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Materials

A new sol-gel process for preparing $Ba(Mg_{1/3}Nb_{2/3})O_3$ nanopowders

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Abstract: Commercially available niobium (V) oxide [Nb_2O_5], with barium acetate [$Ba(CH_3COO)_2$] and magnesium acetate [$Mg(CH_3COO)_2{\cdot}4H_2O$] was used as the starting material in the sol-gel process for preparing $Ba(Mg_{1/3}Nb_{2/3})O_3$ (BMN) nanopowders. At first, Nb_2O_5 reacted with melting sodium hydroxide and transformed into dispersible oxide. The resulting glassy substance after cooling was dispersed and washed several times in distilled water to remove the Na^+ ions. The as-prepared colloidal $Nb_2O_5{\cdot}nH_2O$ was subsequently mixed with acetic solution of barium acetate and magnesium acetate according to the required molar proportions and followed by gelation. The ultrafine BMN powders were finally obtained after heat-treating the gel at 820°C for 1 h, and the as-sintered nanoceramics revealed a high relative density of 98.2%, and a high microwave Q-factor, of 10397 at 1.45GHz.

Key words: $Nb_2O_5{\cdot}nH_2O$ colloid; $Ba(Mg_{1/3}Nb_{2/3})O_3$ nanopowder; sol-gel processing; microwave Q-factor

1 Introduction

With the development of advanced communication systems, there is an ever-increasing demand for cheap but high performance microwave dielectrics. The effective dielectric materials should have a sufficiently high relative permittivity, low dielectric losses and a temperature coefficient of resonant frequency near zero [1]. The complex perovskite $Ba(Mg_{1/3}Nb_{2/3})O_3$ (BMN) [2] and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) [3-5] are currently available dielectric ceramics. It is known that tantalum is a much more expensive metal, the ore tantalite (60% Ta_2O_5) costing $150 per kg, but niobium is over 20 times cheaper [6]. So the BMN would be one of candidate materials of relative cheap and high performance dielectric ceramics.

As reported, the preparation routes of BMN powders are primarily based on the solid-state reaction method [7-8], in which high temperature is often required to promote the ion diffusion among various oxides. And the so obtained BMN powders are usually coarse and agglomerated, which are harmful to the properties of the final ceramics.

Wet-chemical processes have been widely regarded as an efficient route to synthesize homogeneous nanocrystalline particles at low temperatures. Some works have been reported to synthesize the BMN powders *via* a necessary precursor, niobium alkoxide derived from the expensive starting powders $NbCl_5$. However, the process for preparing niobium alkoxide would take a so long time and need the protected atmosphere [9,10]. Furthermore, the $NbCl_5$ was more difficult to be prepared experimentally because of its unstable chemical characteristics. This paper presents a simple and novel approach to prepare BMN nanopowders with high sinterability. Nb_2O_5, due to its lower cost and abundant resource, was selected as the starting material to prepare a high quality colloidal $Nb_2O_5{\cdot}nH_2O$, instead of the currently used $Nb(OC_2H_5)_5$ precursor. The fine BMN powders could be finally obtained after mixing the as prepared colloidal $Nb_2O_5{\cdot}nH_2O$ with Mg-acetate and Ba-acetate and followed gelation and heat treatment. The microstructure and the infrared absorption spectra of the synthesized powders were characterized and examined. In addition, the microwave dielectric properties were reported.

2 Experimental procedure

2.1 Preparation of BMN powders and ceramic

Nb_2O_5 is a kind of almost insoluble substance, except in alkali bisulfate, alkali carbonate or caustic alkali. It must be transformed into dispersible oxide so as to improve the activity of Nb_2O_5 to be used as a key precursor. In the present work, caustic soda was chosen as a fluxing agent to melt Nb_2O_5. These mixture powders of Nb_2O_5 and NaOH were put in corundum crucible and vigorously stirred while heating to 200-300°C on a hot plate for about 15 min. The molten mixture was then moved into a muffle furnace and

