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ScienceDirect

Ceramics International 34 (2008) 1059–1062

CERAMICS INTERNATIONAL

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Colossal dielectric response in barium iron niobate ceramics obtained by different precursors

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Abstract

$Ba(Fe_{0.5}Nb_{0.5})O_3$ (BFN) ceramics were synthesized by a traditional mixed oxide method (BFN-M), as well as a columbite method (BFN-C) with $FeNbO_4$ precursor. X-ray diffraction reveals that both the ceramics and precursor have a pure monoclinic phase. BFN-C samples showed improved microstructure with less pores and smaller grain size. Dielectric properties of the BFN ceramic were characterized in a broad frequency range (0.1 Hz to 10 MHz) and a temperature range from -120 to 300 °C. A Debye-like relaxation was found in a low-frequency range, where a high-temperature dielectric anomaly was observed too. The relative low-dielectric loss suggests that columbite method should be a better choice for the synthesis of $A(Fe_{0.5}B_{0.5})O_3$ ceramics.

Keywords: B. Grain size; E. Capacitors; Colossal dielectric constant; BFN

1. Introduction

As driven by the impetus of smaller and smaller feature sizes of devices in microelectronics, researchers are looking for the so-called high-k materials. Perovskites such as lead zirconate titanate (PZT) usually possess high-dielectric constant of a few hundreds at room temperature [1,2] and are widely used as capacitive components. Another well-known example is $CaCu_3Ti_4O_{12}$, which exhibits very high-dielectric constant ε'in the order of 10^4 around room temperature. Since the complex perovskite $Ba(Fe_{0.5}Nb_{0.5})O_3$ (BFN) ceramics were first reported to have high values of ε', several works have been done on BFN and it was regarded as a ferroelectric relaxor [4,5]. Moreover, Raevski et al. pointed out that the temperature and frequency dependence of both the real (ε') and imaginary ε'' parts of the dielectric permittivity of BFN resemble those of $CaCu_3Ti_4O_{12}$, and a Maxwell–Wagner mechanism is responsible for the high values [6]. It seems that the dielectric permittivity of BFN arise from both the intrinsic (dipole polarizability) and the extrinsic effects.

As reported in previous works on iron-doped systems, the occurrence of Fe^{2+} and oxygen vacancies created during the sintering process increases electrical conductivity, dielectric loss, and space charge accumulation at the grain boundaries, which are detrimental to material performance [7,8]. A B-site precursor (columbite) method, using $FeNbO_4$ as the precursor, has been proposed to be a suitable precursor for $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) with no secondary pyrochlore or iron-oxide phases generated [9]. The grain boundaries play an important role in PFN ceramics derived from different precursor [9,10]. The similar idea can also be applied to the BFN system. To understand in details the role of this kind of precursor played in BFN ceramics, we have performed a comparative study on the BFN-C and BFN-M ceramics. The giant dielectric response of BFN ceramics has been observed.

2. Experimental procedure

$FeNbO_4$ (FN) precursor with a monoclinic phase was synthesized by solid-state reaction of reagent grade Fe_2O_3 and Nb_2O_5. First, the starting powders were mixed and ball milled

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doi:10.1016/j.ceramint.2007.09.079

in ethyl alcohol for 12 h. As reported by Raymond et al. [9], monoclinic and orthorhombic phases can be obtained when the calcination temperature is 1075 and 1200 °C, respectively. In this study, we chose 1075 °C in order to obtain monoclinic FN. Powders of FN were then mixed with $BaCO_3$ and ball milled in ethyl alcohol again for 12 h. Calcination of dried powders was conducted at 1200 °C for 8 h. The calcined BFN powders were then compacted into pellets by cold isostatic pressing and sintered in air at 1250, 1300 and 1350 °C, respectively, for 6 h. The samples obtained from this route are named BFN-C.

The BFN-M ceramics were synthesized by direct mixing of the reagent grade Fe_2O_3, $BaCO_3$, and Nb_2O_5, which was then followed by ball milling, calcination, and sintering in air at 1250, 1300 and 1350 °C, respectively. The heating rates were 5 °C/min for all the samples with a furnace cooling. Calcined powders and BFN ceramics were examined by X-ray diffraction (XRD, Philips X'Pert) with Cu Kα radiation. Morphological and microstructural features were examined by scanning electron microscope (SEM, Leica Stereoscan 440) and energy dispersive spectroscopy (EDS). For dielectric property measurement, silver paints were coated on the top and bottom surfaces of the sintered disks and fired at 650 °C for 20 min. The sample pellets were 10 mm in diameter and about 1 mm in thickness. The dielectric properties were then measured by a frequency–response analyzer (Novocontrol Alpha-analyzer) over a broad frequency range (0.1 Hz to 10 MHz) at different temperatures down to −130 °C.

