

# Effect of A-site substitution on crystal component and dielectric properties in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ceramics

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## Abstract

A-site replacement is common used in optimizing the electric properties of  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (abbreviated to BNT). The effect of  $\text{Ba}^{2+}$  doping in BNT capacitor ceramics is investigated here. After the samples containing 6 at.%  $\text{Ba}^{2+}$  was sintered at  $1180^\circ\text{C}$  for 2 h, capacitor ceramics with enhanced dielectric properties was fabricated, compared with pure BNT ceramics. It can be concluded from the experiment results that  $\text{Ba}^{2+}$  replaced the ions in A-site, and the lattice structure was altered, which led to the improvement of dielectric properties in BNT ceramics. Then we discussed the phase transformation process from room temperature to  $400^\circ\text{C}$  according to the dielectric properties–temperature graphs.

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**Keywords:** Bismuth sodium titanate; Dielectric properties; Doping effects; Phase transitions

## 1. Introduction

Bismuth sodium titanate is an attractive lead-free A-site complex perovskite ferroelectric relaxor material, which is regarded as a new candidate to replace the widely used lead-contained ceramics, because of the free control of sintering atmosphere and none lead pollution during the fabrication process [1–5]. But the applications of pure BNT ceramics are limited by some of its shortcomings in electric properties, for example: low relative dielectric permittivity ( $\epsilon_r$ ); narrow sintering temperature range and high conductivity at room temperature [6–8]. In this case, it is necessary to improve BNT ceramics on dielectric properties for applications.

It is reported that  $\text{BaTiO}_3\text{--}(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$  system appears arresting because of the enhancement in dielectric properties [9,10]. To summarize and grasp the principle, further research on  $\text{Ba}^{2+}$  doping BNT system is necessary.

In this experiment, we synthesized the BNT-based ceramics in ambient atmosphere in conventional ceramics fabrication technique. Defect reactions were used to reveal the

principle of  $\text{Ba}^{2+}$  doping, which is well matched with the results.

## 2. Experimental procedure

The metal oxide and carbonate powder of high purity, such as:  $\text{Bi}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{TiO}_2$  and  $\text{BaCO}_3$ , were used as the raw materials. Mixing them in ethanol with nylon balls and ball-milling for 4 h, then calcining at  $850^\circ\text{C}$  for 1 h, then ball-milling in ethanol again for 6 h. The dried powder was formed into discs, 12 mm in diameter and 1.5 mm in thickness. The samples with different  $\text{Ba}^{2+}$  content, which is over the range of 0–20 at.%, were sintered at  $1140\text{--}1200^\circ\text{C}$  for 2 h, the samples without additives were sintered at  $1100^\circ\text{C}$  for 2 h.

The microstructure of the well-sintered sample was observed with ESEM (Philip XL 30 ESEM). The X-ray diffraction pattern, as shown in Fig. 1, was obtained with X-ray diffraction meter (BDX 3300, Beijing). After supersonic cleaning, fired-on silver pasted was used as the electrodes for dielectric properties measurement with Automatic LCR meter (4425, Tianjin) at 1 kHz. Temperature dependence of

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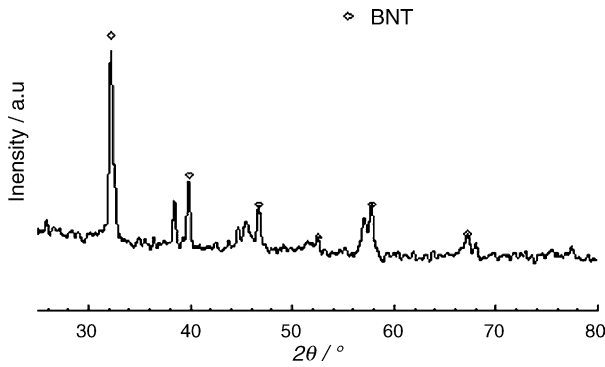


Fig. 1. XRD pattern for 0.94(Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-0.06BaTiO<sub>3</sub> sample.

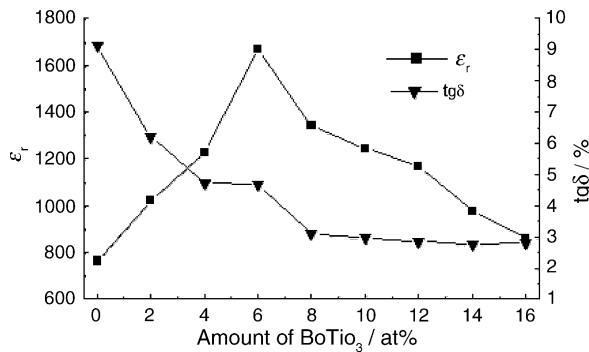


Fig. 2. *x* dependence of relative permittivity and dissipation factor of *x*BaTiO<sub>3</sub>-(1 - *x*)(Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>.

dielectric relative permittivity and loss tangent were drawn with an automated dielectric system, which consisted of the Automatic LCR meter and a temperature control unit.

