

Progress in the synthesis of $\text{Ba}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ceramics: A versatile co-precipitation method

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$\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (BFN) is a class of material that exhibits a very high value of the dielectric constant over a wide range of temperature, rendering it a promising candidate for capacitor application. In this contribution, we report a versatile route for synthesis of a BFN ceramic via a co-precipitation process. The method simply involved mixing of solutions of precursors in ambient conditions. The mixed solution was dried at 110 °C and subsequently calcined at 850 °C for different periods of time. The formation of the perovskite structure of BFN was followed by utilizing X-ray diffraction and Fourier transformed infrared spectroscopy. The pure perovskite phase was obtained upon the calcination at 850 °C for 14 h, a much milder conditions compared to the normal solid-state reaction. The powder samples were pressed into pellets and sintered at 1250 °C for 4 h. The examination by scanning electron microscopy observed an average grain size of the BFN ceramic of about 1.53 μm . The field dependences of the dielectric response and dielectric loss were measured in a frequency range of 20 Hz to 2 MHz at room temperature. The maximum values of the dielectric constant and dielectric loss are ~ 9000 and ~ 1.1 , respectively.

Key words: Niobates, Dielectric properties, Perovskite, Ferroelectric properties.

Introduction

Complex perovskites such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)$, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ are very promising for electroceramic applications. This is mainly due to their high values of the dielectric constant over a wide range of temperature [1]. $\text{Ba}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (BFN) is one of the materials in this family that has been known to exhibit temperature- and frequency-dependent dielectric values [2–4]. A maximum value of 30,000 was detected at around 170 °C [2, 3]. The synthesis of BFN can be achieved via a routine solid state reaction, which normally takes place at a temperature above 1000 °C [2, 3, 5–10]. However, the apparent disadvantage of this method is that it is rather difficult to control stoichiometry and homogeneity of the BFN powder. Moreover, this method requires a high temperature to obtain a complete solid solution and phase-pure BFN powder. Continuous efforts have been made in order to improve the methods of synthesis that yield a BFN ceramic with, at least, comparable dielectric properties [8, 11–14]. A recent study by Intatha *et al.* showed that the addition of LiF into the system caused a reduction of the sintering temperature by about 150–200 °C [11]. However, the values of the dielectric constant were found to decrease with an increase in the amount of the dopant LiF. Other studies have shown that the dielectric constant of the BFN ceramic can be increased by doping with some

metals such as bismuth and lanthanum [12, 13].

The method of synthesis of BFN can be reduced to milder conditions by utilizing a wet chemical process. The method also provides a route for thin film fabrication of the ceramic and has a better control over the final composition. It was demonstrated by Chung *et al.* that the synthesis of BFN can be accomplished via a sol-gel route [15]. The calcination temperature required to obtain pure perovskite BFN was much lower than that of the solid state reaction. It was found that the crystallization into the perovskite BFN occurred at 550 °C and was eventually completed at 850 °C. In this study, a co-precipitation route for fabrication of a BFN ceramic was explored. It was recently shown that this method was successfully used to prepare $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ [16]. The procedure simply involved the mixing of precursor solutions in atmospheric conditions. The pure perovskite powder was obtained using mild conditions for the calcination comparable to those of the sol-gel method.

Experimental procedure

The $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ powders were prepared by a co-precipitation process using barium chloride [$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$], ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], niobium chloride [NbCl_5] and citric acid anhydrous. The purities of all the chemicals were over 99.9%. A diagram depicting the details of the experimental procedure is shown in Fig. 1. The citric acid, ferric nitrate and barium chloride were dissolved in deionized water while the niobium chloride was dissolved in ethanol. All solutions were thoroughly mixed in an ambient atmos-

