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Low-temperature synthesis of β -BiNbO₄ powder by citrate sol–gel method

Ning Wang*, Mei-Yu Zhao, Zhi-Wen Yin, Wei Li

Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 DingXi Road, Shanghai 200050, PR China

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Abstract

β -BiNbO₄ powder with nanometer sized (\approx 65 nm) particles was prepared by citrate sol–gel technique. Using Bi-citrate and Nb-citrate as the starting precursors, the crystalline phase of β -BiNbO₄ could be obtained by thermal decomposition of citrate complex precursors at a low temperature (600 °C). Infrared spectrum, thermogravimetry–differential thermal analysis (TG–DTA), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) technique and transmission electron microscopy (TEM) were used to characterize the citrate precursors and the calcined powders.

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1. Introduction

Recently, increasing efforts have been directed towards achieving even further miniaturization of microwave components and devices by employing passive integration [1]. This passive integration is performed using multilayer ceramics technology, whereby green ceramic tapes of different materials—corresponding to the different passive functions—are laminated and co-fired, usually at rather low temperatures. Therefore, it is necessary to develop dielectric ceramic materials that can be sintered at temperatures lower than the melting point of internal

conductor. Most of the known commercial microwave dielectric ceramics, such as (Zn,Sn)TiO₄, Ba₂Ti₉O₂₀ and Ba(Mg_{1/3}Ta_{2/3})O₃, possess good microwave dielectric properties but high sintering temperatures [2–4]. Although low melting glass additions, chemical processing and smaller particle sizes of the starting materials were, three methods normally, used to reduce the sintering temperature of those dielectric materials; the sintering temperatures for those ceramics were still too high to co-fire with low melting point electrodes of Ag or Cu.

BiNbO₄ ceramics have attracted many researchers' attention because of their excellent microwave dielectric properties and their low sintering temperatures [5–8]. It is well known that BiNbO₄ ceramics have a crystal structure of the orthorhombic-SbTaO₄ type (α) below 1020 °C and then transform to the triclinic phase (β) as the temperature is increased [9–11]. BiNbO₄ ceramics with α -phase have been

* Corresponding author. Tel.: +86-21-52412014; fax: +86-21-52413903.

E-mail address: wningemail@163.net (N. Wang).

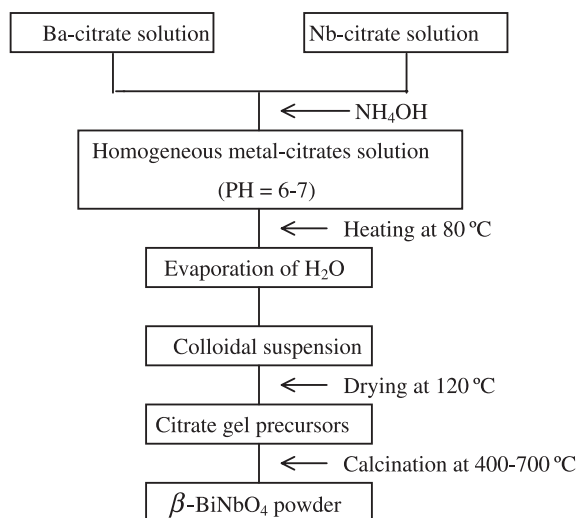


Fig. 1. Schematic diagram for the preparation of β -BiNbO₄ powder by citrate sol-gel process.

investigated worldwide and their microwave dielectric properties were also reported in many literatures. For example, BiNbO₄ ceramics with CuO–V₂O₅ mixtures addition sintered at 875 °C were found to be in the low-temperature α modification and possess a Q value of 4260 (at 4.3 GHz), ϵ_r value of 43 and τ_f value of +38 ppm/°C [5]. The microwave dielectric properties of (Bi_{1-x}Nd_x)NbO₄ with $x=0.025$ sintered at 940 °C were $\epsilon_r=43.7$, $Q \times f=11046$ GHz, and $\tau_f=-1.82$ ppm/°C [6]. At a sintering temperature of 920 °C and x value of 0.01, (Bi_{1-x}La_x)NbO₄ ceramics exhibited the microwave dielectric properties of $\epsilon_r \sim 43.36$, $Q \times f \sim 10600$ GHz, and $\tau_f \sim -2$ ppm/°C [7]. On the other hand, the β -BiNbO₄ has received little attention and the microwave dielectric properties of pure β -BiNbO₄ are not yet studied. The reason might be that the β -BiNbO₄ could be obtained only when the preparation temperature was above 1020 °C; however, such a high preparation temperature might lead to the compositional deviation from stoichiometry as a result of the evaporation of Bi₂O₃. To get a dense and well-sintered BiNbO₄ ceramics with β -phase, it is important to get the β -BiNbO₄ powder at low temperature. However, there are no previous reports, to the best of our knowledge, on the synthesis of β -BiNbO₄ at low temperature.