3. Results and discussion

The XRD pattern of the calcined FN powders is shown in Fig. 1. The pattern for FN powders synthesized at 1075 °C can be assigned to a monoclinic phase (JCPDS card no. 71–1849). It agrees well with the result obtained by Raymond et al. [9], while the FN powders show an orthorhombic phase when the calcination temperature is raised to 1200 °C. Fig. 2 shows the XRD patterns of the BFN-M and BFN-C powders calcined at 1200 °C. All the diffraction peaks of the XRD pattern can be indexed according to a monoclinic structure. Since the early 1960s, BFN has been known as a cubic perovskite with the lattice parameter $a = 0.4045$ nm [11]. However, recent structural studies using XRD indicate that BFN has monoclinic structure at room temperature with $\beta = 90.11°$, $a = 0.40743$ nm, $b = 0.40388$ nm and $c = 0.28759$ nm [3]. As shown in Fig. 2, no

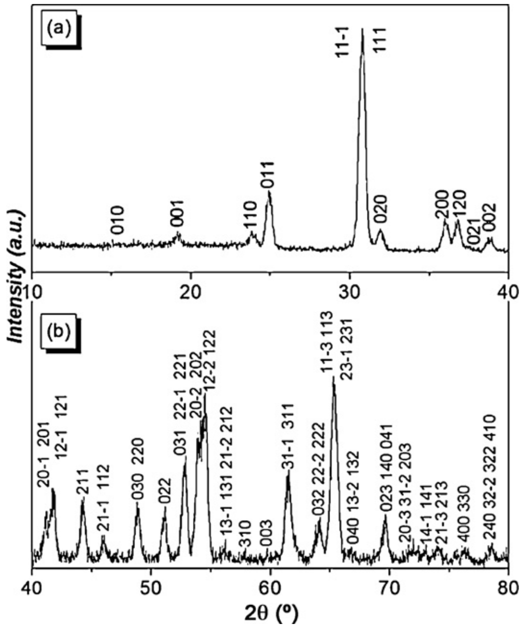

Fig. 1. XRD pattern of monoclinic $FeNbO_4$ precursor: (a) $2\theta = 10°$ to 40° and (b) $2\theta = 40°$ to 80°.

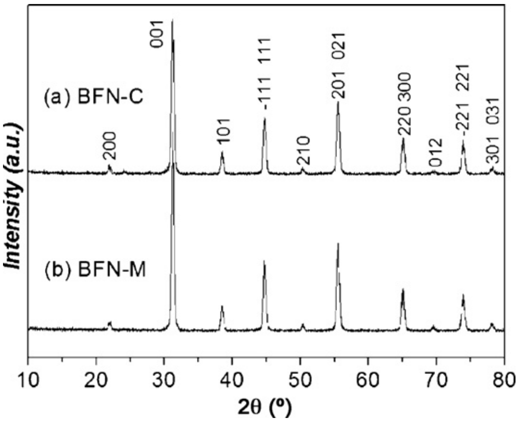

Fig. 2. XRD patterns of: (a) BFN-C and (b) BFN-M powders calcined at 1200 °C.

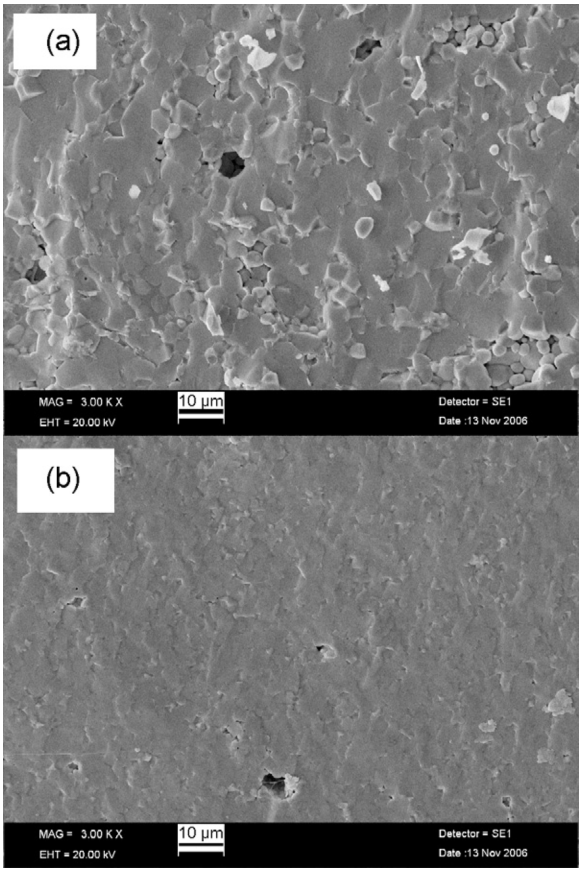

Fig. 3. Cross-section SEM of: (a) BFN-M and (b) BFN-C ceramics sintered at 1300 °C.

