

# Synthesis and dielectric behavior of lead-free $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Ti}_{1-y}\text{Ta}_y\text{O}_3$ piezoelectric ceramics

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Solid solution of  $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Ti}_{1-y}\text{Ta}_y\text{O}_3$  in the composition range  $x = 0.06$  and  $0.0 \leq y \leq 0.05$  were prepared by conventional ceramics sintering technique. These new group of lead-free piezoelectric ceramic were studied for their crystal structure, dielectric and piezoelectric properties. It is shown that the system possess pure perovskite phase in its as calcined state. A morphotropic phase boundary (MPB) between tetragonal and rhombohedral phases appears at  $x = 0.06$  and  $y = 0.05$ . The room temperature measurements of dielectric and piezoelectric properties reveal that the obtained ceramics with MPB composition has potential for use as piezoelectric material.

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## 1. Introduction

Recently, lead-free piezoelectric materials have attracted increasing attention as an alternative to lead zirconate titanate (PZT) materials for the sake of environmental protection [1-5]. Lead is known to be health and environmental hazard, and requires special precautions during handling and processing. It would be highly desirable to find a suitable alternative for lead in these compositions, and still maintain satisfactory electromechanical properties of new ceramics.  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$  (NBT) is one of the rare relaxor ferroelectric perovskites in which the ratio of two different ions  $\text{Na}^{1+}$  and  $\text{Bi}^{3+}$  at the A-sites is 1:1. This composition was found to have an excellent potential for application as piezoelectric [6]. However, its high coercive field ( $E_C \approx 73\text{kV/cm}$ ) and high electrical conductivity at room temperature causes the problem in poling process [7] that has to be overcome. Recent results suggest that BNT-based solid solutions might solve these problems [8-9]. BNT-based solid solution with  $\text{BaTiO}_3$  is reported to exhibit morphotropic phase boundary (MPB) similar to what is well known for  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  system. MPB for Ba substituted compound is situated at  $x = 0.06$  [11], which is why this composition had been chosen as a fixed amount of Ba that was introduced into A-sites. On the other side, the role of Ta is not known. On the other side, However, the introduction of  $\text{Ta}^{5+}$  in the B-site of BNT could disorder perovskite structure. For that reason in the present study,  $\text{Ba}^{2+}$  and  $\text{Ta}^{5+}$ , the so-called "soft" doping cations usually used in PZT system, were introduced into both A-sites and B-sites of  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ , with an attempt to explain the phase transition behavior and piezoelectric properties.

## 2. Experimental

Designed compositions (Table 1) were prepared by the conventional mixed-oxide solid state reaction technique using commercially available metal oxide or carbonate powders:  $\text{Bi}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{BaCO}_3$ ,  $\text{TiO}_2$  and  $\text{Ta}_2\text{O}_5$ . The powders were weighted and mixed with  $\text{ZrO}_2$  balls in DI water in polyethylene bottle for 12 hours. The calcinations were then conducted at  $850^\circ\text{C}$  for 6 hours. The calcined mixtures were mixed with PEG (3-5wt %) and ball milled in DI water again for 12 hours. The as-granulated powders were uniaxially pressed into disk samples with diameter of 20 mm and a thickness of 3 mm. Sintering is accomplished in an electrical furnace at ambient atmosphere in temperature range from 1000 to  $1150^\circ\text{C}$ . The sintering schedule is given in Fig. 1. The proposed schedule was used to enable burning out the organic binder.

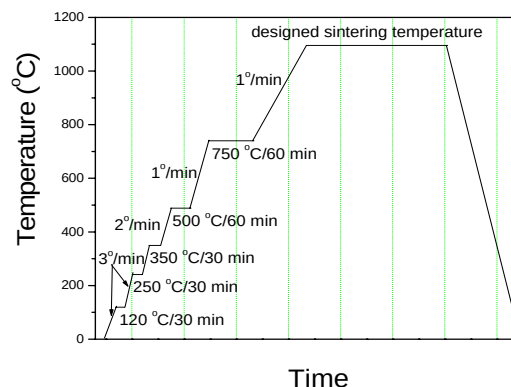


Fig. 1. Heating profile during sintering.

