Crossover from a nearly constant loss to a superlinear power-law behavior in Mn-doped Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$−PbTiO$_3$ ferroelectrics

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Mn-doped Bi(Mg$_{1/2}$Ti$_{1/2}$)−PbTiO$_3$ disordered ferroelectric ceramics were studied under ac electric fields and a crossover from a nearly constant loss to a superlinear power-law behavior was observed. Our results confirmed that the nearly constant loss behavior also exists in disordered ferroelectrics. The exponent of the superlinear power-law was found to be temperature dependent. Such a behavior was related to the local movements of oxygen vacancies. © *2010 American Institute of Physics.*
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I. INTRODUCTION

The frequency dependent ac conductivities of a wide variety of materials satisfy the following sublinear power-law behavior:

$$\sigma(2\pi f) = \sigma(0) + A(2\pi f)^s, \qquad (1)$$

where $\sigma(0)$ is the dc conductivity and s is a fractional exponent of frequency f. Both $\sigma(0)$ and A are thermally activated quantities. This type of behavior has been called the "universal dielectric response" (UDR) by Jonscher *et al.*[1,2] At relatively low temperatures or high frequencies, a different power-law behavior has been found valid for a diverse range of materials[3–7]

$$\sigma(2\pi f) = B(2\pi f)^n, \qquad (2)$$

where n is very close to unity and B is not thermally activated. The exponent $n=1$ implies a negligible frequency dependence of the imaginary part of dielectric permittivity through the relation $\varepsilon''(\omega) = \sigma'(f)/2\pi f$. Nowick *et al.*[3] named this behavior as the "nearly constant loss" (NCL).

According to existing investigations on ionic conductors,[3–6] polymers,[7] polaronic conductors, and amorphous semiconductors,[8,9] the NCL response appears to be a universal feature in highly disordered materials. Up to now, however, interpretations of the NCL behavior remain speculative. Our recent study on polymers shows that the NCL is more likely caused by the vibrational relaxation of the polymer chains.[7] Recently, Lunkenheimer and Loidl[10] have studied the broadband [up to terahertz (THz)] dielectric responses of different disordered materials, "including molecular and ionic liquids, supercooled liquids, glasses, ionic conductors, and doped semiconductors." They claimed that a new universality, where Jonscher's UDR (characterized by a sublinear power-law at intermediate frequencies) is

followed by a superlinear power-law (SLPL) with an exponent smaller than 2, is valid for most of the disordered materials.

It seems that NCL is a mediate behavior between UDR and SLPL.[10] However, there has been no reported work on the relationship among UDR, NCL, and SLPL. Experimentally, the relatively "simple" NCL behavior is best observed in highly disordered systems. But as the dopant and/or defect concentration is lowered, the ac response becomes more complex.[11] The theoretical details are somewhat unclear. There are questions of how the exponent varies with temperature or frequency and what the limiting value of the exponent is. It is worthy to be noted that the UDR response has already been found in triglycine sulfate ferroelectric crystals.[12] Unlike UDR, NCL has not yet been found in ferroelectrics though it has been reported in a wide variety of disordered materials. In the present work, we present the experimental evidence of a NCL behavior below 273K in lightly Mn-doped Bi(Mg$_{1/2}$Ti$_{1/2}$)−PbTiO$_3$ (BMT–PT) ferroelectric ceramics with a perovskite structure. This is an important result demonstrating the coexistence of NCL and SLPL-like behaviors in a disordered ferroelectric system.

II. EXPERIMENTAL

Because of the small ionic size of Bi^{3+} on the A-site, which makes the Bi-based ABO$_3$ perovskite structure unstable, pure BMT cannot be synthesized under the normal atmospheric pressure and a high pressure technique is required.[13] Recently, by introducing polyethylene glycol (PEG) to the conventional solid state reaction process, we have successfully synthesized Pb- and Bi-based relaxor-type ferroelectrics.[14–17] It has been found that PEG interacts with Bi in a way aiding the formation of the perovskite phase. The compounds of BMT–PT with a composition at the morphotropic phase boundary at $x=0.38$ were selected. The detailed processing conditions for the synthesis of BMT–PT ceramics can be found elsewhere.[15] For the measurement of dielectric properties, silver pastes were painted onto both sides of pel-

