regard as a layered structure, consisting of a $[Bi_2O_2]+[NbO_4]+[Bi_2O_2]+[NbO_4]$ stacking sequence. The orthorhombic structure can be described to consist of two bismuth layers and two separated NbO_6 octahedral layers with different distortions, as shown in Fig. 4(c). By comparison among these three kinds of crystal structures carefully, it is found that the triclinic β-$BiNbO_4$ and the $Bi_5Nb_3O_{15}$ have similar stacking units of $[Bi_2O_2]$ and $[NbO_4]$. With the increase of thermal treatment temperature, for $Bi_5Nb_3O_{15}$ phase, the selective volatilization of Bi atoms from $[BiNb_2O_7]$ structure and preservation of $[NbO_4]$ and $[Bi_2O_2]$ units lead to the formation of triclinic β-$BiNbO_4$ (Low-β). In other words, the $Bi_5Nb_3O_{15}$ turns into triclinic β-$BiNbO_4$ instead of α-$BiNbO_4$ with the relatively lower barrier-activation energy due to the structure similarity between $Bi_5Nb_3O_{15}$ and β-$BiNbO_4$. So, although α-$BiNbO_4$ is the thermodynamically stable phase below 1040 °C, the larger structure difference between α-$BiNbO_4$ and $Bi_5Nb_3O_{15}$ leads to higher barrier-activation energy and α-$BiNbO_4$ is difficult to form from the decomposition of $Bi_5Nb_3O_{15}$ at low thermal treatment temperature of 600–750 °C. In one word, on one hand the formation of Low-β is attributed to the appearance of the intermediate phase of $Bi_5Nb_3O_{15}$, on the other hand the fine $Bi_5Nb_3O_{15}$ particles with large reactive surface area after pyrolysis of the citrate precursor might be an effective factor to activate the decomposition of the $Bi_5Nb_3O_{15}$ phase into Low-β [21]. Such a phenomenon is also observed in the preparation of β-$BiTaO_4$ powders using the citrate method [22].

The phase transition from β-$BiNbO_4$ to α-$BiNbO_4$ occurs only in the β-$BiNbO_4$ samples prepared below 750 °C. We think that the grain size might play a key role during this procedure. Fig. 5 shows the TEM and SEM images of $BiNbO_4$ thermally treated at 700 and 1050 °C, respectively. The grain size of $BiNbO_4$ powders thermally treated at 700 and 1050 °C is about 200 nm and 2 μm, respectively. The shape of $BiNbO_4$ powders seems irregular, and the samples

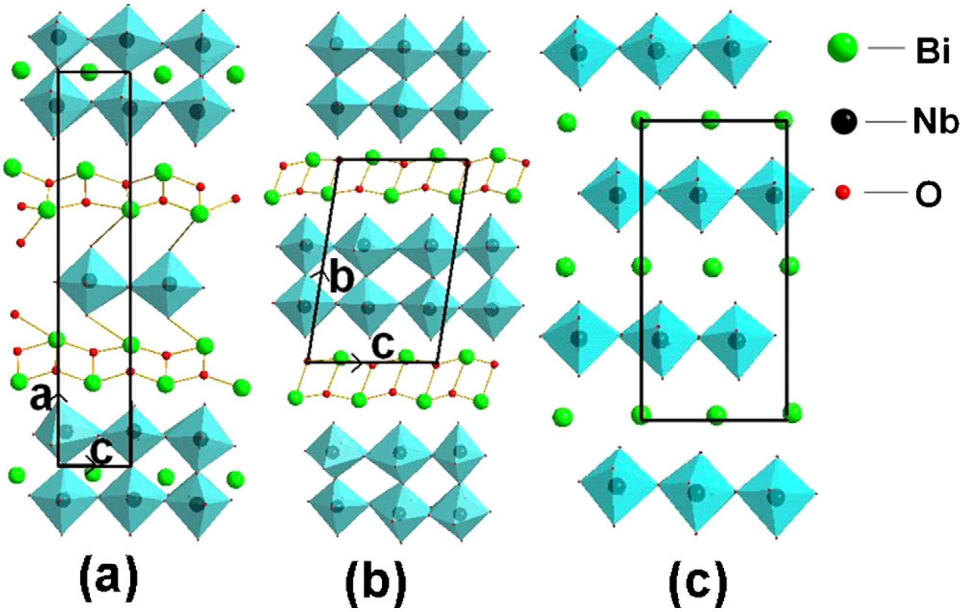

Fig. 4. Schematic illustrations of crystal structures of (a) $Bi_5Nb_3O_{15}$, (b) β-$BiNbO_4$ and (c) α-$BiNbO_4$.