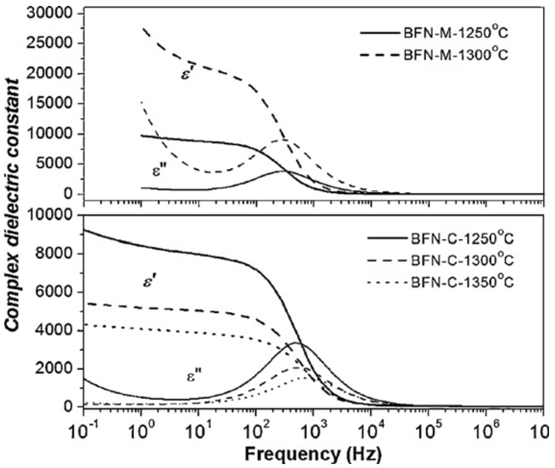

Fig. 4. Frequency dependence of the complex dielectric constant at −120 °C.

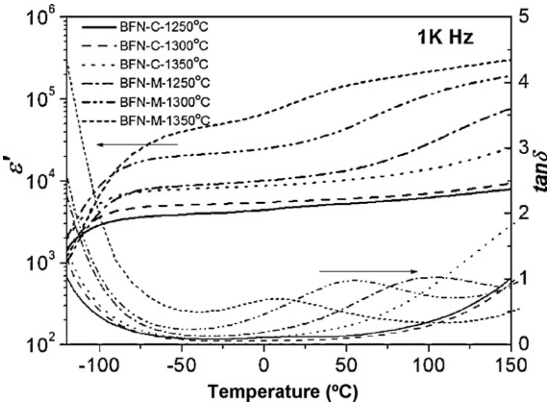

Fig. 5. Temperature dependence of dielectric constant ε' and tan δ at 1 KHz.

perceivable differences can be found between the BFN-M and BFN-C samples, regardless of the sintering temperature. Fig. 3 displays typical cross-section SEM photographs of BFN-M and BFN-C sintered at 1300 °C for 6 h. The average grain size of BFN-C samples was found to be much smaller (Fig. 3(b)) than BFN-M samples (Fig. 3(a)), and the porosity was reduced by the columbite method.

Fig. 4 shows the frequency dependence of the complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ for the BFN-M and BFN-C ceramics sintered at different temperatures. As shown in Fig. 4, each sample has a similar dielectric behavior at −120 °C. They all have a Debye-like relaxation, i.e. the real part of the complex dielectric constant ε' displays a step decrease at the frequency where the imaginary part ε'' shows a relaxation peak, and the relaxation peak in all samples shifts to higher frequencies at higher temperatures (figure not shown). For both BFN-M and BFN-C samples, ε' is much more frequency dependent below the relaxation frequency as the sintering temperature is increased. Moreover, BFN-M sample shows much larger ε' than BFN-C sample sintered at the same temperature. The Debye-like relaxation peaks can be fitted to the empirical Cole–Cole equation [12]:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^\beta} \qquad (1)$$

where ε_s is the static dielectric constant, ε_∞ the dielectric constant at high frequencies, ω the angular frequency, τ the mean relaxation time, and β is the constant. For an ideal Debye relaxation $\beta = 1$. $\beta < 1$ implies that the relaxation has a distribution of relaxation times. The broader peak in BFN-C samples indicating a smaller β value at −120 °C.

The temperature dependence of the dielectric properties at 1 KHz for BFN-M and BFN-C ceramics is shown in Fig. 5. For both samples, ε' exhibits a step increase at lower temperatures and at higher temperatures, ε' of BFN-M shows another relatively small step increase while BFN-C maintains at an almost constant value of ε'. Meanwhile, the dielectric loss of BFN-M shows a peak, moving to higher temperatures with decreasing sintering temperatures. There are no loss peaks in BFN-C samples in the temperature range of −120–150 °C. It is worth noting that the columbite samples have relatively low-dielectric loss and an almost temperature independent high-dielectric constant. These dielectric behaviors are similar to those reported in large dielectric constant materials, such as CCTO [13], Li- and Ti-doped NiO [14], and so on. In these materials, the dielectric properties could be explained using the Maxwell–Wagner relaxation arising from the grain boundaries. According to Maxwell–Wagner relaxation, the differences in dielectric properties between BFN-M and BFN-C can be explained by the difference in their grain and boundary structures. However, several authors [3–5] have suggested that BFN is a relaxor ferroelectric. We also observed a relaxor behavior in CCTO ceramics [15]. The ferroelectric hysteresis loops can also be detected in our BFN samples, indicating that both the intrinsic and the extrinsic effects contribute to the dielectric properties of BFN.

4. Conclusions

$Ba(Fe_{0.5}Nb_{0.5})O_3$ ceramics were prepared by a direct solid-state reaction (BFN-M) and a columbite method (BFN-C), respectively. Monoclinic $FeNbO_4$ was synthesized as the columbite precursor. Both BFN-M and BFN-C ceramics show a single monoclinic phase and large dielectric constant with small temperature dependence from −80 to 80 °C. Compare to BFN-M ceramics, BFN-C ceramics have smaller grain size and lower dielectric loss.

Acknowledgements

This work has been partially supported by the Program of YET and NCET and the Specialized Research Fund for the Doctoral Program of Higher Education of MOE of China, as well as by a grant from the Research Grants Council of Hong Kong Special Administrative Region (project no. PolyU5166/05E).

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