

# The variation of Curie temperature and dielectric relaxor behaviour in the nominal $(1-x)\text{BaTiO}_3-x\text{BiAlO}_3$ system

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**Abstract**  $\text{BiAlO}_3$  is a perovskite ferroelectric with a high Curie temperature above  $520^\circ\text{C}$ . However, it is difficult to prepare pure perovskite phase by the conventional method. In this experiment,  $\text{BaTiO}_3$  has been selected as host to incorporate  $\text{BiAlO}_3$ , and the nominal binary system of  $(1-x)\text{BaTiO}_3-x\text{BiAlO}_3$  has been investigated with regard to its Curie temperature ( $T_c$ ) and dielectric relax behaviors. It was found that the pure perovskite phase can be retained below  $x=0.08$ . However, the value of  $T_c$  in the system doesn't follow the normal Vegard's law, on the contrary, shows the decreasing trend with the increase of  $x$ . According to the compared experiments about  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  doping in  $\text{BaTiO}_3$ , it can be safely concluded that the combined substitution of  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  played the dominant role to decrease the  $T_c$  and increase the relaxor behavior in  $(1-x)\text{BaTiO}_3-x\text{BiAlO}_3$  system.

**Keywords** Ceramics · Defects · Dielectric properties · Microstructure

## 1 Introduction

There is an increasing demand for the environment friendly materials like lead-free ceramics for applications in piezoelectric device. In 2005, density functional theoretical studies on bismuth aluminate predicted that  $\text{BiAlO}_3$  could be a promising lead-free ferroelectrics with a polar rhombohedral system and a Curie temperature ( $T_c$ ) about 800 K [1]. Later,

the characterization of the  $\text{BiAlO}_3$  ceramics synthesized by the high-pressure method demonstrated that  $\text{BiAlO}_3$  is indeed a perovskite ferroelectric with a Curie temperature  $T_c > 520^\circ\text{C}$  [2, 3]. Especially, it was found that  $\text{BiAlO}_3$  has no structural phase transitions between  $-133$  and  $550^\circ\text{C}$  and the  $d_{33}$  value of  $25\text{--}28$  pC/N can be maintained until  $520^\circ\text{C}$ . It showed great potential as application in high temperature piezoelectric device. However,  $\text{BiAlO}_3$  could only be prepared by a high-pressure high-temperature technique and it would decompose above 820 K [4]. Thus, two main factors, the poor thermal stability and extreme synthetic conditions, have limited the practical usability of  $\text{BiAlO}_3$ .

It is well-known that lead-based relaxor ferroelectrics, such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN),  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZN), *etc.*, are difficult to be prepared by the conventional oxide mixing method [5, 6]. To stabilize the pure perovskite phase, addition of other ideal perovskite materials with simple crystal structure, such as  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$ , to these compounds to form solid solutions, is an effective method. So it was expected that this method can be extended to the preparation of pure  $\text{BiAlO}_3$  perovskite phase, meanwhile, the properties of both the host compound and  $\text{BiAlO}_3$  could be modified. In this way, many solid solutions, such as  $\text{BaTiO}_3\text{-BiAlO}_3$  [7],  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-BiAlO}_3$  [8],  $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-BiAlO}_3$  [9] and  $\text{PbTiO}_3\text{-BiAlO}_3$  [10], have been proposed. However, it should be noted that the Curie temperatures of these solid solutions strongly decrease with the increase of  $\text{BiAlO}_3$  content, even lower than that of the host compound. So this venue is unsuccessful in respect to developing high Curie temperature ferroelectrics.

As we know, the mixed ferroelectrics solid solutions, composed by two different ferroelectric crystals with similar structure, showed compositionally dependent ferroelectric parameters such as the Curie temperature  $T_c$  (or  $T_m$ ) corresponding to the maximum value of the dielectric

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permittivity  $\epsilon_m$ ), following a famous linear relationship of Vegard' rule [11],

$$T_c(x) = (1-x)T_c(0) + xT_c(1) \quad (1)$$

Where  $T_c(x)$  is the Curie temperature of the solid solution,  $T_c(0)$  and  $T_c(1)$  are the Curie temperature of two end members. Although this law is often broken and the theoretical backing needs to be further clarified, in some instances, it serves as a useful rule and also can be extended to the more complicated system with multiplicity of phases, such as (1- $x$ )PNN-  $x$ PZT [12], (1- $x$ )PZN-  $x$ PZT [13] and (1- $x$ )KNN-  $x$ LiNbO<sub>3</sub> [14].