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heated at 650°C for 1 h to ensure the extensive reaction of Nb_2O_5 with NaOH. The resultant glassy substance after cooling was dispersed into distilled water and the excess alkali in the solution was neutralized by 0.1 mol/L CH_3COOH until the pH value to 7. Colloidal $Nb_2O_5 \cdot nH_2O$ particles could be obtained by washing and filtrating the mixture for at least five times to remove the remaining sodium ions. Portions of the as-prepared colloidal substances were dried and heat-treated to evaluate the content in Nb_2O_5. Finally the colloidal $Nb_2O_5 \cdot nH_2O$ were diluted and blended with the acetic solution of barium acetate $[Ba(CH_3COO)_2]$ and magnesium acetate $[Mg(CH_3COO)_2 \cdot 4H_2O]$ in the molar ratio of Ba^{2+}: Mg^{2+}: Nb^{5+} = 3: 1: 2, followed by continuous stirred in 80°C water bath for 2 to 3 h. With the solvent volatilization, an opaque gel was formed and converted to white powders after drying at 120°C. The resulting powders were calcined at the temperature of 680, 820 and 1000°C respectively in air for 1 h. In order to measure the microwave dielectric properties, the BMN powders were formed to the disk ceramic body (6 mm in diameter and 1.5 mm in thickness) by uniaxial pressing at 100 MPa, and then the samples were sintered in air at 1000°C for 1 h.

2.2 Characterization of samples

X-ray diffraction (XRD) analysis using CuK_α radiation (model Rigaku Dmax-RB) and transmission electron microscope (TEM, model H-800, Hitachi, Japan) were carried out for phase identification and microstructure characterization. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were performed on the dried powders in air at a heating rate of 5°C/min. Infrared (IR) spectra of the heat-treated specimens were measured by potassium bromide (KBr) method and fourier transform-infrared (FT-IR) spectrophotometer (Model IR-10300E, Mattson Co., USA) at the wavenumbers range of 400-4000 cm^{-1}. The density of the bulk ceramics was measured by the Archimedes methods in water. The microwave dielectric properties of BMN samples were determined by a HP4291B impedance analyzer at the frequencies range of 1.0-3.0 GHz.

3 Results and discussion

The DTA-TG curves of the powders are illustrated in **figure 1**. Two endothermic peaks are observed at 80°C and 190°C in the DTA curve which are accompanied with mass loss in TG. It may be attributed to the evaporation of residual and combined water respectively. The exothermal peak near 420°C in DTA corresponds with the large mass loss in TG which is possibly due to the decompose and combustion of acetic acid and acetate. The sharp peak at 475°C maybe result from the formation of some crystalline phase associated with BMN. A small exothermic peak at 680°C could be related to the crystallization of BMN phase as indicated in XRD patterns shown in **figure 2**. A wide exothermic band is found at the temperature range of 700-860°C. It has been considered as the process of further crystallization and ordering of the B-site atom in BMN phase.

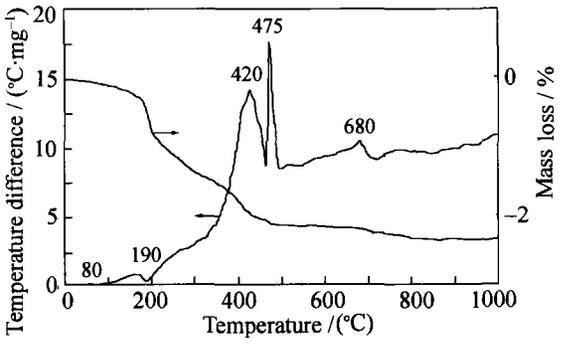


Figure 1 DTA/TG curves for the synthesized powders.

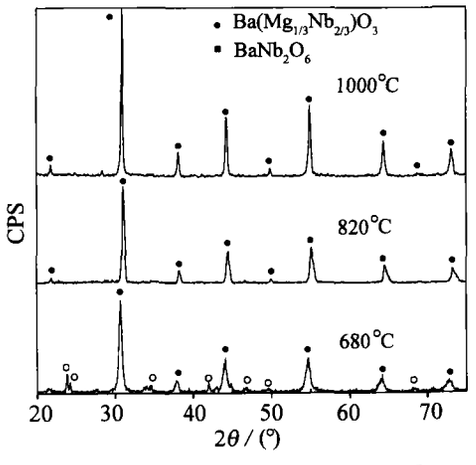


Figure 2 XRD patterns of BMN powders under calcined at different temperatures.