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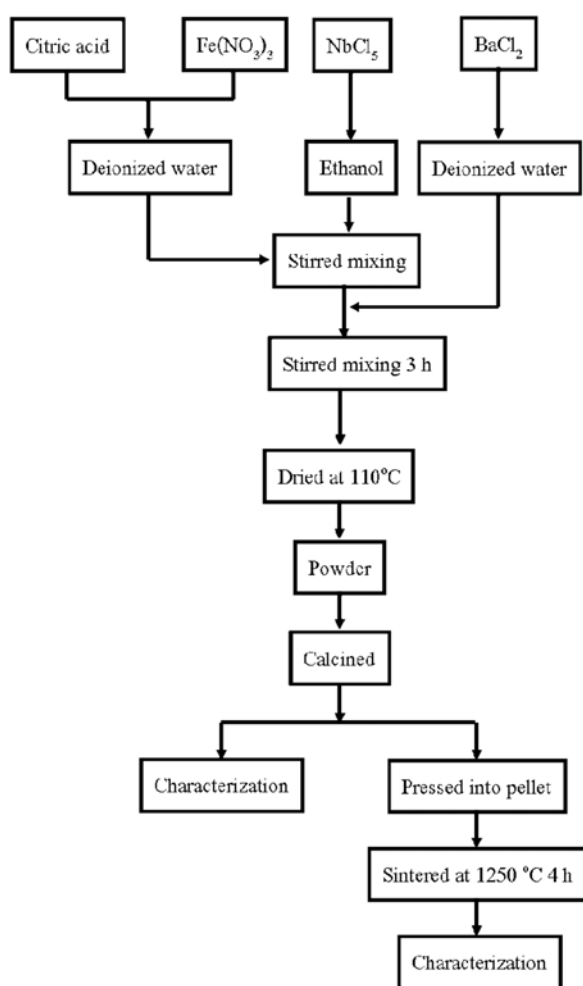


Fig. 1. Illustration of the preparation of the BFN powders and BFN ceramic via a co-precipitation process.

sphere using a magnetic stirrer. Precipitates of the precursors were obtained after continuous stirring for 3 h. The solutions containing the co-precipitates were dried at 110 °C for 10 h. The samples were subsequently calcined at 850 °C for various times. The progress of the reaction was followed utilizing X-ray diffraction (XRD) with Cu K α ($\lambda = 1.54$ Å) radiation (XRD; Philips PW 3040/60 X'PERT PRO Console) and Fourier transformed infrared spectroscopy (FT-IR; Perkin-Elmer). The powder samples were pressed into pellets and sintered at 1250 °C for 4 h under heating and cooling rates of 5 K·min⁻¹. The microstructures of the ceramics were examined by scanning electron microscopy (LEO 1455 VP). The sintered samples were polished to obtain parallel surfaces and gold sputtered electrodes made for dielectric measurements. The dielectric properties of the pellet samples were measured at room temperature and various frequencies ranging between 20 Hz-2 MHz using an LCR meter (Hioki model 3532-50).

Results and Discussion

The preparation of BFN powders by a sol-gel route in

a previous study showed that a pure perovskite phase was obtained when calcined at 850 °C [15]. Therefore, we selected this temperature for calcination of our samples. Structural evolution of the sample was then followed utilizing XRD and FT-IR. Fig. 2 gives the XRD patterns of powder samples obtained from the calcinations at 850 °C for different times. A crystallization of BFN into the perovskite structure is observed when the soaking time is 9 h. However, a considerable amount of residual phases still remains. The crystallization progresses with an increase of the soaking time. It is clear that nearly a single perovskite phase is obtained when the soaking time reaches 14 h. A further increase of the soaking time to 20 h hardly affects the structure of the powder sample. Our XRD pattern is consistent with previous studies, reporting a monoclinic structure of BFN with $\beta = 90.11^\circ$, $a = 4.0743$ Å, $b = 4.0388$ Å and $c = 2.876$ Å [2, 3].

Fig. 3 shows FT-IR spectra of BFN powders prepared using different conditions for calcination. The intense broad band detected at approximately 600 cm⁻¹ is attributed to the absorption of metal oxide bonds in the perovskite structure of BFN. The existence of some H₂O and a hydroxyl group in the system contributes to the broad band at 2700-3400 cm⁻¹ while the peaks at about 1633 cm⁻¹ are due to an asymmetric stretching vibration of the COO⁻ group.