Bulk densities were measured by the Archimedeian displacement method using distilled water. After removing 0.2 mm of the material from the surface by grinding, crystalline phases were identified by X-ray diffraction (XRD) using  $\text{Cu K}\alpha$  radiation (Siemens D5000). The microstructural observation of polished and chemically etched specimens was performed by scanning electron microscopy (SEM).

All dielectric properties were measured from 1 Hz to 1 MHz by impedance analysis (Solartron Impedance Analyzer) at room temperature. The samples were polished and painted with silver paste. For piezoelectric measurement, samples were immersed in silicon oil and poled by applying an electric field from 1 to 4 kV/cm at room temperature. The  $d_{33}$  piezoelectric coefficient measurements were made on poled samples using a  $d_{33}$  meter.

### 3. Results and discussion

Stability of perovskite structure depends on the relative sizes of the A and B elements as well as on the electronic configuration of the B sites ions. The size factor is expressed by a tolerance factor “ $t$ ” obtained by considering the structure as derived from a close-packed stacking of the A and oxide ions [12]. It is defined by the relationship:

$$R_A + R_O = t \cdot \sqrt{2} \cdot (R_B + R_O) \quad (1)$$

where  $R_A$  and  $R_B$  are the ionic radii (of the A and B ions taken from the Shannon and Prewitt [13]). The ideal close packing corresponds to  $t = 1$ . The perovskite structure is found for  $t$  values ranging from 0.8 to 1.1. Table 1 shows that the  $t$  values for designed compositions are in the range of stable perovskite structure.

Table 1. Tolerance factor in function of chemical compositions.

| No | Composition                                                                                    | Tolerance factor, $t$ |
|----|------------------------------------------------------------------------------------------------|-----------------------|
| 1  | $(\text{Bi}_{0.47}\text{Na}_{0.47}\text{Ba}_{0.06})\text{Ti}_{0.99}\text{Ta}_{0.01}\text{O}_3$ | 0.9509                |
| 2  | $(\text{Bi}_{0.47}\text{Na}_{0.47}\text{Ba}_{0.06})\text{Ti}_{0.97}\text{Ta}_{0.03}\text{O}_3$ | 0.9506                |
| 3  | $(\text{Bi}_{0.47}\text{Na}_{0.47}\text{Ba}_{0.06})\text{Ti}_{0.95}\text{Ta}_{0.05}\text{O}_3$ | 0.9503                |

The XRD patterns of the ceramics with BNT-based solid solutions  $[(\text{Bi}_{0.47}\text{Na}_{0.47})\text{Ba}_{0.06}\text{Ti}_{1-x}\text{Ta}_x\text{O}_3]$  in show that all the samples have pure perovskite structure (Fig. 2).

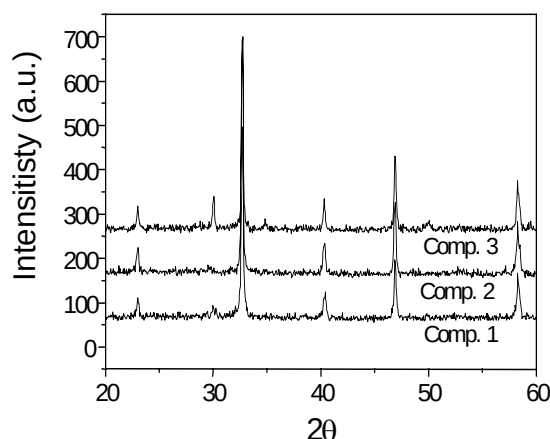


Fig. 2 X-ray diffraction patterns of  $[(\text{Bi}_{0.47}\text{Na}_{0.47})\text{Ba}_{0.06}\text{Ti}_{1-x}\text{Ta}_x\text{O}_3]$ , where  $x$  ranges from 1 to 5 at % of  $\text{Ta}^{5+}$ . Comp 1 (1 at %), Comp. 2 (3 at%) and Comp. 3 (5 at%).

Effect of sintering temperature on sintered density for each composition is given in Table 2. For all compositions, the density increased with increasing sintering temperature and time as well as with higher Ta concentration.