So there aroused the suspicions that what is the main reason responsible for the large deviation of Curie temperature from Vegard's law in the reported BiAlO<sub>3</sub> based system [7–10]. It is believed that the Curie temperature reflects the stability of oxygen octahedron, which can be influenced by the occupation state of A or B ions in ABO<sub>3</sub> perovskite structure [15]. Thus, we speculate that both the substitutions of Bi<sup>3+</sup> at A site and Al<sup>3+</sup> at B site can adjust the Curie temperature of solid solution. In order to verify this speculation, we selected classical ferroelectric BaTiO<sub>3</sub> as host material to incorporate BiAlO<sub>3</sub>. For comparison, Al<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> were selected independently to add to BaTiO<sub>3</sub> to evaluate the doping effect on Curie temperature and relaxor behaviors.

## 2 Experimental

Three series of ceramic specimens, (1- $x$ )BaTiO<sub>3</sub>- $x$ BiAlO<sub>3</sub> ( $x=0, 0.02, 0.05, 0.08, 0.10, 0.12$ , hereafter designated as BA0, BA2, BA5, BA8, BA10 and BA12, respectively), BaTiO<sub>3</sub>- $y$ Bi<sub>2</sub>O<sub>3</sub> ( $y=0.002, 0.005, 0.008$  and  $0.010$ , hereafter designated as Bi2, Bi5, Bi8 and Bi10, respectively) and BaTiO<sub>3</sub>- $z$ Al<sub>2</sub>O<sub>3</sub> ( $z=0.002, 0.005, 0.008$  and  $0.010$ , hereafter designated as Al2, Al5, Al8 and Al10, respectively), were synthesized using the conventional solid state reaction method. Stoichiometric amount of analytical grade BaCO<sub>3</sub> (99.0%), TiO<sub>2</sub> (99.0%), Bi<sub>2</sub>O<sub>3</sub> (99.0%), and Al<sub>2</sub>O<sub>3</sub> (99.0%) were thoroughly mixed and calcined at 1100°C for 4 h. The calcined powders were pressed into disk samples with a diameter of 11.5 mm and then sintered in closed crucibles at 1300°C for 2 h. The crystal structures of the samples were recorded on x-ray diffractometer (XRD) (model Bruker 8D Advance, Karlsruhe, Germany) using Cu  $K\alpha$  radiation. The dielectric property and its dependence on temperature were measured using a LCR analyzer (model E4980A; Agilent Technologies, Santa Clara, CA) with an automated temperature controller.

## 3 Results and discussion

Figure 1 shows the XRD patterns of (1- $x$ )BaTiO<sub>3</sub>- $x$ BiAlO<sub>3</sub> ceramics. All the prominent peaks in this figure can be indexed with BaTiO<sub>3</sub> type perovskite structure. Impurity peak appeared at  $2\theta=28^\circ$  for  $x\geq 0.08$ , which arises from the formation of Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub>-type secondary phase [16]. Lattice parameters were obtained by least-squares refinement of the peak positions of 6–7 prominent Bragg peaks, and the results are shown in Fig. 2. For  $x=0.00$ , i.e., BaTiO<sub>3</sub>, the lattice parameters were refined as  $a=0.3994$  nm and  $c=0.4034$  nm which are very close to the values found in JCPDF card No.83-1880 (e.g.,  $a=0.3994$  nm and  $c=0.4033$  nm). The  $c$  parameter decreases continuously on increasing  $x$  while the  $a$  parameter increases until  $x$  up to 0.08, beyond which it shows decreasing trend. The appearance of turn point at 0.08 can be attributed to the formation of second phase. Thereby, the single phase formation is possible under conventional synthesis conditions only in the low composition range of  $0\leq x\leq 0.08$  [7].