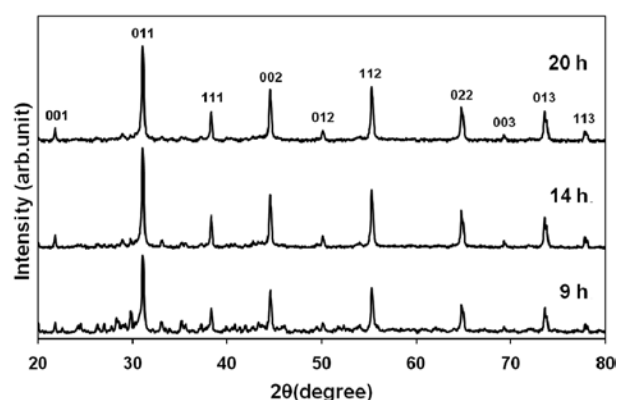


Fig. 2. XRD patterns of BFN powders calcined at 850 °C for various times.

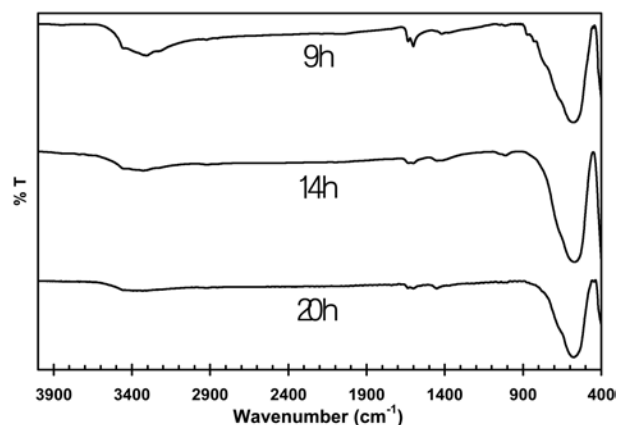


Fig. 3. FT-IR spectra of BFN powders calcined at 850 °C for various times.

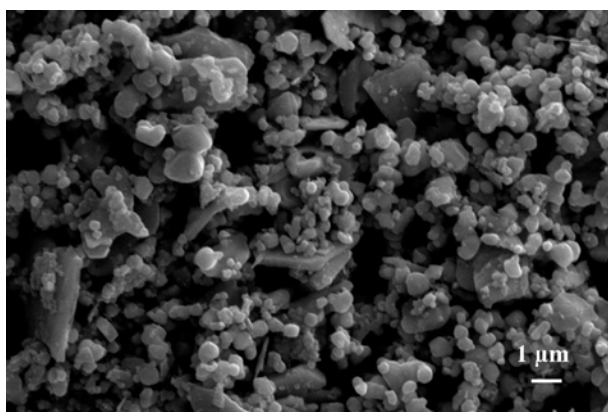
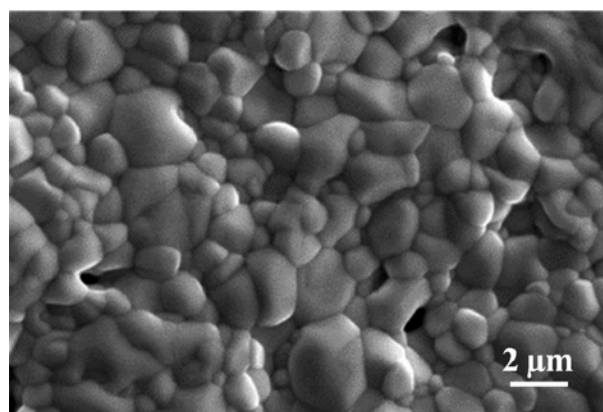


Fig. 4. SEM micrographs of BFN powder calcined at 850 °C for 14 h.

