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Preparation and dielectric properties of barium iron niobate by molten-salt synthesis

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Abstract

In this work, barium iron niobate; $BaFe_{0.5}Nb_{0.5}O_3$ powder has been successfully synthesized by molten salt method. The power was characterized by a variety technique. Pure phase perovskite was obtained at relative low calcination temperature of <700 °C. The powder exhibits a fine grain with a relatively uniform particle size and microstructure. In addition, $BaFe_{0.5}Nb_{0.5}O_3$ ceramics were prepared and its dielectric properties were investigated. The result suggested that the ceramic prepared from molten-salt synthesis may be has a better properties than that of the ceramics synthesized by a conventional method.

Keywords: A. Calcination; A. Sintering; C. Dielectric properties; D. Perovskite

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1. Introduction

Barium iron niobate: $BaFe_{0.5}Nb_{0.5}O_3$ (BFN) is an interesting high dielectric lead free material. This material exhibits a very high value of dielectric constant ($\varepsilon_r \sim 10^4$–10^5) covering a wide range of temperature [1–8]. BFN was first synthesized via solid state reaction by Saha and Sinha in 2002 [3]. After that, many workers have studied properties of the BFN [4–9]. Rama et al. [10] reported that the structure of BFN is cubic. However, the XRD analysis of Saha and Sinha [7] using a standard computer program (POWD) indicated BFN with a monoclinic type structure. It has been also reported that BFN is a relaxor ferroelectric material characterized by a board dielectric transitions with frequency dependent [7].

In order to achieve a better performance of BFN ceramics, a high quality of starting powder is required. Various approach have been applied to synthesis the BFN powders. The conventional mixed-oxide method has been often used to synthesize BFN powders; however, it requires a high calcination temperature which cause the particle coarsening and aggregation of the powders. Other chemical routes including sol–gel process and hydrothermal and microwave synthesis have been reported for producing the fine BFN powders [11]. However, the costs of raw materials for these routes are quite high. Further, the yield product that obtained from these methods is so small. Recently, it is reported that molten salt synthesis is one of the simple and practical techniques with low cost for preparing fine powder with the desired composition [9]. In the present work, therefore, the molten salt synthesis was applied to synthesize the BFN powder. The characteristic of BFN powder prepared by the molten salt method was investigated. It is expected that fine particles with a narrow particle size distribution should be obtain this technique. The BFN ceramics were fabricated by using the obtained BFN powder. Properties of the ceramics were also investigated.

2. Experimental procedures

$Ba(Fe_{0.5}Nb_{0.5})O_3$ powder was synthesized by molten salt method. An equal molar ratio of inorganic salt mixtures, NaCl (99.5%, Fluka) and KCl (99.5%, Riedel de Haen) were mixed by hand-grinding for 20 min. The stoichiometric amounts of Ba_2CO_3 (99.0%, Sigma–Aldrich), Fe_2O_5 (99.5%, Riedel de

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Haen), and Nb_2O_5 (99.9%, Aldrich) were mixed in a vibro-mill for 2 h in ethanol medium, and then dried at 110 °C for 12 h. The mixed precursors and mixed salts were weighed into 1:1 ratio. After hand-grinding for 30 min, the obtained powder was heated at temperatures ranging from 700 to 900 °C for 4 h at a heating and cooling rate of 300 °C/h. To determine the calcination temperature of BFN powder, DTA technique was performed at the temperature ranging 30–950 °C (DuPont Instruments, USA). The products were washed with hot deionized water several times until no trace of anion was detected by $AgNO_3$ aqueous solution. The calcined powders were characterized by a variety technique. Phase formation was determined by XRD analysis (Bruker AXS D8 Advance diffractometer, Germany). The morphologies of particles were examined by FE-Scanning Electron Microscopy (SEM, JEOL JSM6335F, Japan). Chemical analysis was determined by X-ray fluorescence (XRF) technique (JEOL, JSX-3400R, Japan). The obtained powder was pressed into a disc shape and then sintered at 1250 °C for 3 h. For the dielectric investigation, silver paste was painted on both sides of the samples. The samples with silver paste were fired at 650 °C for 15 min. Dielectric measurements were carried out using a dielectric measurement system (Agilent LCR meter, Malaysia) in conjunction with a tube furnace.

