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Hydrothermal synthesis of $Ba_5Nb_4O_{15}$ ultrafine powders

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Abstract

$Ba_5Nb_4O_{15}$ ultrafine powders were prepared by hydrothermal method using $Ba(NO_3)_2$ and Nb_2O_5 precursors. The synthesis characteristics were influenced by the chemical form of precursors, reaction temperature, mole ratio of Ba/Nb and pH value. The chemical form of the precursors has a strong influence on the products of $Ba_5Nb_4O_{15}$. There was no requisite compound in the final product when Nb_2O_5 powder was used as Nb-precursor. In addition, the reaction completeness was also dependent on the synthesis temperature. The best single phase $Ba_5Nb_4O_{15}$ ultrafine powders were obtained at a temperature of 230 °C. The most appreciate Ba/Nb molar ratio was 3/2. The reactions were only carried out in a solution with pH value between 12 and 14. When pH was equal or larger than 14, there was no product of $Ba_5Nb_4O_{15}$ powder in the reactor.

Keywords: Powders-chemical preparation; X-ray methods; Chemical properties; Niobates; Microwave dielectric materials

1. Introduction

Dielectric materials with dielectric constant greater than 20 and high quality factors ($Q_f > 2000$ GHz) have attracted increasing interests for microwave applications. The hexagonal perovskite oxide $A_5B_4O_{15}$ (A = Ba, Sr; B = Nb, Ta) system have been characterized at microwave frequencies. These systems combine a relatively high permittivity ($39 < \varepsilon_r < 46$) with a low dielectric loss ($11{,}583\,\text{GHz} < Q_f < 31{,}839\,\text{GHz}$) and small temperature coefficient of resonant frequency ($-36\,\text{ppm/°C} < \tau_f < 79\,\text{ppm/°C}$) and these were expected as good candidates for microwave dielectric materials.[1] Among $A_5B_4O_{15}$ (A = Ba, Sr; B = Nb, Ta) system, $Ba_5Nb_4O_{15}$ is the most attractive due to the low cost and good dielectric properties. The structure of $Ba_5Nb_4O_{15}$ has been well studied.[2–5] It has hexagonal structure and crystallizes in the P3m1 space group with one formula unit per cell ($Z = 1$). The compounds have five-layer closet packing of oxygen and barium ions. The Nb^{5+}ions are positioned at the octahedral sites of five AO_3 layers which altogether constitute the unit cell. All the $Ba_5Nb_4O_{15}$ powders were prepared by the conventional solid-reaction method in the concerned reports.[1–9] Sreemoolanadhan et al. synthesized $Ba_5Nb_4O_{15}$ by blending stoichiometric amounts of $BaCO_3$ and Nb_2O_5 and heating at 1250 °C for 4 h, while Srivastava et al. synthesized $Ba_5Nb_4O_{15}$ at 1100 °C for 10 h.[8]

The present paper reports the hydrothermal synthesis of $Ba_5Nb_4O_{15}$ powder. The major advantage of hydrothermal processing is that there is no need for high-temperature calcination. This, in turn, eliminates the need for milling. Powders are formed directly from solution by taking advantage of the complex reactions taking place in high-temperature water. By controlling these reactions, it is possible to produce anhydrous crystalline powders with controlled particle size, controlled stoichiometry and, in some cases, controlled particle morphology. Chemically synthesized ceramic powders often posses better chemical homogeneity and a finer particle together with better control of particle morphology than those produced by the mixed oxide route, and these features often result in the improved sinterability.[6]

2. Experiment procedures

Analysis-grade barium nitrate and 4N niobium oxide were adopted as the raw materials. Hydrothermal synthesis of $Ba_5Nb_4O_{15}$ powders was carried out in a 200 cm^3 stainless autoclave with a Teflon line under autogenous pressure. First, the niobium oxides were dissolved in hot hydrofluoric acid, and the mixture was heated at 80 °C inside a ventilator to remove the residuary HF. Then, the niobium oxide solution was mixed with the barium nitrate which was dissolved in distilled water. After that, sodium hydroxide was vigorously added to the mother solutions until the pH value attained the desired value. Then, the resultant suspension was transferred to the autoclave and heated at 200–250 °C for 5 h, where the filling factor was 80 vol%.

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After cooling, the product was filtered and washed with distilled water until the pH was between 7 and 8. Finally, the product was poached ultrasonically with distilled water and dried at 80 °C in an oven.

