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Chemical composition and tolerance factor at the morphotropic phase boundary in $(Bi_{0.5}Na_{0.5})TiO_3$-based piezoelectric ceramics

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Abstract

A quantitative relation between the morphotropic phase boundary (MPB) composition and the tolerance factor (t) in $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT)-based piezoelectric ceramics was established. The t value of the MPB compositions in BNT-based ceramics is around 0.990–0.993 and is independent of the types of added compounds. In order to experimentally demonstrate it, two piezoelectric ceramic systems $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x(Ba_{1-a}Sr_a)TiO_3$, $a = 0.05$ and 0.3 (BNBST5-x and BNBST30-x, $x < 12\%$), were used. X-ray diffraction patterns and the lattice parameter investigations revealed that these two systems formed solid solutions within the studied stoichiometry and showed a rhombohedral–tetragonal phase transformation. Furthermore, both the structure analysis and electric properties measurements indicated that the MPB compositions were BNBST5-6 and BNBST30-8 and their corresponding t value were 0.9900 and 0.9903, respectively. The results confirm the relation between the MPB composition and t value and provide a method for designing new piezoelectric materials.

Keywords: Perovskites; Piezoelectric properties; X-ray method; Tolerance factor; (Bi, Na)TiO_3

1. Introduction

The most used piezoelectric materials are $PbTiO_3$–$PbZrO_3$ (PZT)-based ceramics because of their excellent piezoelectric properties. However, PZT-based ceramics are environmentally burdened materials. Therefore, it is necessary to investigate and develop environment-friendly materials to replace PZT-based ceramics.

Lead-free piezoelectric materials, such as langasite single crystal, ferroelectric ceramics with the perovskite structure, and Bi-layered structure oxides have been reported.[1] Among these materials, bismuth sodium titanate $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT), firstly reported by Smolenskii et al.,[2] is considered to be a candidate to replace the widely used lead-contented perovskite materials due to its high remanent polarization ($P_r = 38\ \mu C/cm^2$). Nevertheless, the applications of BNT are limited by its high coercive field ($E_c = 7.3$ kV/mm) and its high conductivity. To solve these problems and improve the electric properties, various types of compounds were added into BNT to form solid solutions, such as $CaTiO_3$, $NaNbO_3$, $BaTiO_3$, etc.[3–17] It is found that the piezoelectric properties of these "modified" BNT-based materials were effectively enhanced when a MPB composition was attained. Usually the determination of MPB composition requires a series of time-consuming experiments and a method that allows a prediction of the MPB composition in BNT-based ceramics has not yet been reported. The present work demonstrates a relation between the MPB composition and tolerance factor and suggests a simple method to evaluate the feasibility of new BNT-based lead-free piezoelectric ceramics.

2. MPB–tolerance factor relation in BNT-based ceramics

The tolerance factor (t) is a concept for the arrangement of interpenetrating dodecahedra and octahedra in a ABO_3 perovskite structure introduced by Goldschmidt,[18] which is given by,

$$t = \frac{R_a + R_o}{\sqrt{2}(R_b + R_o)}$$

where R_a, R_b, and R_o are the ionic radii of cation A, B and oxygen, respectively. For complex perovskite system,

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Table 1
The optimal piezoelectric constant (d_{33}) and electromechanical coupling factor (k_p) of the composition in various BNT-based piezoelectric ceramics

BNT-based solid solution	MPB	d_{33} (μC/N)	k_p (%)	t	Ref.
BNT	–	58	12	0.9857	3
0.99BNT–0.01$CaTiO_3$	–	50	13.8	0.9855	4
0.87BNT–0.13$(Sr_{0.5}Ca_{0.5})TiO_3$	–	–	12	0.9855	5
$(Bi_{0.5}Na_{0.5})_{0.9742}La_{0.0172}TiO_3$	–	91	13	0.9812	3
0.98BNT–0.02$BiScO_3$	–	74.7	14.4	0.9844	6
0.995BNT–0.005$Ba(Cu_{0.5}W_{0.5})O_3$	–	80	18.1	0.9862	7
0.985BNT–0.01$EuTiO_3$	–	46	–	0.9828	8
0.98BNT–0.02$NaNbO_3$	–	88	17.9	0.9853	9
0.993BNT–0.007$Bi(Mg_{2/3}Nb_{1/3})O_3$	–	94	–	0.9854	10
0.994BNT–0.006$BaNb_2O_6$	–	94	–	0.9844	11
0.94BNT–0.06$BaTiO_3$	O	125	20	0.9902	12
0.88BNT–0.12$PbTiO_3$	O	106.6	33.2	0.9907	13
0.84BNT–0.16$(Bi_{0.5}K_{0.5})TiO_3$	O	–	31.4	0.9926	14
0.9BNT–0.05$(Bi_{0.5}K_{0.5})TiO_3$–0.05$BaTiO_3$	O	163	28	0.9922	15
0.91BNT–0.09$Ba(Ti_{0.942}Zr_{0.058})O_3$	O	147	–	0.9922	16
$Bi_{0.49}Na_{0.3775}K_{0.075}Li_{0.02}Ba_{0.02}TiO_3$	O	205	29.0	0.9915	17
$Bi_{0.495}Na_{0.3825}K_{0.075}Li_{0.02}Ba_{0.01}TiO_3$	O	178	37.0	0.9907	17

