

Dielectric Properties and Relaxation of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-LiNbO}_3$ Lead-Free Ceramics

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Abstract— A new member of lead-free piezoelectric ceramics of the BNT-based group, $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{LiNbO}_3$ ($x=0.002, 0.004, 0.01, 0.014$), was prepared by conventional solid state reaction and its dielectric properties and relaxation was investigated. X-ray diffraction showed that LiNbO_3 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.

Key words: Diffusion Phase Transitions; Dielectric Properties; Relaxor Characteristics

I. 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 Smolensky 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 $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{LiNbO}_3$ (abbreviated as BNT–LN) ceramics.

II. EXPERIMENTAL

A conventional ceramic fabrication technique was adopted to prepare BNT–BN ceramics with $x = 0.002, 0.006, 0.010, \text{ and } 0.014$. 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, 10mm 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. 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 $20\text{--}410^\circ\text{C}$.

III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of BNT–LN ceramics in the 2θ range of $20\text{--}80^\circ$. 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 LN 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–LN 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)

$$1/\epsilon - 1/\epsilon_m = C(T - T_m)^{-\nu}$$

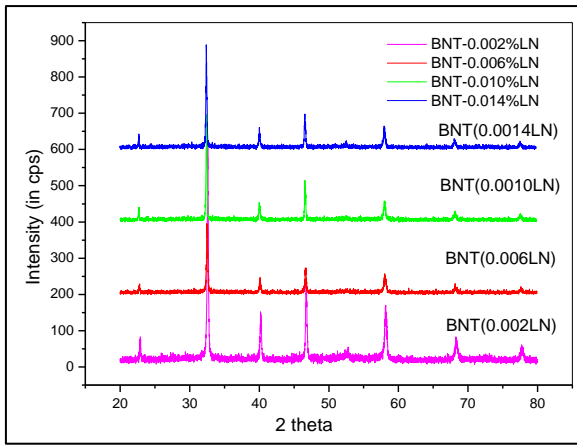


Fig. 1: Shows the X-Ray Diffraction Patterns of Pure BNT and BNT-LN in the 2θ Range Of 20–80°.

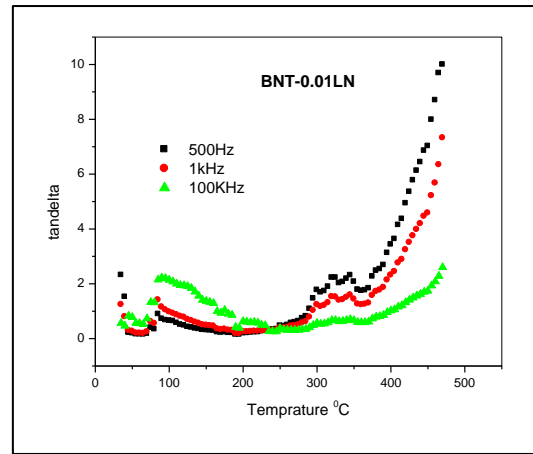


Fig. 2: The Temperature Dependence Of Dielectric Constant, ϵ_r And Dielectric Loss, $\tan\delta$, Of BNT-LN Samples At Frequencies Of 500Hz, 1kHz And 1000 KHz.