Figure 2 shows the evolution of phase transformation during calcination. At low temperature (680°C), a predominant phase BMN and a subsidiary $BaNb_2O_6$ can be found. With the temperature increasing to 820°C, the subsidiary $BaNb_2O_6$ disappeared and the pure BMN phase was formed. So it implied that $BaNb_2O_6$ transformed into cubic perovskite type BMN at about 800°C. According to literatures, however, the formation of the single BMN phase from the conventional process (solid state reaction method) would require a much high temperature of over 1200°C. In order to elucidate the stirring dependence of the final phase compositions, an additional group experiment was especially performed, only without the stirring during the melting process of Nb_2O_5 with NaOH. The latter routes, which involved neutralizing, filtering, washing, *etc*, kept the consistent with that of the

above-mentioned. The phase compositions of so resultant powders after heat-treatment at 1000°C were quite different from the former, as shown in **figure 3**. Besides BMN phase, there are Nb_2O_5, $MgNb_2O_6$ and BaO impurity substance in the sample. It is reasonable to state that a uniformly controlled process in melting Nb_2O_5 to obtain a high quality colloidal $Nb_2O_5 \cdot nH_2O$ is a prerequisite for the synthesis of pure BMN nanopowders.

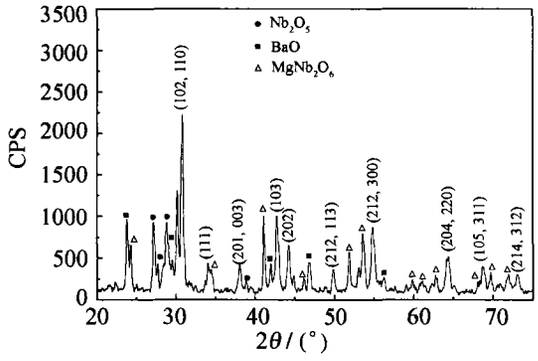
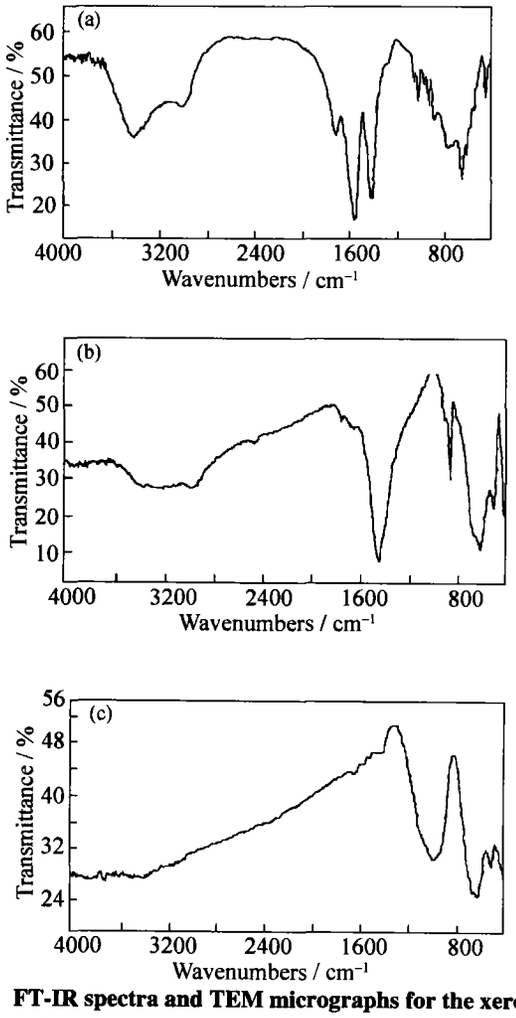


Figure 3 XRD patterns of BMN powders calcined at 1000°C without vigorous stirring in the melting of Nb_2O_5 with NaOH.