The XRD analysis using Cu Kα radiation (Rigaku D/MAX2550PC) was conducted to determine the crystal structure. The microstructure and morphology of the product powders were examined using a scanning electron microscope (XL-30-ESEM) with a field gun. An accelerating voltage of 20 kV was used.

3. Results and discussion

Two kinds of differently pretreated Nb_2O_5-precursors are used to synthesis $Ba_5Nb_4O_{15}$. Fig. 1 shows the products XRD patterns of the two kinds of precursors: (a) the product derived from the Nb_2O_5 powders dissolved in 40% hot HF solution, (b) result of Nb_2O_5 powders in 40% HF solution without dissolution. Only Nb_2O_5 powders dissolve in hot HF solution, can lead to $Ba_5Nb_4O_{15}$ powders in the product. Otherwise, there are only NaF and BaF_2 in the product.

In precursor (a) the following reactions take place:

$$Nb_2O_5 + (10 + 2n)HF = 2H_n[NbF_{5+n}] + 5H_2O \tag{1}$$

$$\begin{aligned}&4H_n[NbF_{5+n}] + 5Ba^{2+} + 30OH^- \\ &\quad = Ba_5Nb_4O_{15} + 4nHF + 20F^-\end{aligned} \tag{2}$$

In precursor (b) the reaction is

$$Ba^{2+} + 2F^- = BaF_2 \tag{1}$$

$$Na^+ + F^- = NaF \tag{2}$$

$$2Na^+ + Nb_2O_5 + 2OH^- = 2NaNbO_3 + H_2O \tag{3}$$

BaF_2 is not resolvable in water, so, when mixed, Ba-precursor and (b), Ba^{2+} ions react with dissociative F^- ion passionately in the mixture.

$NaNbO_3$ has good solubility in water, it is washed away by distilled water, so there is no $NaNbO_3$ phase in XRD pattern of the resultant product.

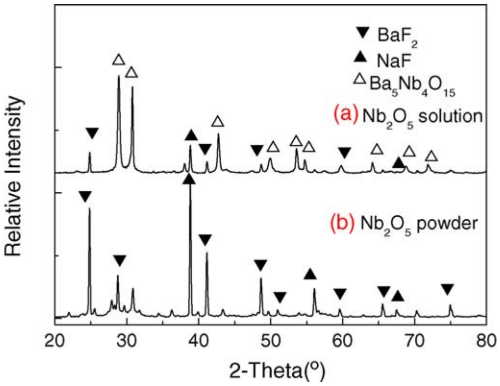

Fig. 1. The XRD patterns of (a) Nb_2O_5 powders dissolved in 40% HF solution, (b) Nb_2O_5 powders not dissolved in 40% HF solution.

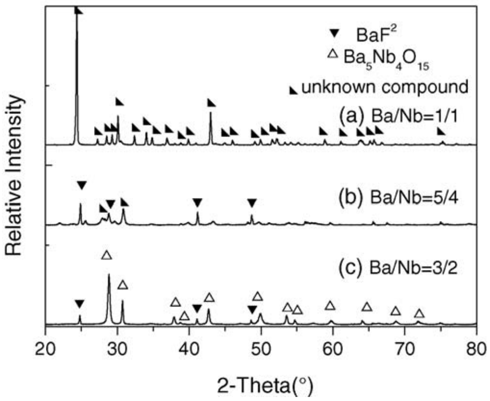

Fig. 2. XRD spectra of hydrothermal powders synthesized at 250 °C from different molar ratio of $Ba(NO_3)_2$ and Nb_2O_5: (a) m(Ba)/m(Nb) = 1/1; (b) m(Ba)/m(Nb) = 1.25/1; (c) m(Ba)/m(Nb) = 1.5/1.

Eight grams of $Ba(NO_3)_2$ and Nb_2O_5 precursors having various Ba:Nb molar ratios were hydrothermally treated at pH 12, 230 °C for 5 h. Fig. 2 shows the XRD spectra of the products. The products are dominated by the Ba/Nb ratio. When Ba/Nb ratio is 1/1, whether there is a product we cannot make a conclusion from the XRD pattern. BaF_2 is synthesized as Ba/Nb ratio is 1.2/1. Only when Ba/Nb ratio is 1.5/1 $Ba_5Nb_4O_{15}$ can be formed.