Here, a new route to synthesize the β -BiNbO₄ at low temperature is presented. The citrate sol-gel process is

thought to be highly promising for achieving homogeneous mixing of the component cations on the atomic scale. Therefore, the adjacent ions can immediately react with each other at a relatively low temperature [12]. This method has been applied to the synthesis of BaTiO₃, Ba-polytitanate and Ba(Mg_{1/3}Ta_{2/3})O₃ powder [13–16]. In the present study, the citrate sol-gel method is used to synthesize the β -BiNbO₄ powder at low temperature. The formation and evolution of crystalline BiNbO₄ from the amorphous citrate precursors are investigated and the resultant powders are characterized. Our self-prepared Nb-citrate was adopted as the starting precursor.

2. Experimental

Bismuth citrate and niobium citrate solutions were prepared for use as starting materials. The experimental procedure for preparing the BiNbO₄ citrate gels and powder is shown in Fig. 1. The aqueous bismuth and niobium citrate solutions were intermixed to the corresponding mole ratio of BiNbO₄. Then the pH value of the solution was adjusted to about 6–7 by adding ammonia solution. The water was evaporated from the solution at 80 °C in a water bath under vigorous stirring and a colorless colloidal suspension was formed. Further heating at 120 °C resulted in dark colored, amorphous citrate gels, which were then subjected to calcination at various temperatures (400–700 °C).

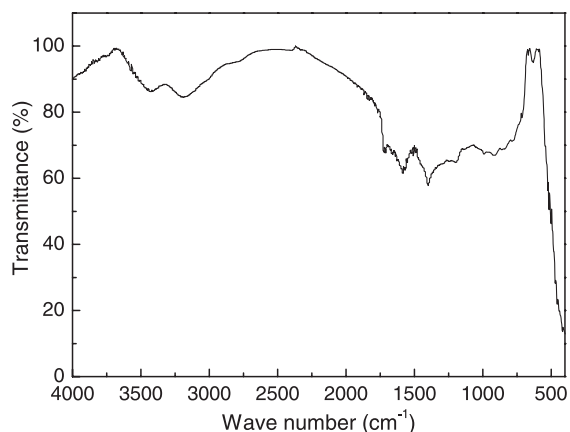


Fig. 2. Infrared spectrum of the citrate precursors of BiNbO₄.

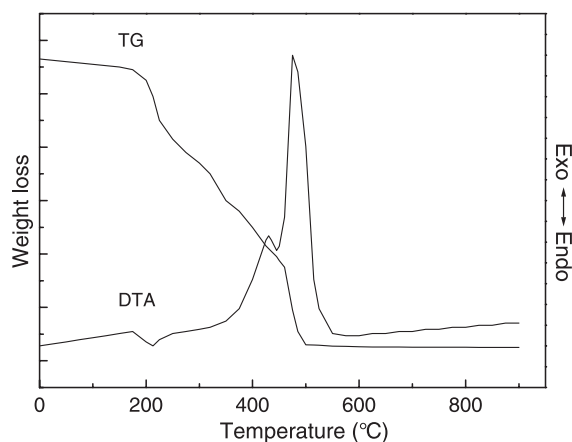


Fig. 3. TG–DTA curves for the amorphous citrate gel precursors of BiNbO_4 .

The structure of the citrate precursors was examined by infrared spectrometry, using KBr as the medium. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out to understand the decomposition and synthesizing processing at a

heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Crystalline phases of the calcined powder were examined by X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation. The specific surface area (SSAS) of the calcined powder was measured using a conventional three points Brunauer–Emmett–Teller (BET) technique with N_2 absorption. The morphology of the selected calcined powder was observed by means of transmission electron microscopy (TEM).