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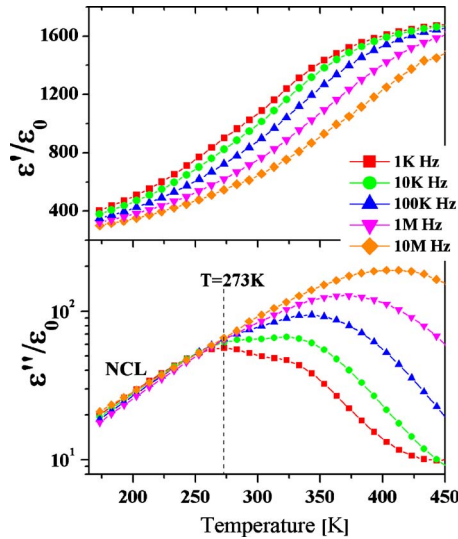b)Author to whom correspondence should be addressed. Electronic address: yuushu@gmail.com.

FIG. 1. (Color online) Temperature dependence of the relative dielectric permittivity of Mn-doped BMT–PT ferroelectric ceramics at various frequencies.
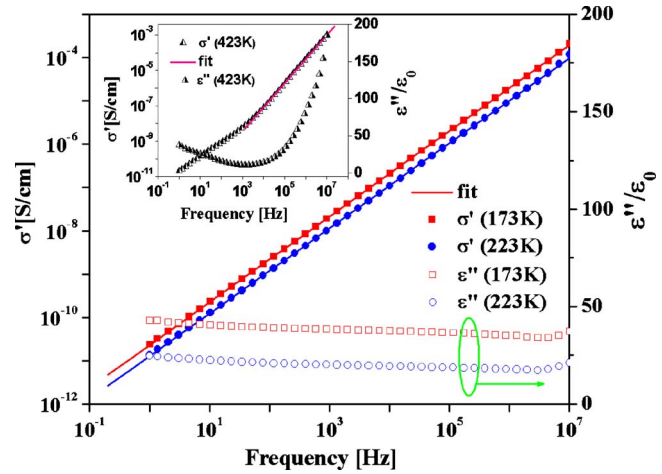

FIG. 2. (Color online) Frequency dependence of the conductivity and the imaginary part of the relative dielectric permittivity at selected temperatures for Mn-doped BMT–PT ferroelectric ceramics. Inset shows the high temperature behavior.

lets as electrodes. The dielectric responses of the ceramics were measured as a function of temperature using a frequency-response analyzer (Novocontrol Alpha-analyzer, Germany) and a LCR meter (HP4284A, Hewlett-Packard, CA).

III. RESULTS AND DISCUSSION

The temperature dependence of the relative dielectric permittivity of Mn-doped BMT–PT at various frequencies is shown in Fig. 1. The measurement was taken over a temperature range of 175–450 K, which is far below its Curie temperature $T_C(\sim 694$ K).[18] Two regions can be easily identified with the boundary located at around 273 K. The imaginary part of dielectric permittivity ε'' in the low temperature region (below 273 K) is almost independent of frequency, reflecting a genuine NCL behavior. In the high temperature region (above 273 K) it becomes quite dispersed with frequency. Similar behaviors cannot be observed in pure BMT–PT ferroelectric ceramics, where the dielectric permittivity increases monotonously over the entire temperatures range (175–450 K) investigated with a weak frequency dependence. These results imply that the NCL response and dielectric dispersion are mainly due to the doping of Mn.

The frequency dependence of the ac conductivity and the imaginary part of dielectric permittivity of Mn-doped BMT–PT at selected temperatures of 173 and 223 K are shown in Fig. 2. It can be observed that experimental conductivity at a low temperature exhibits a linear frequency dependence [with an exponent $n \approx 1$ following Eq. (2)] and therefore a negligible frequency dependence of ε'', an unambiguous NCL behavior. The frequency dependence of σ' and ε'' of Mn-doped BMT–PT at 423 K is shown as the inset of Fig. 2. It can be seen that, at an elevated temperature, ε'' displays a strong frequency dependence, indicating the disappearance of an NCL behavior. By fitting to Eq. (2), the exponent n and coefficient B can be obtained and their temperature dependence is shown in Fig. 3 and its inset. Two

