

Dielectric properties and relaxation of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--BaNb}_2\text{O}_6$ lead-free ceramics

CHANG-RONG ZHOU* and XIN-YU LIU

Department of Information Material Science and Engineering, Guilin University of Electronic Technology, Guilin Guangxi 541004, China

Also at School of Material Science and Engineering, Central South University, Changsha Hunan 410083, China

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Abstract. A new member of lead-free piezoelectric ceramics of the BNT-based group, $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}x\text{BaNb}_2\text{O}_6$, was prepared by conventional solid state reaction and its dielectric properties and relaxation was investigated. X-ray diffraction showed that BaNb_2O_6 diffused into the lattice of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ to form a solid solution with perovskite-type structure. A diffuse character was proved by the linear fitting of the modified Curie–Weiss law. The temperature dependence of dielectric constant at different frequencies revealed that the solid solution exhibited relaxor characteristics different from classic relaxor ferroelectrics. The samples with $x = 0.002$ and 0.006 exhibited obvious relaxor characteristics near the low temperature dielectric abnormal peak, T_f , and the samples with $x = 0.010$ and 0.014 exhibited obvious relaxor characteristics between room temperature and T_f . The mechanism of relaxor behaviour was also discussed according to the macro-domain to micro-domain transition theory.

Keywords. Diffusion phase transitions; dielectric properties; relaxor characteristics.

1. Introduction

Relaxor ferroelectrics are characterized by their broad dielectric transition, known as diffuse phase transition with frequency dispersion (Smolenski 1970; Isupov 1989). These materials have great scope for applications such as a high capacitance capacitor, hysteresis free actuator and high performance sensor. It is generally accepted that the relaxor phenomenon is related to the micropolar regions induced by B-site substitution, and the atomic radii and chemical valence differences of ions will often affect the relaxor effect. But until now, the main focus had been on B-sites lead-based complex perovskite relaxors such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and derived compounds (Yamashita 1994; Yuan 2005). Recently, lead-free alternate materials are increasingly in demand because of their environmental friendly applications.

Bismuth sodium titanate, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (abbreviated as BNT), discovered by Smolenski *et al* in 1960, is one of the important ferroelectrics with perovskite structure (Smolenski *et al* 1961). Moreover, it is an A-site substituted distorted perovskite compound (ABO_3) which is rarer than the B-site one. Its dielectric properties reveal two anomalies. The well known corresponds to the ferroelectric–paraelectric transition whose Curie temperature

is 320°C . The other one is frequency dependant and is not yet well understood, since no structural transition is observed. Although most investigations have been concentrated on the modifications of BNT for applications such as piezoelectric and pyroelectric devices, this material is considered to be a good candidate for a high temperature relaxor. Moreover, BaNb_2O_6 (abbreviated as BN)-based compounds are receiving great attention as a new ferroelectric tungsten bronze niobate material (Sakamoto and Mizuno 2006). Therefore, in this work, we have studied the dielectric properties and relaxation behaviour of $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}x\text{BaNb}_2\text{O}_6$ (abbreviated as BNT–BN) ceramics.

2. Experimental

A conventional ceramic fabrication technique was adopted to prepare BNT–BN ceramics with $x = 0.002$, 0.006 , 0.010 and 0.014 . Reagent grade oxide or carbonate powders of Bi_2O_3 , TiO_2 , Nb_2O_5 , BaCO_3 and Na_2CO_3 were used as starting materials. The powders were ball-milled for 12 h and calcined at 900°C for 2 h. After calcination, the mixture was ball-milled for 24 h, dried and granulated with PVA as a binder. The granulated powders were pressed into disc with diameter, 18 mm and thickness, 1.2 mm. The compacted discs were sintered at 1190°C for 2 h in air. Silver paste was fired on both faces of the discs at 650°C as electrodes.

*Author for correspondence (zcr750320@yahoo.com.cn)

X-ray diffraction patterns were taken on a Bruker D8-Advance X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and graphite monochromator. The temperature dependence of dielectric constant was investigated using an LCR meter (TH2818) in the temperature range 20–410°C.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of BNT–BN ceramics in the 2θ range of 20–80°. It can be seen from figure 1 that a solid solution with perovskite-type structure has been formed for all samples without any detectable impurity phases. The lattice and angle parameters were indexed to be a rhombohedral symmetry structure, implying that BN diffused into the BNT lattice and does not cause an obvious change in the phase structure.

