

# Effects of bismuth doping on the dielectric properties of $\text{Ba}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ceramic

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Received 9 March 2006; received in revised form 18 June 2007; accepted 15 October 2007 by T.T.M. Palstra  
Available online 30 October 2007

## Abstract

The ferroelectric ceramic  $\text{Ba}_{1-x}\text{Bi}_x(\text{Fe}_{0.5}\text{Nb}_{0.5})_{1-x/4}\text{O}_3$  (BBFN) is synthesized by a solid-state reaction. It has a partially disordered perovskite structure and shows a maximum plateau of the dielectric permittivity depending upon the temperature. The X-ray diffraction of the sample ( $x \leq 0.06$ ) at room temperature shows a monoclinic phase. When the doped contents of Bi are over 6 mole% the structure changes from monoclinic to tetragonal. The dielectric constant initially remains constant with increasing temperature up to a particular temperature  $T_d$ , beyond which it increases rapidly. The temperature variations of the real and imaginary components of the dielectric permittivity show a broad maximum. The frequency dependence of the loss peaks is found to obey an Arrhenius law with activation energy of 0.155 eV. The Cole–Cole plot analysis of BBFN shows that the high dielectric constant is not grain responsive, but is a grain boundary effect as a typical barrier layer capacitor. All these observations show the dielectric relaxation properties of BBFN perovskites.

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PACS: 77.22.-d; 77.22.Gm

Keywords: A. Sintering; C. Dielectric properties; D. Perovskites; E. Capacitors

## 1. Introduction

Recently, compounds with perovskite structures ( $\text{ABO}_3$ ) have contributed greatly to research because of the diversity of their physical properties. These compounds have found applications in several industrial fields, such as high density capacitors, memory devices, actuators and so on [1].

Most dielectric materials with perovskite structures contain lead, which pollutes the environment. Therefore, lead-free materials with high dielectric constants are becoming increasingly attractive.

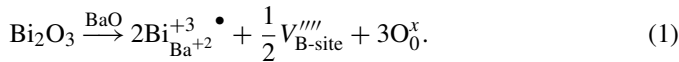
A lead-free perovskite-like oxide,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) [2, 3], was recently reported to have an extraordinarily high static dielectric constant  $\epsilon_0 \approx 10^5$  at room temperature. Furthermore, Li and Ti-doped NiO is a new oxide with a high dielectric constant [4], it does not have a perovskite structure and is

nonferroelectric, but it does have a low-frequency dielectric constant  $\epsilon_0 \approx 10^4\text{--}10^5$  at room temperature.

$\text{Ba}(\text{FeNb})_{1/2}\text{O}_3$  is a relaxor-type ferroelectric material which has a partially disordered perovskite structure [5–7]. The  $\text{Fe}^{+3}$  and  $\text{Nb}^{+5}$  ions are randomly distributed in the octahedral positions and have small lattice distortion. Dielectric study revealed the existence of a large dielectric constant at low frequency over a wide temperature range. The present dielectric behavior was interpreted on the basis of the interfacial polarization at the grain boundary region [8]. These dielectric relaxation properties follow from broad dielectric transitions, known as the diffused-phase transitions (DPT) with strong frequency dispersion [9,10].

Bismuth ions doped in  $\text{Ba}(\text{FeNb})_{1/2}\text{O}_3$  normally occupy the Ba sites. The lattice will carry positive charges which can, in order to keep charge balance, be compensated by electron or B-site vacancies. This may be represented by the Eq. (1) for  $\text{Ba}_{1-x}\text{Bi}_x(\text{Fe}_{0.5}\text{Nb}_{0.5})_{1-x/4}\text{O}_3$  ( $0 < x < 0.2$ ).

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The small Bi ions were compensated by the appearance of B-site vacancies. Incorporating  $\text{Bi}_2\text{O}_3$  into the A-site sublattice of the perovskite structure stabilizes it in the monoclinic phase, and the polycrystalline materials of such modified dielectrics were prepared by a solid-state reaction method. The microstructures and the corresponding dielectric properties were then examined.

## 2. Experimental

The compounds used in this investigation were prepared by a routine solid-state reaction. The starting materials were  $\text{BaCO}_3$  (99.9% pure, NOAH technologies corporation, San Antonio),  $\text{Fe}_2\text{O}_3$  (99.9% pure, Alfa Aesar Co.),  $\text{Nb}_2\text{O}_5$  (99.9% pure, Aldrich Chemical Co.) and  $\text{Bi}_2\text{O}_3$  (99.99% pure, Showa Chemical Inc.). The doping concentration of Bi was varied from 0.02 to 0.2 mole%. The raw powders were based on the formula  $\text{Ba}_{1-x}\text{Bi}_x(\text{Fe}_{0.5}\text{Nb}_{0.5})_{1-x/4}\text{O}_3$ . The columbite precursor method was used for the  $\text{FeNbO}_4$  powders, which were first synthesized by ball milling the  $\text{Fe}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  with acetone in a polypropylene jar for 24 h. The mixture was then dried at 100 °C and calcined at 1100 °C for 4 h in air. Second, the  $\text{Ba}_{1-x}\text{Bi}_x(\text{Fe}_{0.5}\text{Nb}_{0.5})_{1-x/4}\text{O}_3$  powders were prepared by mixing the  $\text{FeNbO}_4$ ,  $\text{BaCO}_3$  and  $\text{Bi}_2\text{O}_3$  with acetone in a polypropylene jar for 24 h again, and after drying, they were calcined at 950 °C for 5 h in air. The calcined powders were reground and pressed at 200 MPa into disks of 10–11 mm in diameter and thicknesses of 2–4 mm. Finally, pellets placed on an aluminum oxide crucible were sintered in air at 1200–1300 °C for 4 h at a ramping rate of 5 °C/min. The electrodes for measurements were deposited on the ground disk surface by rubbing on In–Ga alloy.