The temperature dependence of the dielectric constant of the BaTiO<sub>3</sub>-BiAlO<sub>3</sub> nominal binary system at different frequency is shown in Fig. 3. For pure BaTiO<sub>3</sub>, the dielectric peak appears relatively sharp at  $T_c=120^\circ\text{C}$ , similar to that reported in the textbook. An increasing broadness of the dielectric peak with frequency dispersion can be observed clearly with increasing  $x$ , indicating the enhancement of relaxor features. It should be noted that  $T_c$  shifts to lower temperature with increasing  $x$ , referring to the large deviation from Vegard's Law. As reported, both BaTiO<sub>3</sub> and BiAlO<sub>3</sub> belong to the perovskite phase, and the  $T_c$  of BaTiO<sub>3</sub> is about 120°C while that of BiAlO<sub>3</sub> is near 520°C.

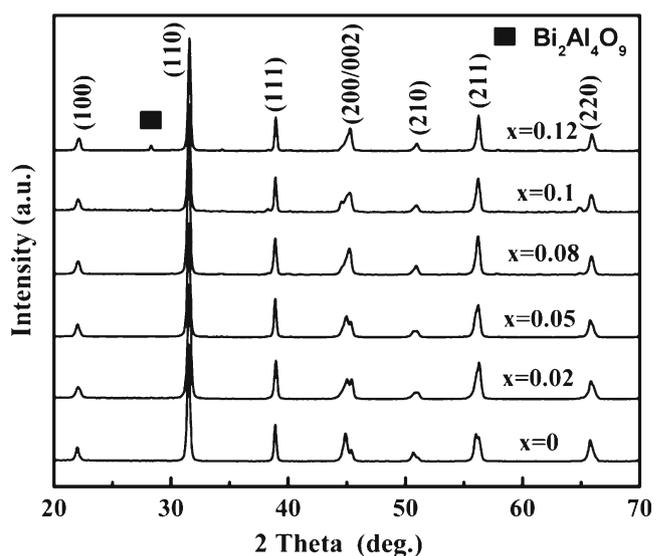
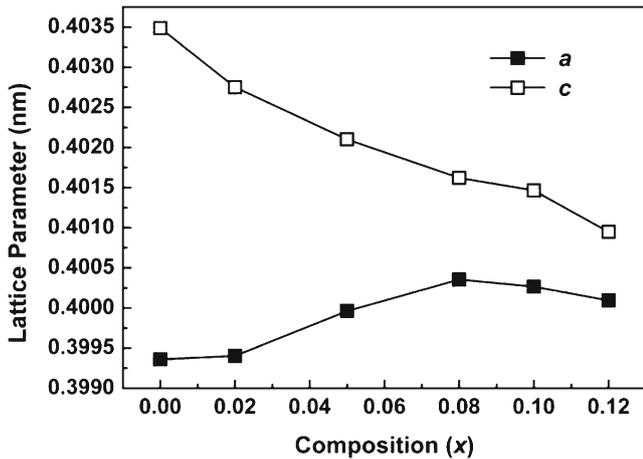


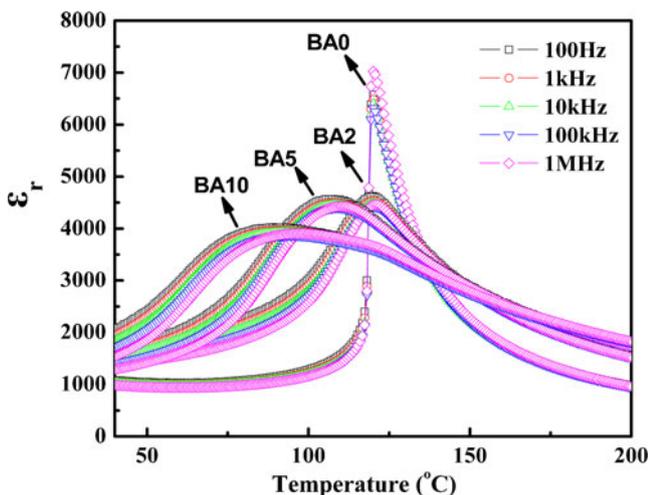
Fig. 1 XRD patterns of (1- $x$ )BaTiO<sub>3</sub>- $x$ BiAlO<sub>3</sub> ceramics recorded at room temperature