Figure 2 shows the temperature dependence of dielectric constants, ϵ_r , of BNT–BN ceramics as a function of x at 1 kHz. Two abnormal dielectric peaks have been observed, which originated from phase transition from ferroelectric to anti-ferroelectric (at T_f) and anti-ferroelectric to paraelectric phase (at T_m), and is consistent with the previous reports of NBT (Yangfang *et al* 2005), NBT–NN (Li *et al* 2004), NBT–PT (Said and Mercurio 2001) and lead-free ceramics system. It was found that the ϵ_r -temperature curves of the compositions exhibit a strongly diffused phase transition characteristics with broad dielectric peaks. A modified Curie–Weiss law is used to explain the dielectric behaviour of complex ferroelectrics with diffuse phase transition, which is described as follows (Fulcher 1925; Tang *et al* 2004)

$$\frac{1}{\epsilon} - \frac{1}{\epsilon_m} = C(T - T_m)^\gamma,$$

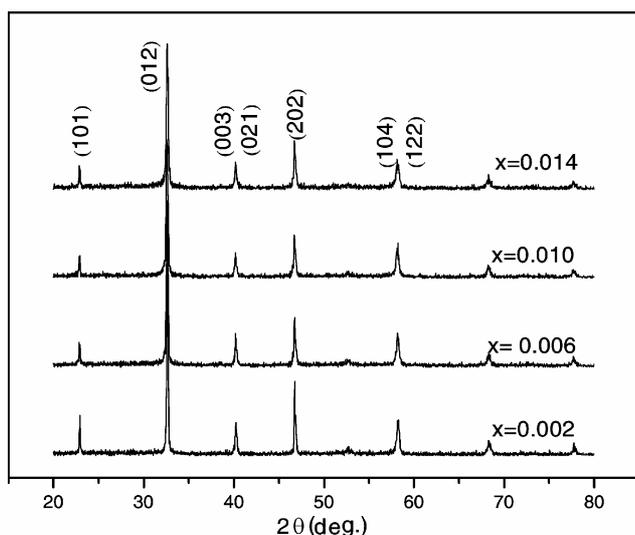


Figure 1. XRD pattern of BNT–BN ceramics sintered at 1190°C for 2 h.

where γ and C are assumed to be constants, the γ value is between 1 and 2. When $\gamma = 1$, the materials with this type of phase transition are called normal ferroelectrics and when $1 < \gamma < 2$, they are called relaxor ferroelectrics; whereas $\gamma = 2$ corresponds to a so-called ‘complete’ diffuse phase. Figure 3 shows the plot of $\ln(1/\epsilon - 1/\epsilon_m)$ as a function of $\ln(T - T_m)$ for all ceramics samples at 1 kHz. A linear relationship was obtained by linear fitting to the experimental data. The slope of the fitting curves was used to determine the γ value. The γ value varies from 1.33 to 1.73, indicating that the BNT–BN solid solution showing more diffuse phase transition behaviour with increasing doping of BN. It is generally accepted that more the cations co-occupy the same lattice of unit cell, the more the chemical composition and crystal structure is homogeneous at the nanometer scale, and the diffuse characteristics is more obvious (Smolenski 1970). So it is considered that the higher amount of Ba^{2+} ions substituting $(\text{Bi}_{1/2}\text{Na}_{1/2})^{2+}$ ions and Nb^{5+} ions substituting Ti^{4+} ions distorts the unit cell, changes the dipolar moment, induces strain in the lattice and may induce diffuse phase transition characteristics.

The temperature dependence of dielectric constant, ϵ_r and dielectric loss, $\tan \delta$, of BNT–BN samples under various frequencies is shown in figure 4. The samples of BNT–BN with $x = 0.002$ and 0.006 indicate obvious relaxor characteristics near T_f having strong frequency dependence. The frequency dependence vanishes when the temperature is higher or lower than T_f . The phenomenon is different from classic relaxor characteristics. The relaxor behaviour can be induced by many reasons such as the macro-domain to micro-domain transition theory (Yao *et al* 1983), local compositional fluctuation (Setter and Cross 1983), superparaelectric (Cross 1987) and dipolar glass model (Viehland 1990). According to the macro-domain to micro-domain transition theory, with the temperature

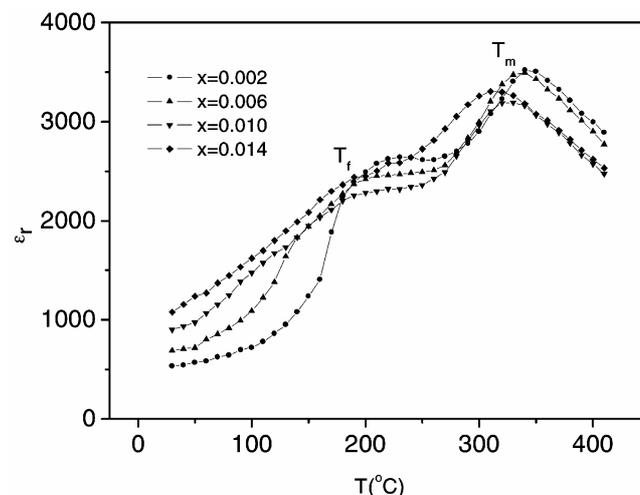


Figure 2. Temperature dependence of dielectric constant, ϵ_r , of BNT–BN ceramics at 1 kHz.