### 3. Results and discussion

#### 3.1. The effect of Ba<sup>2+</sup> on the dielectric properties

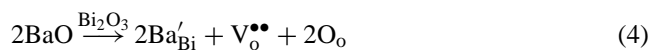
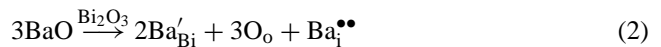
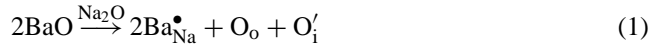
Fig. 2 shows the relationship between the ε<sub>r</sub>, loss tangent and *x* in BNBT system [(1 - *x*)(Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-*x*BaTiO<sub>3</sub>], and Table 1 shows the relative density, respectively. It can be seen that Ba<sup>2+</sup> doping can improve the dielectric properties remarkably. When *x* was less than 0.06, the dielectric permittivity became higher with the increasing of *x*, while the loss

Table 1  
Relative density of BNT samples with different Ba<sup>2+</sup> content

Content of Ba <sup>2+</sup> (at.%)	Relative density (%)
0	92.5
2	92.7
4	93.2
6	93.9
8	95.1
10	97.4
12	98.4
14	98.6
16	98.5

tangent decreased. When *x* was 0.06, the ε<sub>r</sub> reaches its maximum (1670); meanwhile, the loss tangent was 4.66%. When the *x* kept on increasing, the ε<sub>r</sub> and loss tangent declined.

During the synthesis process, BaCO<sub>3</sub> decomposed into BaO and CO<sub>2</sub>, and BaO can enter the crystal lattice and replace the ions in lattice site. The ionic radius of Ba<sup>2+</sup> is 0.160 nm when its coordination number is 12, and ionic radii of Na<sup>+</sup>, Bi<sup>3+</sup> and Ti<sup>4+</sup> are 0.139, 0.128 and 0.061 nm, respectively, so Ba<sup>2+</sup> ions are most likely to occupy A- site of perovskite structure (ABO<sub>3</sub>). The reactions below are likely to occur:



Since bismuth sodium titanate is perovskite structured, in which close packing consist of O<sup>2-</sup> and A-site ions, O<sub>i</sub>' and Ba<sub>i</sub>'' will increase the internal energy of BNT crystal. So reactions (1) and (2) seem hard to occur compared with the other two, so it can be concluded that the defect reactions mainly occurred in the BNBT system are (3) and (4).

Ba<sup>2+</sup> is more likely to substitute the ions whose radius is closer to Ba<sup>2+</sup>. So reaction (3) will occur in initial period. The V<sub>Na</sub>' will decrease the lattice density, so the lattice structure becomes incompact, which is favor for domain wall motion [11], so the relative permittivity increases. Meanwhile, Ba<sup>2+</sup> doping also leads to series of space charge center as we known, weak-bonded ions play an important role in dielectric loss, and the space charge centers can disorder the distribution of electric potential (shown in Fig. 3), which can increase the potential barrier and the migration of the ions are restrained, so the loss tangent declines.

When *x* is more than 0.06, ε<sub>r</sub> begins to decline, because Ba<sup>2+</sup> begins to replace Bi<sup>3+</sup>, which will create oxygen vacancies, when the content of Ba<sup>2+</sup> reach certain critical value. It has been known that oxygen vacancies are the main cause of wall domain clamping [12]. This clamping will restrain the macro-micro domain switching in some degree; this is the

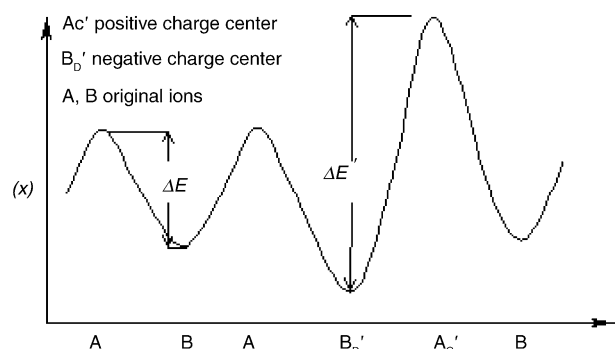


Fig. 3. Lattice potential energy pattern.

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