Well-crystallized $Ba_5Nb_4O_{15}$ powders can be synthesized at 230 °C when pH = 12, as shown in Fig. 3. But a small amount of BaF_2 phase is found in the XRD pattern of the product. Because HF is superfluous, when Nb_2O_5 is dissolved in hot 40% HF solution, there are $H_n[NbF_{5+n}]$ and dissociative F^- ions in the Nb-precursor. When Ba-precursor and Nb-precursor are mixed together, following reaction takes place:

$$Ba^{2+} + 2F^- \rightarrow BaF_2\downarrow$$

The XRD patterns of the product with differently pretreated Nb-precursors are showed in Fig. 3. In sample (a), Nb-precursor is volatilized in an aerator for 12 h. Because when Nb_2O_5 dissolves in 40% HF, it stays in HF solution as H_nNbF_{5+n}, after volatilization almost all the dissociative HF has been removed, there is no byproduct of BaF_2 in the resultant product.

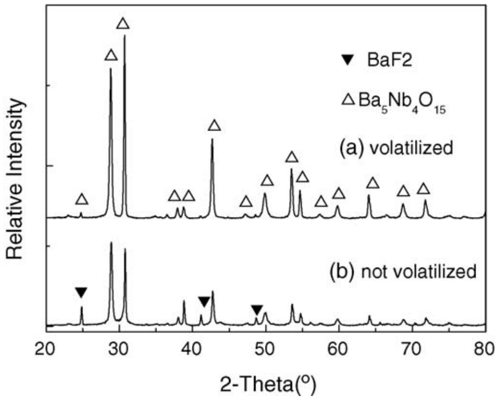

Fig. 3. XRD patterns of synthesis powders: (a) HF has been volatilized from the precursor before reaction; (b)HF has not been volatilized from the precursor before reaction.

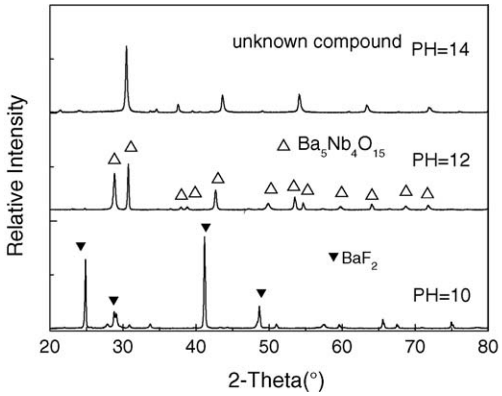

Fig. 4. XRD patterns of hydrothermal powders synthesized at 230 °C for 5 h from Ba/Nb molar ratio 1.5/1 under the pH value 10, 12 and 14.

Fig. 4 shows the XRD patterns of the product with different pH value at 230 °C for 5 h. $Ba_5Nb_4O_{15}$ phase is obtained when pH 12–13. When pH ≥ 14, a new compound is produced. The reaction conversion value for Nb_2O_5 is 99.13% when pH 12 and that is 101.02% when pH = 13, but it is more difficult to make a conclusion for pH = 13–14. So, we selected pH 12 as the reaction condition.

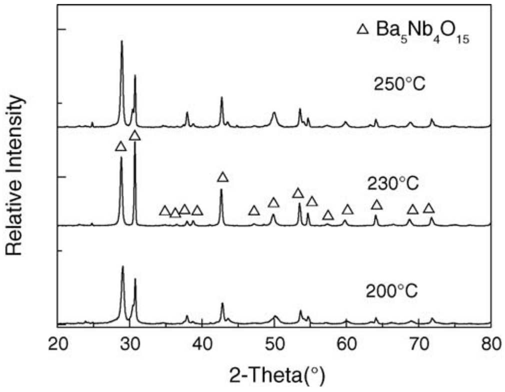

Fig. 5. XRD pattern of hydrothermal powders synthesized at pH 12 for 5 h with Ba/Nb molar ratio 1.5/1 at 200, 230 and 250 °C.

Fig. 5 shows the XRD pattern of the products formed at 200, 230 and 250 °C, when pH is 12, Ba/Nb molar ratio is 1.5/1. All the products form at these temperatures are composed only $Ba_5Nb_4O_{15}$ phase, but the reaction conversion values for Nb_2O_5 are different. Table 1 gives the reaction conversion values for Nb_2O_5. When the synthesis temperature increases from 200 to 230 °C, the reaction conversion values increases obviously, but it changes little when the reaction temperature