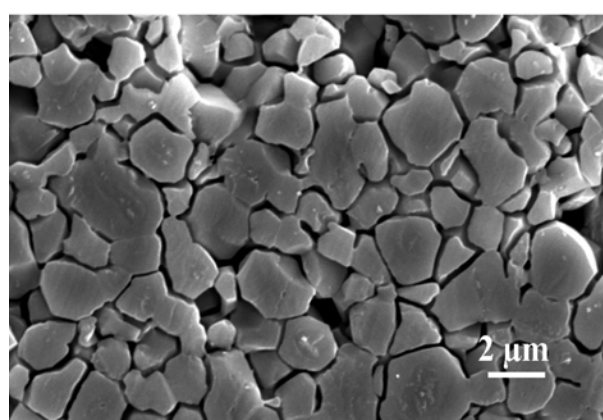
The measurements by FT-IR are in agreement with the XRD results. The broad absorption band at a low frequency, mainly associated with the vibrations of metal-oxygen bonds, is detected after 9 h of calcination. However, the spectrum also is constituted of other absorption bands from residual organic fractions. These concentrations indicated by the intensity of their corresponding absorption bands decrease with an increase of the soaking time of the calcination. Only a small fraction of the organic residuals remains in the samples when the soaking times of the calcination reach 14 h and 20 h.

The microstructure of the BFN powder revealed by scanning electron microscopy is illustrated in Fig. 4. The powder consists of fine particles with an average grain size of about 0.64 μm . It also shows a good homogeneity of the sample. Fig. 5(a) shows a surface micrograph of the BFN ceramic sintered at 1250 °C for 4 h. The pellets were prepared using powder samples obtained from 14 h soaking time calcination. The surface of the sample exhibits an average grain size of about 1.53 μm as measured using the intercept method. The sample was also polished and etched using dilute HF solution to further investigate the grain size within the ceramics. Fig. 5(b) shows that the grain size is approximately the same compared to that measured from the surface of the sample.

The field dependences of the dielectric response and dielectric loss were measured in a frequency range from 20 Hz to 2 MHz at room temperature as shown in Fig. 6. The maximum value of the dielectric constant detected at 20 Hz is ~9,000. The value decreases significantly upon increasing frequency and reaches about 2,500 at 1 kHz. This behavior is due to the fact that the dipoles are able to follow the applied field at a low frequency while it becomes more difficult at a higher frequency. This frequency-dependence of the dielectric constants of the samples suggests that BFN is a relaxor ferroelectric. The values of dielectric loss ($\tan \delta$) are in the range of 1.1 to 0.1. It is important to note that the dielectric response and dielectric loss of our samples are comparable to the values of BFN ceramics prepared by solid state synthesis [12]. However, our sample was obtained by using much milder conditions.



(a)



(b)

Fig. 5. SEM micrographs of BFN ceramic sintered at 1250 °C for 4 h. The pellets were prepared from powders calcined at 850 °C for 14 h (a) non-treated surface, (b) chemically etched polished surface. The grain sizes measured from the two samples are approximately the same.

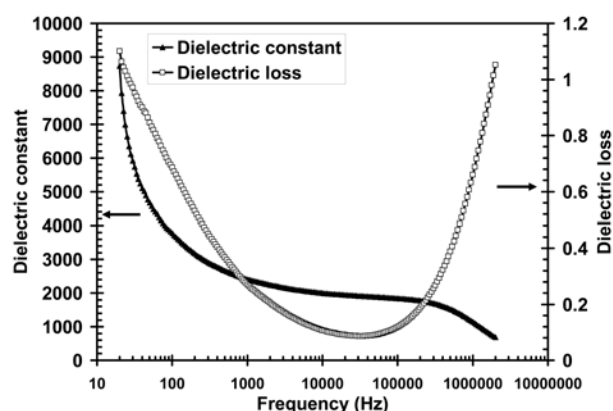


Fig. 6. Dielectric properties at room temperature of BFN ceramics sintered at 1250 °C for 4 h. The pellets were prepared from powders calcined at 850 °C for 14 h.

Conclusions

Our study demonstrated a co-precipitation method for the synthesis of $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ceramics. This novel route

is rather versatile and requires milder conditions compared to the common solid-state reaction. A single phase of perovskite BFN was obtained when calcined at 850 °C for 14 h. The field dependences of the dielectric response and dielectric loss were measured at room temperature and it was found that the dielectric constant of this ceramic decreases with increasing frequency. Our method can be utilized to prepare a large quantity of BFN powder, which is important for the electroceramics industry.

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