Table 2 Sintered densities ( $\text{g/cm}^3$ ) of doped NBT ceramics.

| Temperature<br>°C/time/h/ | Comp.<br>1 | Comp.<br>2 | Comp.<br>3 |
|---------------------------|------------|------------|------------|
| 1000-1h                   | 4.9        | 5          | 5.3        |
| 1000-2h                   | 5.1        | 5.1        | 5.4        |
| 1000-4h                   | 5.3        | 5.4        | 5.7        |
| 1000-8h                   | 5.7        | 5.8        | 5.8        |
| 1050-1h                   | 5.1        | 5.3        | 5.4        |
| 1050-2h                   | 5.3        | 5.2        | 5.6        |
| 1100-4h                   | 5.6        | 5.6        | 5.7        |
| 1150-4h                   | 5.5        | 5.8        | 5.9        |

After sintering, the material reveals fine grained microstructure with homogeneous distribution of perovskite crystals Fig. 3). The chemistry of the grains was analyzed by energy dispersive microanalysis (EDX), which shows Ti, Bi, Na and O elements. However, Ba and Ta are not detected, probably due to low amounts.

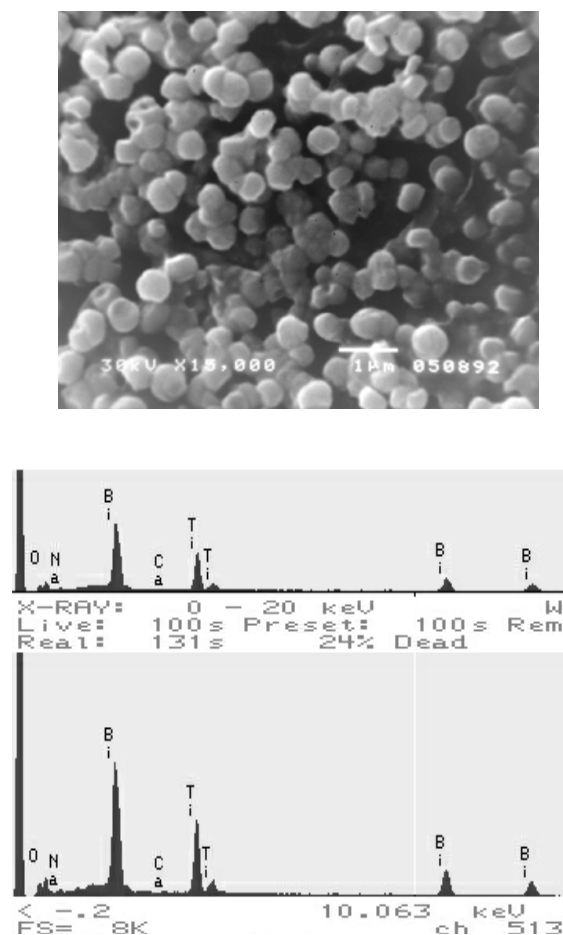


Fig. 3. SEM micrograph (a) and EDX (b) of polished and chemically etched sections of the sample  $[(\text{Bi}_{0.47}\text{Na}_{0.47})\text{Ba}_{0.06}\text{Ti}_{0.95}\text{Ta}_{0.05}\text{O}_3]$  sintered at 1150 °C for 4 h.

Since the highest density is achieved for sample sintered at 1100 °C for 4 h (composition 3), the dielectric properties were measured only for this samples. The properties were measured at frequencies ranging from 1 Hz to 1 MHz. Typical relationships between capacitance and loss  $\tan \delta$  after poling are shown in Fig. 4. It can be seen that the samples poled under lower electrical field have capacitance and  $\tan \delta$  higher than those of samples poled under higher electrical field.

Increasing the electrical field during poling causes decreasing the value for loss  $\tan \delta$  from 5.35% to 3.65%.

The polarization behavior was also measured at room temperature. The  $d_{33}$  piezoelectric coefficient increased from low value to 85 pC/N after the application of an electrical field of 4 kV/cm (Fig. 5). These results suggest that the composition 3 has an attractive polarization performance.