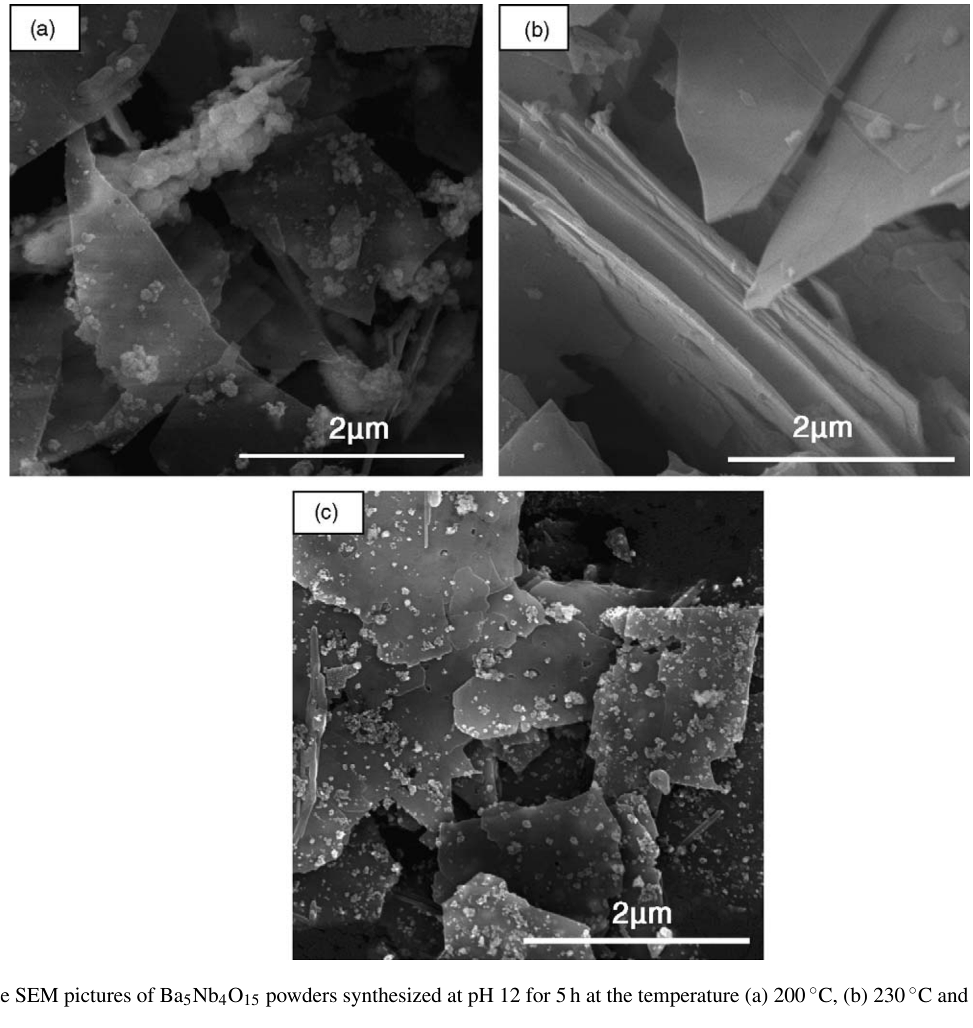

Fig. 6. The SEM pictures of $Ba_5Nb_4O_{15}$ powders synthesized at pH 12 for 5 h at the temperature (a) 200 °C, (b) 230 °C and (c) 250 °C.

Table 1
The relationship between the reaction conversion for Nb_2O_5 and the reaction temperature

Reaction temperature T (°C)	Reaction conversion for Nb_2O_5 (%)
200	88.12
230	99.13
250	99.50

Ba/Nb molar ratio 1.5/1, pH 12, 5 h.

is higher than 230 °C. So we select 230 °C as the best reaction temperature.

Fig. 6 shows the SEM micrographs of the products synthesized at various temperatures for 5 h. It can be easily seen that the particle size increases obviously when the reaction temperature increases from 200 to 230 °C, whereas it decreases from temperature 230 to 250 °C. The size of plate-like particle is more uniform and its surface is more smooth at 230 °C.

4. Conclusion

$Ba_5Nb_4O_{15}$ fine powders were prepared by a hydrothermal synthesis using $Ba(NO_3)_2$ and Nb_2O_5. Nb_2O_5 powders should be dissolved in hot HF when it was used as Nb-precursor. The Ba/Nb molar ratio effected the synthesis product, when Ba/Nb molar ratio was 1.5/1 $Ba_5Nb_4O_{15}$ powders could be obtained. Superfluous dissociative F^- ions in the Nb-precursor produced BaF_2 second phase in the product, so it was volatilized from Nb-precursor. The best reaction condition to synthesize $Ba_5Nb_4O_{15}$ fine powders was 230 °C, pH 12 for 5 h.

Acknowledgements

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