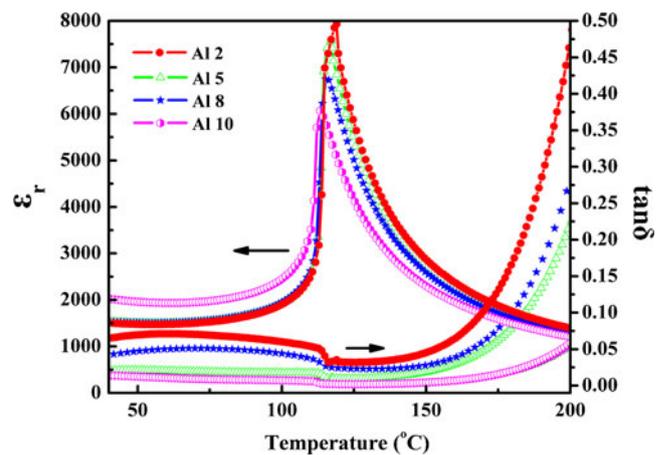
**Fig. 2** Variation of lattice parameters of  $(1-x)\text{BaTiO}_3-x\text{BiAlO}_3$  ceramics

So if Vegard’s Law works well, the introduction of  $\text{BiAlO}_3$  to  $\text{BaTiO}_3$  should increase the  $T_c$ . However, the experimental results show the converse trend. We speculate that this deviation should be attributed to the substitute effect of Bi and Al in host  $\text{BaTiO}_3$ .

In order to further clarify the mechanism which results in decreasing Curie temperature of  $\text{BaTiO}_3\text{-BiAlO}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3$  were selected independently to dope with  $\text{BaTiO}_3$  system. In the experimental substitution content range, both  $\text{BaTiO}_3\text{-Bi}_2\text{O}_3$  and  $\text{BaTiO}_3\text{-Al}_2\text{O}_3$  systems show the pure perovskite structure and no detected second phase can be found, indicating that Al and Bi entered the  $\text{BaTiO}_3$  sublattice. These results are consistent with the report in literatures [17, 18]. Figure 4 shows the temperature dependences of the dielectric constant and the loss tangent of the  $\text{Al}_2\text{O}_3$  doped  $\text{BaTiO}_3$  systems. As seen in Fig. 4, both  $\epsilon_m$  and  $T_c$  show the decreasing trend with increasing  $\text{Al}_2\text{O}_3$  content.



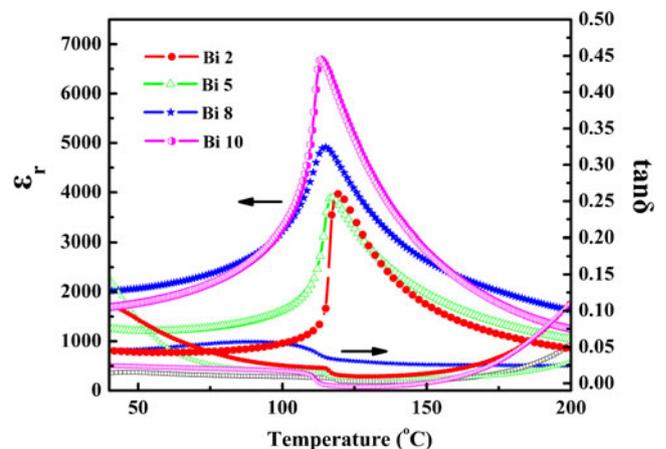
**Fig. 3** (Color online) Temperature dependence of the dielectric constant for  $\text{BaTiO}_3\text{-BiAlO}_3$  nominal binary system at different frequency



**Fig. 4** (Color online) Temperature dependence of the dielectric constant and the loss tangent for  $\text{Al}_2\text{O}_3$  doped  $\text{BaTiO}_3$  system at 1 kHz

According to the crystal data [19], the ionic radii of  $\text{Al}^{3+}$  and  $\text{Ti}^{4+}$  with six coordination are 0.530 and 0.605 Å, respectively. So  $\text{Al}^{3+}$  ions likely replace  $\text{Ti}^{4+}$  ions in  $\text{BaTiO}_3$ , which leads to the creation of oxygen vacancies due to the imbalance of valence. The oxygen vacancies can pin the movement of the ferroelectric domain walls, resulting in a decrease of  $\epsilon_m$  [15]. In addition, for the reason that the bond energy of  $\text{Al-O}$  (512 kJ/mol) is lower than that of  $\text{Ti-O}$  (662 kJ/mol), it is reasonable to deduce that the substitutions of  $\text{Ti}^{4+}$  by  $\text{Al}^{3+}$  can decrease the stability of the B-site ions in the center of  $\text{BO}_6$  octahedra and thus decrease Curie temperature  $T_c$ . This phenomenon can also be seen in other doped ferroelectric systems [20].