regions can be clearly identified. Below 273 K, the exponent n reaches a plateau value close to 1, while at a high temperature well above 273 K, n increases linearly with temperature leading to a SLPL. This behavior is quite different from that of ionic conducting glasses, where n increases toward the limiting value of 1 as the temperature is decreased.[3] For instance, with decreasing temperature, n of $CeO_2:Gd_2O_3$ ceramics increases toward a low temperature plateau value of 1 from the high temperature plateau value of 0.6.[3] In the present case and within the experimental window, no limiting value for n in the high temperature region can be observed for Mn-doped BMT–PT.

As seen from the inset of Fig. 3, the coefficient B is almost temperature independent below 273 K, a typical behavior of NCL, while it shows a strong thermally activated behavior in the SLPL region. To determinate the energy barrier associated with the SLPL process, the temperature dependence of conductivity $\sigma'(T)$ at different frequencies is plotted in Fig. 4. A relaxation peak can be clearly seen in $\sigma'(T)$. It is noted that the peak temperature shifts to higher values with increasing measurement frequencies. By using an Arrhenius expression[19]
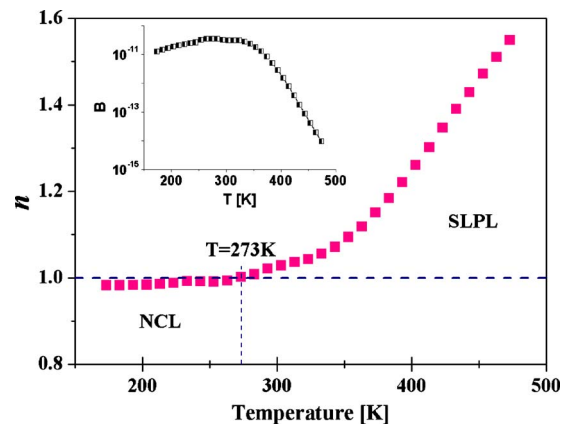

FIG. 3. (Color online) Temperature dependence of the exponent n and B (shown in inset) in Eq. (2).
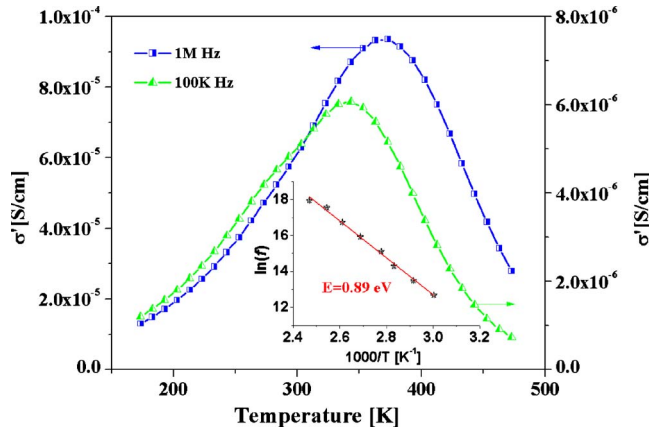
FIG. 4. (Color online) Temperature dependence of conductivity at different frequencies. The inset shows the Arrhenius fit according to Eq. (3).

$$f = f_0 \exp\left(-\frac{E}{k_B T}\right), \tag{3}$$

where E is the activation energy, f_0 is the pre-exponential term, k_B is the Boltzmann constant, and T is the temperature at maximum conductivity. The activation energy for the relaxation processes was calculated to be 0.89 eV.