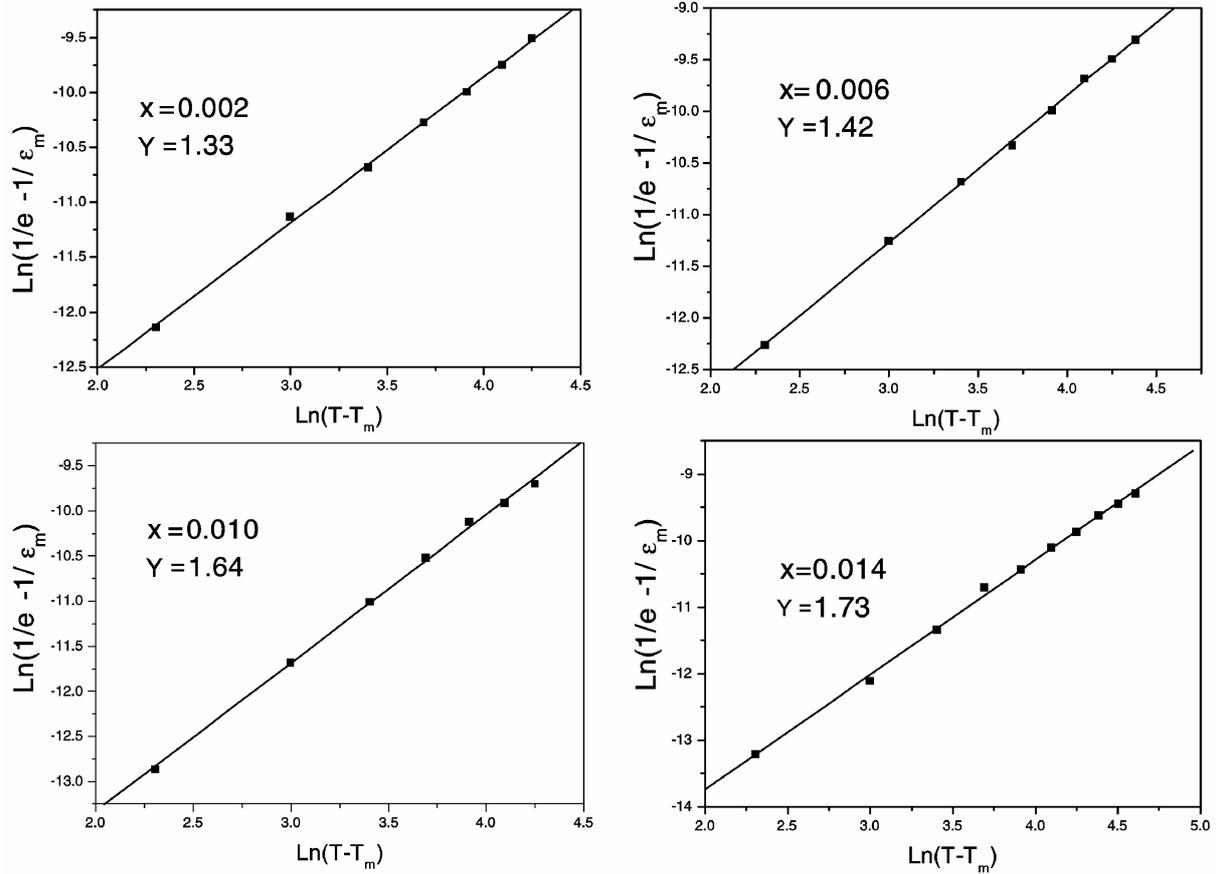


Figure 3. $\text{Ln}(1/\epsilon - 1/\epsilon_m)$ as a function of $\text{Ln}(T - T_m)$ of BNT–BN ceramics at 1 kHz.

increasing, the frequency dependency appears near T_f because of the transition from macro-domains to micro-domains. Subsequently, with the temperature further increasing, the frequency dependence disappears for micro-domains shift to polar micro-regions and anti-ferroelectrics macro-domains. The above results can also be explained by the dielectrics loss–temperature curves. The dielectric loss mainly comes from the domain walls in BNT-based ferroelectrics ceramics, and with the increasing temperature, macro-domains shift to micro-domain and the domain walls sharply increase, which leads to dramatic increase of dielectric loss. With the temperature further increasing, micro-domains change to polar micro-regions and anti-ferroelectrics macro-domains. And domain-walls decrease results in rapid decrease in dielectric loss, which leads to a distinguished peak in dielectric loss–temperature curve corresponding to T_f .