3. Results and discussion

DTA thermogram of the mixed starting materials is displayed in Fig. 1. No peak of water evaporation at 100–120 °C was observed due to the mixed powder was dried before the DTA experiment. A sharp endothermic peak was observed at temperature ~630–670 °C. This result suggests that the reaction between the raw materials started at ~630 °C, and then it finished at temperature ~670 °C. Therefore, the calcinations temperature of the BFN powder prepared by the molten salt method should be higher than 670 °C.

In the present work, the mixed raw materials powder was calcined over a temperature range 600–900 °C. The XRD patterns of the obtained powder calcined at various temperatures are shown in Fig. 2. The XRD result revealed that all samples exhibited perovskite structure. No impurity other than BFN was detected by XRD except the samples calcined at the temperature lower than 700 °C. In general by using the conventional method, the pure phase of BFN can be obtained at the calcination temperature over 1200 °C [5–8,10,11]. Therefore, the existence of pure phase BFN at 700 °C in the present work, suggests that the molten salt method can reduce the calcination temperature by <500 °C. In addition, the chemical analysis showed that there was no evidence of Na and K impurities in the XRF result because several times of washing were performed. The Fe and Nb ration was determined to be <0.8, suggesting that the obtained powder exhibited a non-stoichiometric composition.

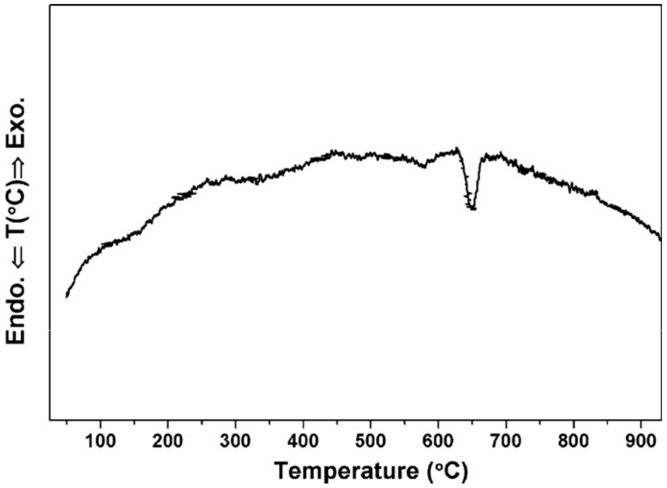

Fig. 1. DTA thermogram of the present powder samples.

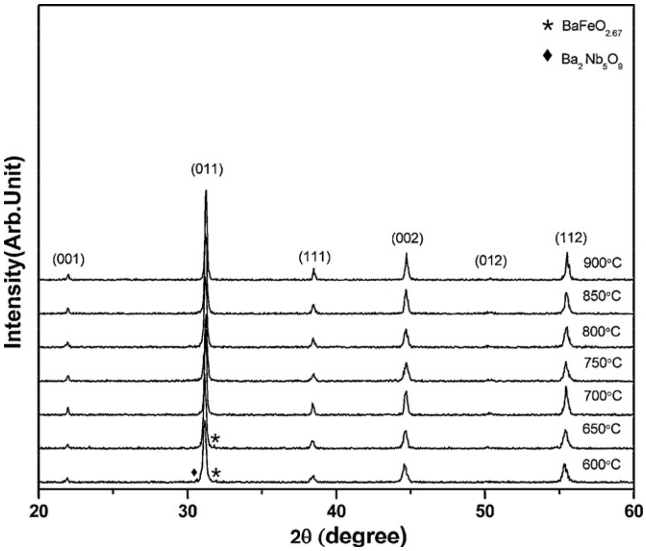

Fig. 2. XRD patterns of the BFN powders calcined at various temperatures.