3. Results and discussion

In citrate sol–gel process, it is important to obtain the component cations citrate complexes in precursors, which can keep the constituent metal cations dispersed homogeneously [15]. Citric acid is a strong complex, which can react with many metal ions under ammonia conditions such Ba^{2+} , Ca^{2+} , Zr^{4+} , Y^{3+} , etc. Therefore, it could be used to prepare the multi-composition solution. Fig. 2 shows the infrared spectrum of the citrate precursors of BiNbO_4 . The broad absorption peak

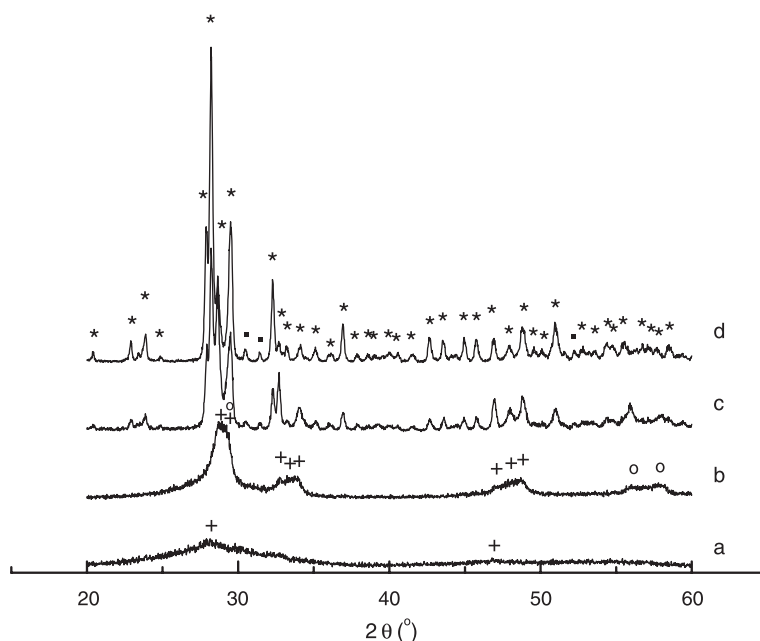


Fig. 4. X-ray diffraction patterns of citrate-derived BiNbO_4 powders as a function of calcination temperature (a) 400, (b) 500, (c) 600, (d) 700 $^\circ\text{C}$ (*: $\beta\text{-BiNbO}_4$, \bullet : $\alpha\text{-BiNbO}_4$, +: $\text{Bi}_3\text{Nb}_{17}\text{O}_{47}$, \circ : $\text{Bi}_8\text{Nb}_{18}\text{O}_{58}$).

Table 1
Characteristics of citrate-derived particles

	600 °C	700 °C
Specific surface area, S_{BET} (m^2/g)	12.42	7.26
ESD ^a (nm)	≈ 65	≈ 110
Particle shape, TEM	nearly round	nearly round
Particle size, TEM (nm)	70–130	140–270

^a ESD: equivalent spherical diameter, $D = 6/(\rho \times S_{\text{BET}})$.

between 3200 and 2900 cm^{-1} corresponds to the stretch of OH in citrate complex. The absorption peaks at 1586 and 1399 cm^{-1} are attributed to the stretch of $-\text{COO}^-$ ions. All kinds of $-\text{COOH}$ have a group of absorption peaks at 3000–2500 cm^{-1} . However, these peaks are not observed in the infrared spectrum of the citrate precursors. The result of infrared spectrum confirms the formation of metal citrate complexes in citrate precursors.

The thermal decomposition of the citrate precursors of BiNbO_4 is shown in Fig. 3. The broad endothermic peak at 213 °C together with drastic weight loss in TG curve is assigned to the evaporation of crystalline water and the melting of remaining citric acid. In the range of 250–400 °C, the weight loss might result from the decomposition of substances present in gels such as ammonia and free citrate [17]. The strong exothermic peaks at 400–500 °C in DTA curve and the abrupt weight decrease in TG might be due to the oxidative decomposition of citrates and the synthesis of $\beta\text{-BiNbO}_4$.