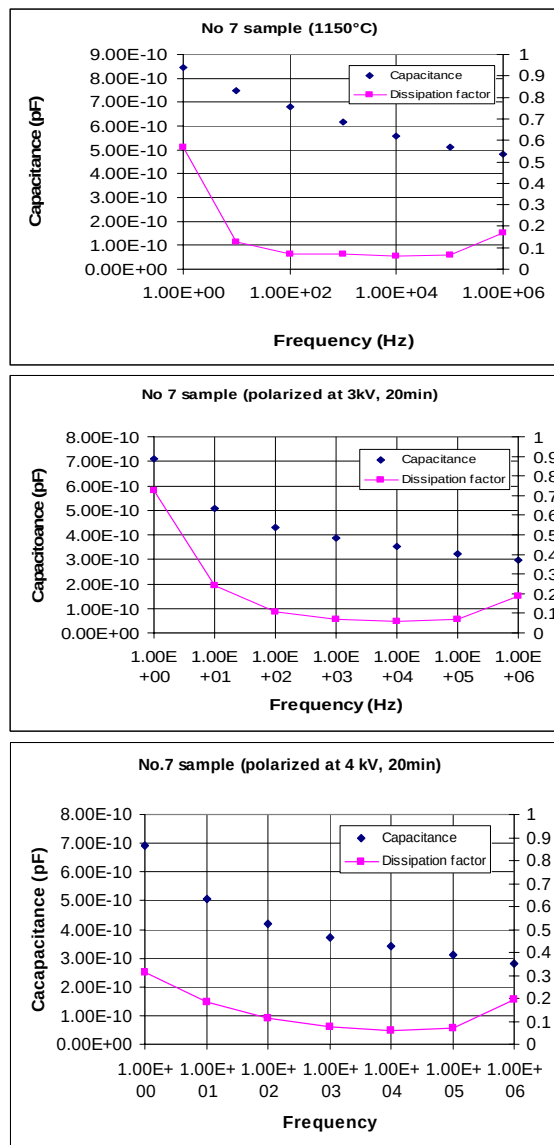


Fig. 4. Capacitance and loss  $\tan \delta$  of BNT ceramics doped with  $\text{Ta}^{5+}$  as a function of frequency (composition 3).

Fig. 6 shows the change in the diffraction peaks of sample after poling. The shifting of peaks in the  $2\theta$  ranges from  $38^\circ$  to  $42^\circ$  and from  $45^\circ$  to  $48^\circ$ , respectively, indicates that the cubic symmetry of samples before poling transforms into tetragonal structure. This is directly related to the change of the domain structure during poling. In order to confirm this assumption, the Rietveld refinement was performed. The results show that poled sample of composition 3 has a good match of peak positions only for tetragonal symmetry. Structural parameters show that  $[(\text{Bi}_{0.47}\text{Na}_{0.47})\text{Ba}_{0.06}\text{Ti}_{0.95}\text{Ta}_{0.05}\text{O}_3]$  is tetragonal phase with nonsymmetrical space group P 4 b m (Table 3 and Fig. 7). The lattice parameters are  $a = b = 5.4886(3)$  Å;  $c = 3.8933(4)$  Å. The final weighted R-factor,  $R_{\text{wp}}$  is 7.34%.

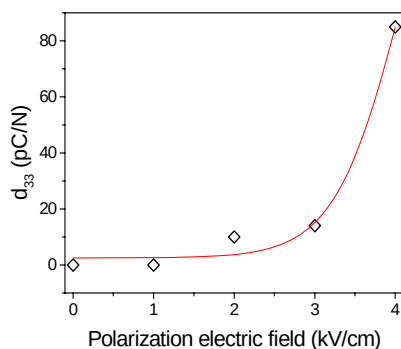


Fig. 5. Polarization behavior of  $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Ti}_{1-y}\text{Ta}_y\text{O}_3]$  ceramics in the composition range of  $x = 0.06$  and  $y = 0.05$  at room temperature.