To check the phase formation in the samples, the XRD phase analysis was carried out based on the Inorganic Crystal Structure Database (ICSD). The XRD data is consistent with cubic symmetry (ICSD code 52835 of pure BFN). Our result consists with the work done by Rama et al. [10] whose samples were also prepared by solid state reaction. In addition, no splitting of the diffraction peaks was observed though the calcinations temperature range, implying there was no change in symmetry with increasing in the calcination temperature. It should be note that an increase calcinations temperature resulted in a decrease in width of the diffraction peaks. Generally, full width at half maximum (FWHM), can be related to crystallite size of the powder. In order to investigate the effect of calcination temperature on the crystallite size of the calcined powders, the Scherer formula as seen in Eq. (1) was used [12]

$$B = \frac{k\lambda}{d\cos\theta} \tag{1}$$

where B is FWHM (the broadening due to the crystallite sizes), λ is the wavelength of the X-rays, d is the average crystallite size, θ is the Bragg angle, and k is a constant ($k < 1.0$ in this work). By assume that the instrumental broadening and the broadening due to lattice strains of all powder samples are

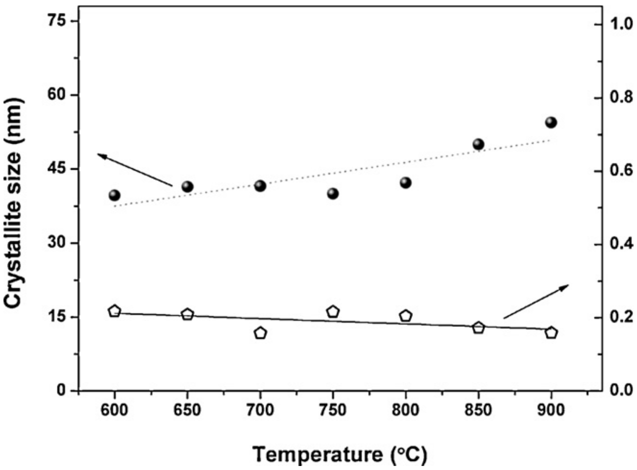

Fig. 3. Crystallite size and FWHM values of BFN as a function of calcination temperature.

similar and small, it can be approximated that B varies linearly to the full width at half maximum (FWHM) of the observed X-ray peak. From Eq. (1), it may be assumed that k, $\cos\theta$, and λ values are constant parameters for the same reflection. Thus, it can be roughly estimated that the FWHM is inversely proportional to the average crystallite size as shown in Eq. (2):

$$\mathrm{FWHM} \propto d^{-1} \tag{2}$$

Plots of FWHM and estimated d for the (0 1 1) reflection from all powder samples were illustrated versus calcination temperature in Fig. 3. The crystallite size increased from 40 nm for the 600 °C sample to 55 nm for the 900 °C sample.

Morphology of BFN powder calcined at 700 °C and 900 °C h is illustrated in Fig. 4(a) and (b). Very fine particles with average diameter of <160 nm were observed for the 700 °C sample. The 900 °C sample showed a slightly increase in particle size (<210 nm). Although the powder exhibited a uniform in particle size, agglomerated particles were observed. This may resulted in the higher value of average particle size (by SEM) comparing to the estimated value from the XRD technique.

In this work, the 700 °C powder was selected to form the BFN ceramics. The sintering was conducted at 1350 °C for 2 h. The dielectric constant of BFN ceramics as a function of frequency at various temperatures up to 300 °C is illustrated in Fig. 5. Very high dielectric >80,000 were observed at 1 kHz and at temperature of 300 °C. This value is higher than that obtained from the conventional method [8]. This may be due to the present ceramics have a higher density (6.12 g/cm^3) than that of the ceramics prepared by the conventional method (<4.60 g/cm^3) [8]. The dielectric constant also exhibited a nearly frequency dependent, especially at a higher temperature. Inset of Fig. 5 shows plots of loss tangent versus frequency at various temperatures. Values of loss tangent at room temperature were less than 1.5 at frequency 100 Hz. At high temperature, the dielectric constant exhibited a dielectric – frequency independent and the values of loss tangent were less than 1.0. These value are closed agree with the ceramics prepared by conventional method (loss tangent < 1.0) [8].