R_a and R_b are the ionic radii of composed ions normalized by the atomic ratio. For the example of $(Ba_{0.7}Sr_{0.3})TiO_3$, $R_a = 0.7 \times 1.61$ Å $+ 0.3 \times 1.44$ Å $= 1.559$ Å ($R_{Ba^{2+}}/R_{Sr^{2+}} = 1.61/1.44$ Å), $R_b = 0.605$ Å ($R_{Ti^{4+}} = 0.605$ Å), $R_o = 1.40$ Å ($R_{O^{2-}} = 1.40$ Å), so that $t = 1.0435$ is deduced. The ionic radii refer to those reported by Shannon.[19] In general, the perovskite structure is stable in the region $0.880 < t < 1.090$,[18] and the symmetry is higher as the t value is close to 1. For example, the t value of a cubic $SrTiO_3$ ($t = 1.001$) is closer to 1 than an orthorhombic $CaTiO_3$ ($t = 0.966$). The t value also provides an indication about how far the atoms can move from the ideal packing positions and be still "tolerated" in the perovskite structure. It reflects the structural modification such as distortion, rotation, tilt of the octahedra.[20] These structure factors consequently affect the electric property. Recently, some investigations are trying to find out the relation between the t and some material properties. For example, Reaney et al. have described that the temperature coefficient of dielectric constant (τ_ε) is controlled by the t, and Suchomel et al. have suggested a MPB-t relation in lead-based piezoelectric ceramics.[21–23] It is believed that a MPB-t relation may also exists in BNT-based lead-free piezoelectric ceramics.

Plenty of research results for the BNT-based lead-free piezoelectric ceramics have been published in the past years,[3–17] and the compositions with optimal piezoelectric properties of each system are summarized in Table 1. It is shown that Table 1 can be separated into two parts according to the existence of the MPB composition and their corresponding t value related to pure BNT ($t = 0.9857$). For the upper part, the chosen non-BNT end compounds cause a decrease of t value in comparison with pure BNT. These systems are either difficult to form a solid solution with BNT or no phase transformation is found. For the lower part, the non-BNT end compounds make the t value increase and results in a phase transformation at their MPB composition where superior piezoelectric properties are observed. The piezoelectric constant (d_{33}) and electromechanical coupling factor (k_p) of the compositions listed in Table 1 is plotted as function of t in Fig. 1. It is obviously found that the t values of the MPB compositions for all the types of compounds are in the range of 0.990–0.993. It implies a fact that the MPB composition for the BNT-based solid solution systems is related to the t value and can be determined by adjusting the t value into this region.

This observation can be explained by the t value because it provides a general information for the crystal structure. For $(Bi_{0.5}Na_{0.5})TiO_3$, whose stable phase is rhombohedral ($R3c$) corresponding to a t value of 0.986. If a non-BNT end compound with a higher t value is added and forms a solid solution with BNT, a phase transformation may take place at certain composition when the added compound is not tolerated anymore in the rhombohedral structure. Moreover, no matter what the non-BNT end compounds are, the "tolerated" limit of the rhombohedral-BNT is approximate. Due to these reasons, the t values of the MPB compositions in BNT-based ceramics should be a definite

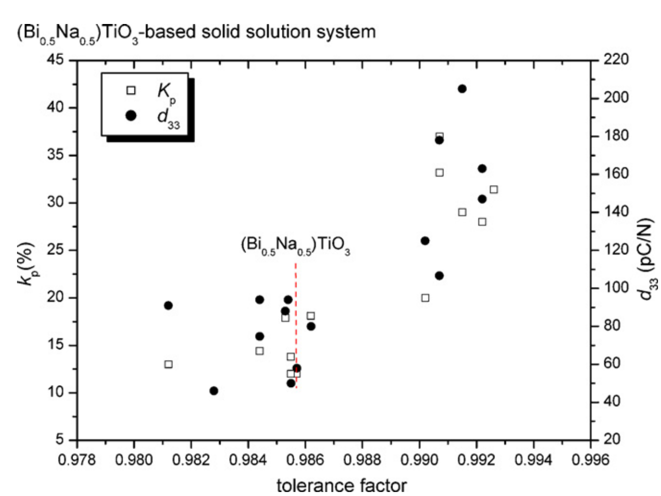

Fig. 1. Piezoelectric constant (d_{33}) and electromechanical coupling factor (k_p) against the tolerance factor (t) in $(Bi_{0.5}Na_{0.5})TiO_3$-based piezoelectric ceramics.