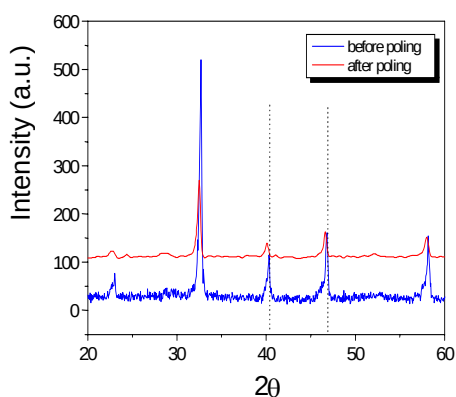


Fig. 6. XRD diffraction patterns of  $[(\text{Bi}_{0.47}\text{Na}_{0.47})\text{Ba}_{0.06}\text{Ti}_{0.95}\text{Ta}_{0.05}\text{O}_3]$  sample sintered at  $1150^\circ\text{C}$  for 4 h before and after poling.

From the result of the structural refinement based on tetragonal phase, it can be concluded that the electric field induces alignment of domains resulting in macroscopic piezoelectric behavior. Therefore, it can be suggested that the MPB of  $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Ti}_{1-y}\text{Ta}_y\text{O}_3]$  ceramics lies in the composition range of  $x = 0.06$  and  $y = 0.05$ .

Table 3. Structural parameters for  $[(\text{Bi}_{0.47}\text{Na}_{0.47})\text{Ba}_{0.06}\text{Ti}_{0.95}\text{Ta}_{0.05}\text{O}_3]$  obtained from the structural refinement using X-ray powder diffraction data at room temperature.

| Atom           | $x$     | $y$     | $z$       |
|----------------|---------|---------|-----------|
| Bi<br>Na<br>Ba | 0.00    | 0.5     | 0.560(1)  |
| Ti<br>Ta       | 0.00    | 0.00    | 0.00      |
| O1             | 0.00    | 0.00    | 0.628(4)  |
| O2             | 0.25(1) | 0.25(1) | -0.072(3) |

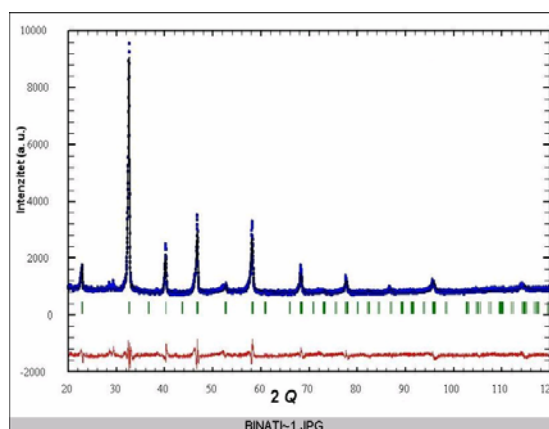


Fig. 7. The structural refinement patterns of the composition  $(\text{Bi}_{0.47}\text{Na}_{0.47})\text{Ba}_{0.06}\text{Ti}_{0.95}\text{Ta}_{0.05}\text{O}_3$  using X-ray powder diffraction data based on the tetragonal phase with space group  $P4bm$ . Point marks (•) represent the observed intensities, while the solid line represents the calculated ones. A difference (measured - calculated) is shown beneath. Thick markers indicate the reflection position.

#### 4. Conclusions

The results showed that powders of lead-free piezoelectric can be obtained by applying traditional solid state process. The ceramics with BNT-based solid solutions  $(\text{Bi}_{0.47}\text{Na}_{0.47})\text{Ba}_{0.06}\text{Ti}_{1-x}\text{Ta}_x\text{O}_3$  possesses perovskite structure. X-ray powder diffraction data, after poling, show the change of rhombohedral to tetragonal structure. It is suggested that the MPB in this material exists in the composition range of  $x = 0.05$  at room temperature. In spite of low applied electrical field, the composition near the MPB exhibits relatively good piezoelectric properties. Thus, lead-free piezoelectric ceramic doped with soft cations ( $\text{Ba}^{2+}$  and  $\text{Ta}^{5+}$ ) has a potential as a material with good piezoelectric properties.

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