Fig. 4 represents the XRD patterns of the powder calcined at various temperatures in air for 2 h. A small amount of $\text{Bi}_3\text{Nb}_{17}\text{O}_{47}$ phase is present after the amorphous citrate precursors were calcined at 400 °C for 2 h (Fig. 4a). The diffraction peaks of $\text{Bi}_3\text{Nb}_{17}\text{O}_{47}$ become strong and apparent and the $\text{Bi}_8\text{Nb}_{18}\text{O}_{58}$ phase is also formed in the powder calcined at 500 °C (Fig. 4b). Almost completely $\beta\text{-BiNbO}_4$ phase could be obtained at 600 °C and the diffraction curve becomes narrower with the calcination temperature increasing to 700 °C, which implies the improvement of the crystallinity and the growth of the crystallite size of the BiNbO_4 powder (Fig. 4c,d). Only very weak peaks of $\alpha\text{-BiNbO}_4$ are detected in Fig. 4. This suggests that the high temperature phase of BiNbO_4 can be synthesized at a very low temperature of 600 °C, which is about 400 °C lower than

that prepared by conventional method. Since the crystal structure of BiNbO_4 is the orthorhombic- SbTaO_4 type ($\alpha\text{-BiNbO}_4$) below 1020 °C and then it will transform to the triclinic phase ($\beta\text{-BiNbO}_4$) as the temperature increases [9–11]. Such a lowering for the formation temperature of $\beta\text{-BiNbO}_4$ might be due to the fact that the formation of citrate complexes in precursors effectively keeps the constituent metal cations dispersed homogeneously, as mentioned above [15].

The characteristics of the powders obtained after calcining the citrate gel precursors at 600 and 700 °C for 2 h are summarized in Table 1. The particle size and shape for the powder were observed by transmission electron micrographs (TEM) (Fig. 5). Both of the calcined powders consist of nearly round shaped particles, as shown in Fig. 5. The diameters for the powders calcined at 600 and 700 °C are estimated as 70–130 and 140–270 nm, respectively. This indicates

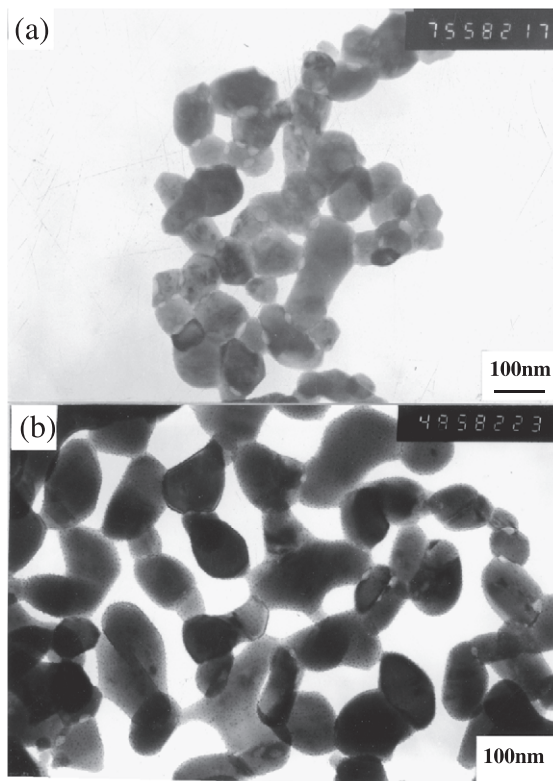


Fig. 5. Transmission electron micrographs of citrate-derived $\beta\text{-BiNbO}_4$ powders calcined at (a) 600 and (b) 700 °C for 2 h.

that the particle size increases as the calcination temperature increases from 600 to 700 °C. The specific surface area was measured as 12.42 and 7.26 m²/g for the powders calcined at 600 and 700 °C (shown in Table 1). Under the assumption of spherical particles, an approximately equivalent spherical diameter (ESD) could be calculated as 65 and 110 nm, respectively. The discrepancy between the particle size estimated by TEM and that by BET might be attributed to the surface roughness of the particles and to the assumption of the perfect spherical geometry [18]. The fine β -BiNbO₄ powders synthesized at temperature as low as 600 °C were supposed to show excellent sinterability.

4. Conclusions

The nanometer sized (\approx 65 nm) β -BiNbO₄ powder with high surface activities were successfully synthesized by the citrate sol–gel method. β -BiNbO₄ phase could be formed almost completely by calcining the citrate complex precursors at 600 °C for 2 h. The diameter of particles was significantly increased and the crystallinity of calcined powder was improved with the calcination temperature increasing from 600 to 700 °C.

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