The phase purity, structure and lattice parameters of the sample were determined by X-ray power diffraction with  $\text{CuK}\alpha$  radiation at room temperature. The particle morphology and grain size were characterized by scanning electron microscopy (SEM). The density of sintered  $\text{Ba}_{1-x}\text{Bi}_x(\text{Fe}_{0.5}\text{Nb}_{0.5})_{1-x/4}\text{O}_3$  was measured using the Archimedes method in deionized water. The dielectric constant and dielectric loss were measured from 100 Hz to 1 MHz at room temperature using an LCR (HP4284A) meter.

## 3. Results and discussion

### 3.1. Crystal structure

Fig. 1 shows the X-ray diffraction patterns (at room temperature) of the ceramics  $\text{Ba}_{1-x}\text{Bi}_x(\text{Fe}_{0.5}\text{Nb}_{0.5})_{1-x/4}\text{O}_3$  sintered at 1250 °C for 1 h with various  $x$  values. All the reflection peaks of the X-ray profiles were indexed and the lattice parameters were determined using the least-square method with the help of a standard computer program. Single-phase monoclinic perovskite structure was obtained for  $x$  (Bi ions) up to 2 mol%–6 mole%. When Bi concentration exceeds 6 mol%, the secondary phase  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ , appears in the X-ray diffraction patterns, as can be seen in the marked peaks in

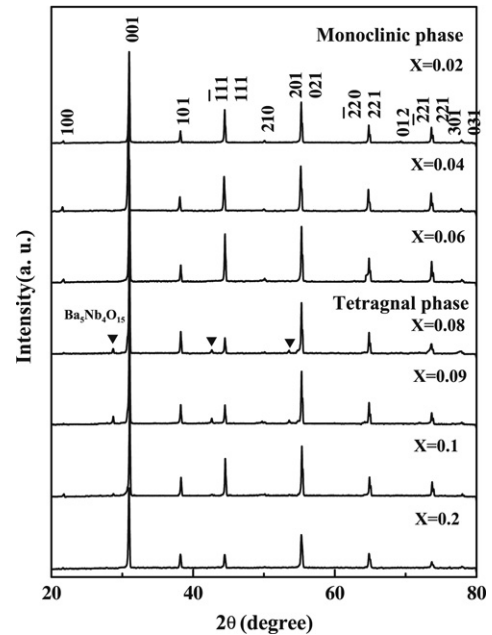


Fig. 1. X-ray diffraction patterns for compositions  $0.02 \leq x \leq 0.2$  of the system  $\text{Ba}_{1-x}\text{Bi}_x(\text{Fe}_{0.5}\text{Nb}_{0.5})_{1-x/4}\text{O}_3$  sintered at 1250 °C for 1 h.

Fig. 1. Moreover, the maximum intensity peak (001) (around 31°) has a small shift towards the higher angle as  $x$  increases. The result is that the BBFN belongs to monoclinic symmetry for  $x$  up to 6 mole%, or a tetragonal symmetry.

The pure  $\text{Ba}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$  has a monoclinic structure at room temperature with  $\beta = 90.16^\circ$  ( $a = 4.0717 \text{ \AA}$ ,  $b = 4.0525 \text{ \AA}$  and  $c = 2.876$ ). If the Bi content increases, the lattice parameter of BBFN decreases in either the monoclinic or tetragonal structure and the beta angle approaches 90°, and this is attributed to the smaller ionic radius of  $\text{Bi}^{3+}$  (0.12 nm) compared to that of  $\text{Ba}^{2+}$  (0.136 nm) [11].

Fig. 2 shows the microstructures of  $\text{Ba}_{1-x}\text{Bi}_x(\text{Fe}_{0.5}\text{Nb}_{0.5})_{1-x/4}\text{O}_3$  ( $x = 0.02, 0.04, 0.06, 0.08$  and  $0.1$ ). By comparing Fig. 2(a)–(c), it can be seen clearly that the growth of grains was significantly suppressed by doping with  $\text{Bi}^{3+}$  ions. However, as the doping level increased up to 8 mol%, the structure changed from monoclinic to tetragonal, and second phase was observed near the grain boundaries. When  $x = 0.1$ , a long needle-shaped second phase appears. Analysed by EDS, the second phase is rich in Ba and Nb compared with the perovskite phase. According to the X-ray result (Fig. 1), this phase is  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ .

### 3.2. Dielectric properties

#### 3.2.1. Temperature and frequency dependences of the dielectric constant

Temperature dependences of the dielectric constant ( $\epsilon$ ) and dissipation factors ( $D$ ) of  $\text{Ba}_{1-x}\text{Bi}_x(\text{Fe}_{0.5}\text{Nb}_{0.5})_{1-x/4}\text{O}_3$  ( $X = 0.1$ ) are shown in Fig. 3(a) and (b). The samples sintered at 1250 °C have the maximum dielectric constant. If the sintering temperature is higher than 1250 °C, the dielectric constant would decrease, because such a high temperature causes the liquid-phase sintering phenomenon, making the

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