Figure 5 shows the temperature dependence of the dielectric constant and the loss tangent of the  $\text{Bi}_2\text{O}_3$  doped  $\text{BaTiO}_3$  system. It can be found that addition of  $\text{Bi}^{3+}$  reduced  $T_c$ , whereas at the same time increased  $\epsilon_m$ . The doped Bismuth ions normally occupy the twelve-fold coordinated crystallographic Ba sites in  $\text{BaTiO}_3$  because of their similar



**Fig. 5** (Color online) Temperature dependence of the dielectric constant and the loss tangent for  $\text{Bi}_2\text{O}_3$  doped  $\text{BaTiO}_3$  system at 1 kHz

ionic radius and similar electronegativity. To compensate the charge imbalance aroused from the substitution of the A-site  $\text{Ba}^{2+}$  by  $\text{Bi}^{3+}$  ions, the off-centered  $\text{Bi}^{3+}$  ions and  $V''_A$  formed  $\text{Bi}^{3+} - V''_A$  dipoles and thus set up a local electric field, which resulted in the decrease of Curie temperature [18]. The increase of  $\epsilon_m$  by  $\text{Bi}_2\text{O}_3$  addition may originate from the special electronic structure of  $\text{Bi}^{3+}$  [10]. Like  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$  ion has the lone  $6s^2$  pair electrons, which can strongly hybridize with O  $2p$  states, whereas the interaction between Ba  $5p$  and O  $2p$  is completely ionic. The Bi-O bonding interaction, and the smaller ionic radius of  $\text{Bi}^{3+}$  (1.11 Å) compared with  $\text{Ba}^{2+}$  (1.60 Å) [19], lead to a large strain that increases the dielectric constant in  $\text{BaTiO}_3\text{-Bi}_2\text{O}_3$  system.

According to the compared results in the  $\text{BaTiO}_3\text{-Bi}_2\text{O}_3$  and  $\text{BaTiO}_3\text{-Al}_2\text{O}_3$  systems, it can be safely concluded that the combined substitution of  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  induced the decrease of Curie temperature in  $(1-x)\text{BaTiO}_3\text{-xBiAlO}_3$  system, which is responsible for the deviation from Vegard's law. Moreover, as seen in Fig. 3, the relaxor features are enhanced in  $(1-x)\text{BaTiO}_3\text{-xBiAlO}_3$  system. In general, relaxor behavior appears when at least two cations occupy the same crystallographic site in  $\text{ABO}_3$  structure, either A or B, which gives rise to random fields that impede the development of long-range polar ordering. The substitution of  $\text{Bi}^{3+}$  for  $\text{Ba}^{2+}$  on the A site and  $\text{Al}^{3+}$  for  $\text{Ti}^{4+}$  on the B site disrupted the long-range dipolar interaction of  $\text{BaTiO}_3$ , resulting in the increase of relaxor behavior.

#### 4 Conclusions

In conclusion, the solid solution of  $\text{BaTiO}_3\text{-BiAlO}_3$  has been prepared in this work. The Curie temperature of the nominal binary system shows the large deviation from the prediction by Vegard's law. Due to the doping effects, the coupled substitutions of  $\text{Bi}^{3+}$  for  $\text{Ba}^{2+}$  on the A site and  $\text{Al}^{3+}$  for  $\text{Ti}^{4+}$  on the B sites play the dominant role to decrease  $T_c$ . Moreover, the heterovalent substitutions of  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  enhance the relaxor behavior of  $\text{BaTiO}_3$ , which can be attributed to the disruption of long-range dipolar interaction due to compositional disorder on both A and B site.

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