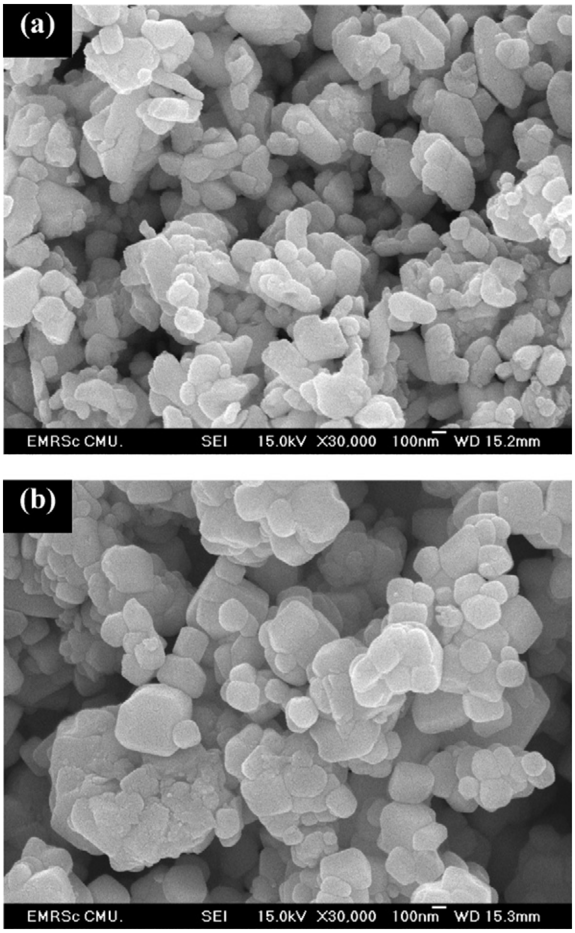

Fig. 4. SEM micrographs of (a) BFN powder calcined at 700 °C and (b) BFN powder calcined at 900 °C.

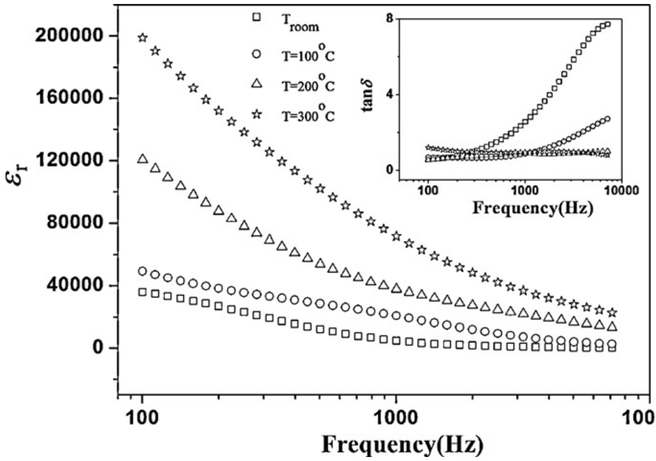

Fig. 5. Dielectric constant and dielectric loss (inset) of BFN ceramic measured at various frequencies over broad temperature range.

4. Conclusions

A molten-salt synthesis was proposed for the preparation of BFN powder for the first time. Pure perovskite phase with cubic symmetry was obtained. The molten-salt method could reduce the calcination temperature to a low temperature. The obtained

BFN powder exhibited very fine particles with a uniform size distribution. The BFN ceramics prepared by the present route exhibited rather high dielectric constant with low loss tangent. Since the molten-salt method shows many advantages for synthesis the lead free electroceramic powder such as BFN, it is interesting to apply it for other lead free materials for future work.

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