From the Kronig–Kramers (KK) (Ref. [1]) relation, it is known that the power-law $(2\pi f)^m$ of ac conductivity will lead to a $(2\pi f)^{m-1}$ behavior for the real part of the dielectric permittivity, that is, $\varepsilon' = B(2\pi f)^{m-1}$. Then we have

$$f\varepsilon' = Cf^m. \tag{4}$$

Therefore, for a NCL response at a given temperature, a straight line with a slop of m should be obtained if $\log(f\varepsilon')$ is plotted as a function of $\log(f)$. Such a plot for Mn-doped BMT–PT at selected temperatures is shown in Fig. 5. Two straight lines can be observed which correspond to the experimental data at two different temperatures. All the experimental data can be well fitted using Eq. (4). As can be seen from the inset of Fig. 5, the exponent m is very close to unity, i.e., close to the value obtained from the conductivity results (Figs. 2 and 3) and decreases slightly with increasing temperatures in the NCL region. While in the SLPL region,
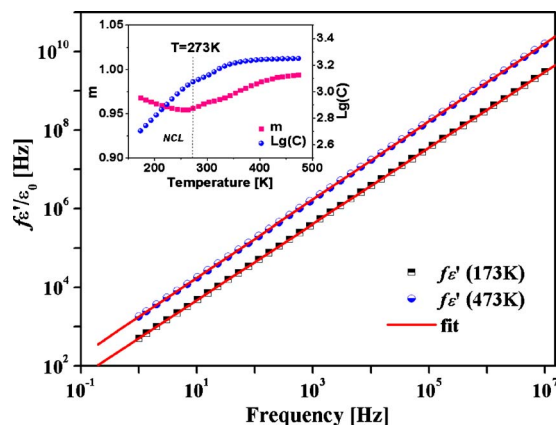

FIG. 5. (Color online) Plots of $f\varepsilon'$ against f for Mn-doped BMT–PT at 173 and 473 K. The solid lines are the best fitted lines according to Eq. (4). The inset displays the temperature dependence of the exponent m and pre-exponential coefficient $\log(C)$.

m increases with increasing temperatures and gradually approaches 1, which is much smaller than that obtained in Fig. 3. This discrepancy results from the fact that the KK relation between dielectric permittivity and conductivity is only valid for an exponent m smaller than 1.

Since the SLPL shows thermally activated characteristics with an activation energy around 0.89 eV, which is quite close to the activation energy for oxygen vacancies jumping in many perovskite structures,[20,21] it is speculated that SLPL is associated with the migration of oxygen vacancies among those nonequivalent oxygen positions in ceramics. This speculation could be further confirmed by reviewing the dielectric loss result shown in Fig. 1. A wide and prominent relaxation peak can be observed in the temperature range 273–450 K. This peak shifts toward a higher temperature and the peak height also increases with increasing measuring frequencies. This characteristic indicates that this peak belongs to a relaxation-type according to the point defect relaxation theory.[22] From the dielectric loss peak, we indeed get an activation energy of 0.98 eV, which is close to 0.89 eV. For Mn-doped BMT–PT, it is known that the Mn dopant (with a valence state of 3+ under its synthesis condition) will occupy the Ti^{4+} site and is charge neutralized by oxygen vacancies.[23] This explains why the NCL and dielectric loss peaks are observed only in Mn-doped BMT–PT but not in pure BMT–PT samples and further confirms that the SLPL behavior observed in Mn-doped BMT–PT is associated with the oxygen vacancy-related relaxation process.

Recent measurements[10] indicated the existence of a universal SLPL with exponents $n = 1.2 - 1.5$ up to THz frequency range. However, the exponent of the SLPL is temperatures independent in the investigated systems. It should be emphasized that the SLPL behavior observed in Mn-doped BMT–PT ferroelectrics is quite different from those reported in Ref. 10. Recent kinetic Monte Carlo simulation[24] of a random dipolar lattice model reveals a transition from Debye relaxation to constant dielectric loss behavior upon lowering of temperature. In this model, the hopping of ions around a random distribution of immobile counter-ions is studied, which includes the dipolar interaction effect. The crossover from the NCL response to the SLPL one in our system reveals such a transition. It shows that a doped ferroelectric material is an ideal system for the theoretical investigation on NCL behavior.

IV. CONCLUSIONS

Mn-doped BMT–PT ferroelectric ceramics were prepared using a PEG-assisted solid state reaction method and a crossover from a NCL to a SLPL behavior was observed. A thermally activated relaxation behavior is observed in the SLPL region and the corresponding activation energy is determined to be 0.89 eV by using an Arrhenius fitting. Such a behavior was discussed in terms of the local movements of oxygen vacancies.

ACKNOWLEDGMENTS

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