Moreover, it can also be found from figure 4 that the samples of BNT–BN with $x = 0.010$ and 0.014 , revealed obvious relaxor characteristics between room temperature and T_f , which is completely different from the samples of BNT–BN with $x = 0.002$ and 0.006 . The results contribute to the BN addition because Nb^{5+} ions are likely to enter B-sites substituted Ti^{4+} ions in the ABO_3 -type BNT

compounds, and A-sites vacancies are created to compensate the charge equilibrium. The A-site vacancies deteriorate the coupling degree of oxygen octahedron and lower stabilization of macro-domains. Therefore, some macro-domains transform to micro-domains at lower temperature, which results in frequency dependency between room and T_f . That can also be explained by dielectric loss–temperature curves which show modest peaks because some macro-domains transformed to micro-domains at lower temperature. Consequently, the increased tendency of domain walls and dielectric loss decrease at T_f .

4. Conclusions

The dielectric properties and relaxation of $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{BaNb}_2\text{O}_6$ ceramics were investigated. X-ray diffraction showed that all samples form a solid solution with perovskite-type structure. The temperature dependence of dielectric constant revealed that all samples exhibited diffuse phase transition character and the diffuse character was more obvious with increasing concentration of BaNb_2O_6 . The temperature dependence of dielectric constant at different frequencies revealed that the solid

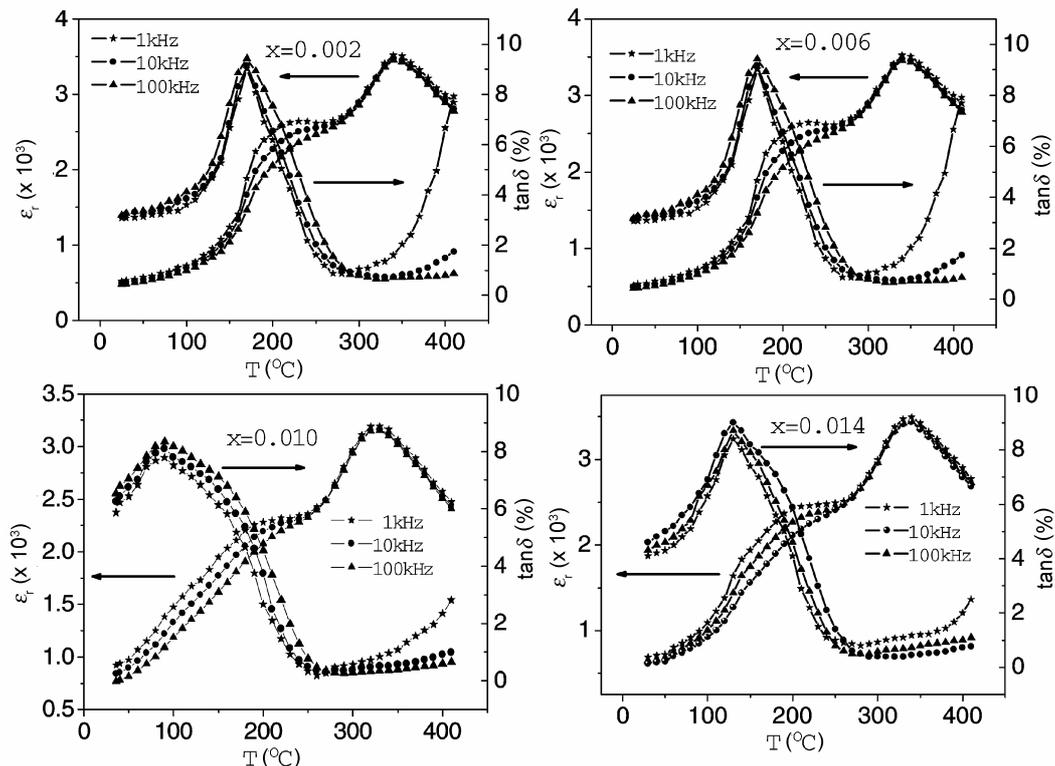


Figure 4. The temperature dependence of dielectric constant, ϵ_r and dielectric loss, $\tan \delta$, of BNT–BN samples at frequencies of 1, 10 and 100 kHz.

solution exhibited different dielectric relaxor characteristics. The samples of BNT–BN with $x = 0.002$ and 0.006 exhibited obvious relaxor characteristics near the low temperature dielectric abnormal peak, T_F , and the samples of BNT–BN with $x = 0.010$ and 0.014 exhibited obvious relaxor characteristics between room temperature and T_F .

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