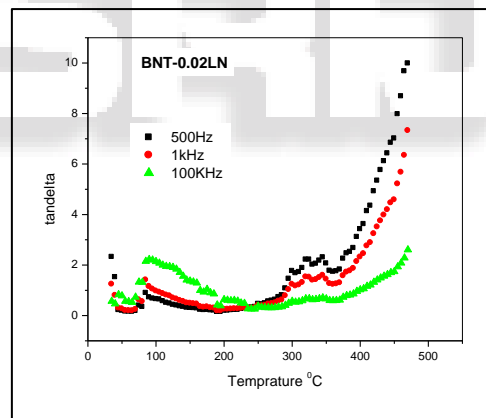
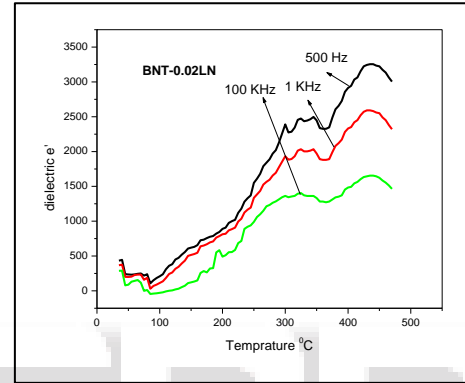
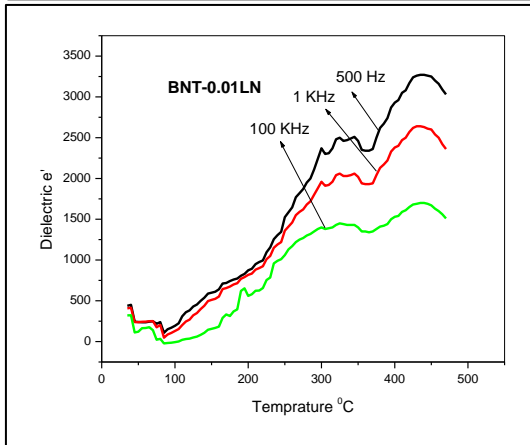
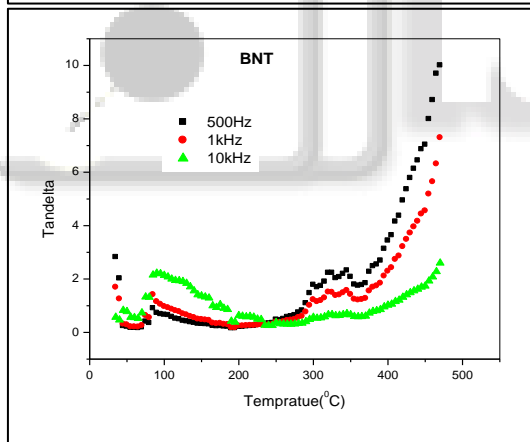
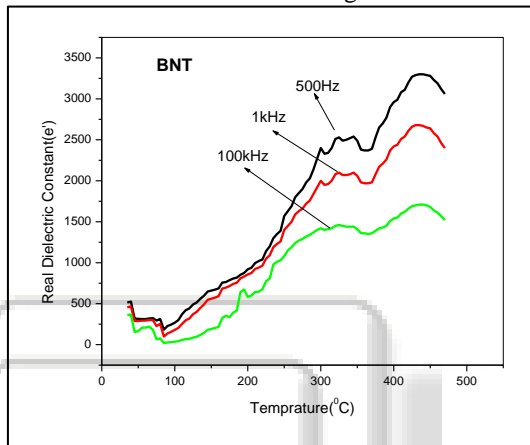
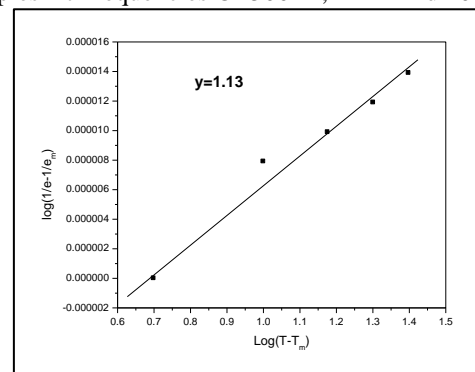


Fig. 3: The Temperature Dependence Of Dielectric Constant, ϵ_r And Dielectric Loss, $\tan\Delta$, Of BNT-BN Samples At Frequencies Of 500Hz, 1kHz And 100 KHz.



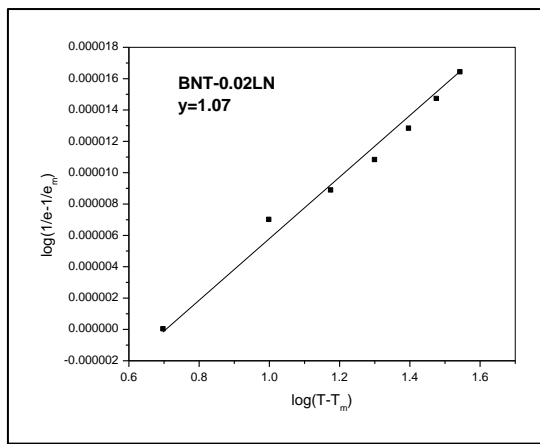


Fig. 4: $\ln(1/\epsilon - 1/\epsilon_m)$ as a function of $\ln(T - T_m)$ of BNT-LN ceramics at 1 kHz.

Increasing, the frequency dependency appears near T_f because of the transition from macro-domains to microdomains. Subsequently, with the temperature further increasing, the frequency dependence disappears for microdomains shift to polar micro-regions and antiferroelectrics 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 antiferroelectrics 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-LN 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 LN 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 macrodomains 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 microdomains at lower temperature. Consequently, the increased tendency of domain walls and dielectric loss decrease at T_f .

IV. CONCLUSIONS

The dielectric properties and relaxation of $(1-x)Bi_{0.5}Na_{0.5}TiO_3-xLiNbO_3$ 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 $LiNbO_3$.

The temperature dependence of dielectric constant at different frequencies revealed that the solid solution exhibited different dielectric relaxor characteristics. The samples of BNT-LN 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-LN with $x = 0.010$ and 0.014 exhibited obvious relaxor characteristics between room temperature and T_f .

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