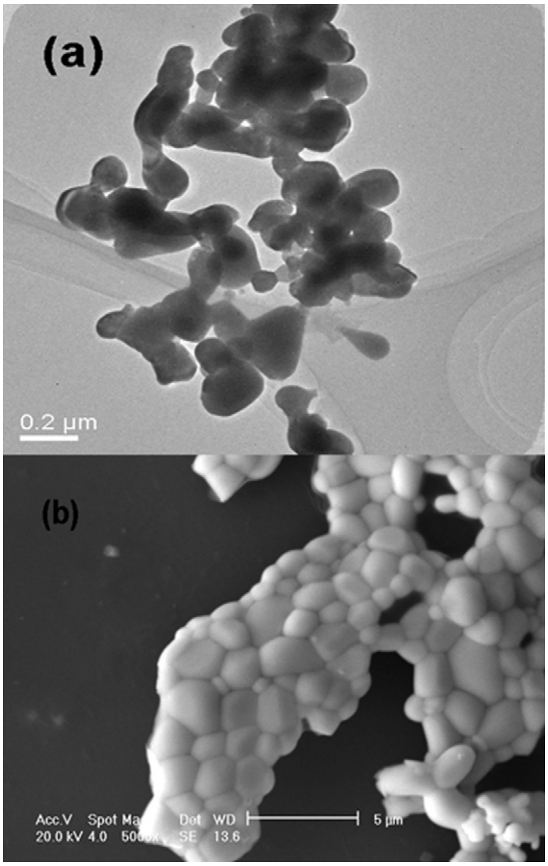

Fig. 5. (a) TEM image of $BiNbO_4$ thermally treated at 700 °C for 3 h, and (b) SEM images of $BiNbO_4$ thermally treated at 1050 °C for 3 h.

thermally treated at 1050 °C have an obvious tendency to form partially sintered aggregates as a result of higher temperature thermal treatment. These images consist with the XRD results shown in Fig. 1(a). The relative intensities of crystal planes in XRD patterns are not very clear for Low-β, especially for the peaks at around 30°, which contains the information of more than one crystal plane. Compared with High-β we consider that the crystal evolution of Low-β has not completed yet. As we know, β-$BiNbO_4$ is thermodynamically stable phase above 1040 °C, below which the Low-β with smaller grain size derived from the decomposition of $Bi_5Nb_3O_{15}$ is in thermodynamically metastable state, and has the trend to transform into α-$BiNbO_4$ of thermodynamically stable phase. Therefore during heating from 750 to 900 °C, the nominally abnormal phase transition from β-$BiNbO_4$ to α-$BiNbO_4$ happens gradually. In fact, the phase transition from Low-β to α-$BiNbO_4$ is reasonable after considering thermodynamic factors, just like the Low-β formation from the $Bi_5Nb_3O_{15}$ due to the kinetic effect.

As discussed above, with the increase of thermal treatment temperature, Low-β begins to transform into α-$BiNbO_4$ due to the thermodynamic requirement. The [NbO_4] structure is opened up and separated by a layer of bismuth. When the temperature is above 1040 °C, the neighboring layers of NbO_6 octahedra join together again with the phase transition from α-$BiNbO_4$ to High-β.

4. Conclusions

In summary, β-$BiNbO_4$ and α-$BiNbO_4$ powders were successfully synthesized by the citrate method and the abnormal phase transition from β-$BiNbO_4$ to α-$BiNbO_4$ was first observed in $BiNbO_4$ powders. This result proves that the phase transition from β to α-$BiNbO_4$ exists in $BiNbO_4$ powder system. The synthesis of Low-β can be attributed to the advantage of citrate method and the formation of the intermediate phase $Bi_5Nb_3O_{15}$. The phase transition from Low-β to α-$BiNbO_4$ may be due to the thermodynamically metastable state of Low-β. We also prove that the influence of activation of stress on the phase transition from Low-β to α phase of $BiNbO_4$ in pellet format. It brings us new understanding of the $BiNbO_4$ system and provides a simple way to obtain $BiNbO_4$ for microwave and photocatalytic applications.

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