Figure 4 shows the IR-spectra (a, b and c) and TEM micrographs (a', b' and c') of the xerogel and the BMN powders after calcined at 820°C and 1000°C, respectively. In figure 4(a) many absorption bands related to acetate anions are apparently observed. The 3500, 3100 and 1710 cm^{-1} peaks correspond to the stretching vibrations of the chemical bonds of −OH, C−H and C=O respectively, while the 1578 cm^{-1} and 1408 cm^{-1} are the results of the asymmetric and symmetric vibration of CH_3COO^- bonds. The peak at 1380 cm^{-1} is related to the vibration of O−H bond in crooked plane direction. Compared with the −COOH absorption in standard spectra of acetic acid, the peak in the xerogel shifts a very short distance to higher wavenumber directions. So it is deduced that O−H bond is deformed, and the hydrogen ion would be substituted by various metal ions. Furthermore, the nearly equal spherical nanoparticles of about 50 nm in diameter are observed in the corresponding micrographs (figure 4(a')). Once the xerogel was calcined at 820°C, all the organic absorption peaks disappear as shown in figure 4(b), and the mean size of the parti-



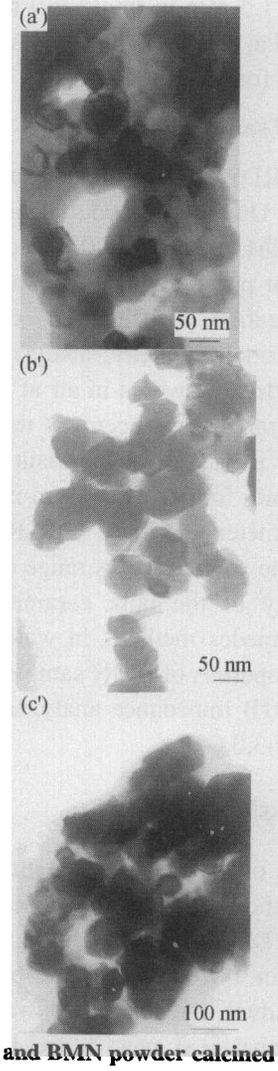


Figure 4 FT-IR spectra and TEM micrographs for the xerogel (a, a') and BMN powder calcined at 820°C (b, b'), 1000°C (c, c') respectively.

cles reach about 90 nm. The FT-IR absorptions at about 500 cm^{-1} exhibit the features of Ba—O, Mg—O and Nb—O vibration. As the temperature increasing to 1000°C, the peaks become sharp shown in figure 4(c). On the other hands, it is found that the shape of BMN crystal grains become irregular, and the sizes in diameter are approximatively double to treble that of xerogel (shown in figure 4(c')).

The density of final ceramic body reached 98.2% of the theoretical density, with its linear shrinkage rate of 14.2%. It reveals that the BMN nanopowders exhibit an excellent sinter-ability. The sintered ceramic body was used to evaluate the microwave dielectric properties after its surfaces were polished in polishing wheel, coated with platinum foil and annealed at 850°C for 30 min to obtain a tight binding layer. The microwave dielectric loss of BMN sample was measured and tabularized in **table 1**. It could be seen that the relatively higher Q value 10397 at 1.45 GHz is attained, compared with that Q value 10165 at the same frequency reported by S.Nomura [2,11]. So the as prepared BMN powders and ceramics might be regarded as a commercial potential candidate product for microwave component. In next paper, some research on the optimizing process of BMN ceramics and the reducing of conductive impurity particles that may bring about leakage loss will be reported and discussed.

Table 1 Microwave dielectric properties of BMN

Sample	ε	$\tan\delta$	Q	Frequency / GHz
BMN	13.8	9.617×10^{-5}	10397	1.45

4 Conclusion

In the work, commercially available Nb_2O_5 was used as the starting material for the synthesis of BMN powders. The obtaining of a high quality $Nb_2O_5{\cdot}nH_2O$ colloid has been a key step with the emphasis on the stirring process in melting Nb_2O_5 with fluxing agent. The spherical BMN powders with the size of 90 nm have been synthesized at 820°C for 1 h. An excellent microwave ceramic with Q value 10397 at 1.45 GHz was also achieved using the as prepared nonapowders. The novel process may provide a potential candidate method for large-scale manufacture of microwave dielectric ceramics.

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