

## Dielectric relaxation behavior of BaTiO<sub>3</sub>/SrTiO<sub>3</sub> composites

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Relaxor ferroelectrics have attracted considerable attention both in fundamental understanding of the structural and physical properties and in practical applications [1–3]. The obvious feature of relaxor ferroelectric is the broad peak that appears in the dielectric constant as a function of temperature and frequency. The positions of the maxima in the dielectric constant are shifted toward higher temperatures as the frequency is increased. Analogs to spin glass in magnetism, the dipolar glass behavior of relaxor ferroelectrics was proposed [4, 5]. It is usually believed that the dielectric behavior of polar species, due to composition and field inhomogeneities, is responsible for the glassy behavior [6–8], although the mechanism of the relaxor ferroelectric behavior has not been fully understood. At the same time, because relaxor ferroelectrics display extremely high coupling coefficients, relative low acoustic impedances, and a wide range of dielectric constants, they have been widely applied to ultrasonic transducers, sensors and ferroelectric random access memories [9, 10].

BaTiO<sub>3</sub>(BTO) has long been known for its ferroelectricity and positive temperature coefficient of resistance (PTCR) [11]. Pure BTO is a typical ferroelectric, which undergoes a sharp dielectric transition when compared to the diffuse transition shown by relaxor ferroelectrics. In recent years it has been shown that many perovskite BTO compounds or doped BTO [12, 13], and solid solution BaTiO<sub>3</sub>/SrTiO<sub>3</sub>(BTO/STO) [14, 15], have anomalous dielectric relaxation behavior. The BTO/STO superlattices have the potential to drastically improve material properties, which have attracted much attention [16, 17].

In this paper we present the results obtained on dielectric permittivity and their relaxation on  $x$ BTO/(1– $x$ )STO composites, where  $x = 1/2; 1/3; 1/4$ .

Samples used in this study were  $x$ BaTiO<sub>3</sub>/(1– $x$ )SrTiO<sub>3</sub> composites of different BTO concentration  $x$ , where BTO and STO powders were prepared using solid state reaction and sintered at 1000 °C, respectively. The BTO and STO powders were grinded in a planetary mill machine for at least 24 hr, and then fully mixed in different BTO concentrations ( $x = 1/2, 1/3, 1/4$ ). Disks were pressed from  $x$ BTO/(1– $x$ )STO mixed powders under a pressure of 100 MPa, and sintered at 700 °C for 1 hr, then rapidly increased to 1000 °C for 10 min. X-ray diffraction was carried out on the samples using CuK<sub>α</sub> radiation. The dielectric spec-

troscopies of BTO/STO composites were measured by an HP4194A Impedance Analyser.

Fig. 1 shows the X-ray diffraction (XRD) obtained for  $x$ BTO/(1– $x$ )STO samples, where  $x = 1/2, 1/3, 1/4$ . It can be seen that there exist two sets of independent crystal structures, tetragonal BTO and cubic STO, in the BTO/STO composite samples. Fig. 2 gives the temperature dependence of dielectric constant for concentration  $x = 1/2, 1/3, 1/4$  of  $x$ BTO/(1– $x$ )STO composites. It is evident that the dielectric constants are dependent on frequency and their values decrease with increasing frequency. Fig. 2a–c show that a change in BTO concentration results in a different dielectric relaxation behavior. When  $x = 1/3$ , a typical relaxor ferroelectric behavior is shown and the dielectric peak looks broader as the diffuse transition described. When  $x = 1/4$ , the dielectric peak becomes sharper. For  $x = 1/2$ , one dielectric peak fissures into two.

Relaxor ferroelectrics have a glassy behavior, which obeys the Vogel–Fulcher(VF) relationship[4, 18], given by

$$f = f_0 \exp(-E_a/K_B(T_m - T_f))$$

where  $f_0$  is the Debye frequency,  $E_a$  is the activation energy for relaxation,  $T_f$  is the freezing temperature, and  $T_m$  is the peak temperature of dielectric constant measured at frequency  $f$ .

Fig. 3 shows the variation of  $T_m$  with frequency  $f$  for  $x = 1/3$  of  $x$ BTO/(1– $x$ )STO. The solid line in Fig. 3 shows the fit to the VF equation. The fit indicates that the present system of ferroelectrics exhibits spin-glass-like characteristics, similar to what is seen in PMN-PT relaxor ferroelectrics. The values of  $E_0$ ,  $f_0$  and  $T_f$  calculated from the fit are 0.039 eV,  $1.76 \times 10^{12}$  Hz and –266.9 K, respectively.

There exist the polar regions (PR's) and un-polar regions in PMN-PT relaxors are believed as the mechanism of its relaxor behavior. The responses of these PR's for temperature and frequency are believed to be responsible for dielectric relaxation behavior [4–7]. Randall *et al.* found evidence for ordering (1:1) of the B site cation in PMN relaxors using transmission electron microscopy (TEM) [19]. The electro-optic and electrostrictive effects revealed that PR's began to appear at several hundred degrees above peak temperature of dielectric constant  $T_m$  [20]. The micro-PR's occupy about one third of the whole volume of PMN by X-ray and

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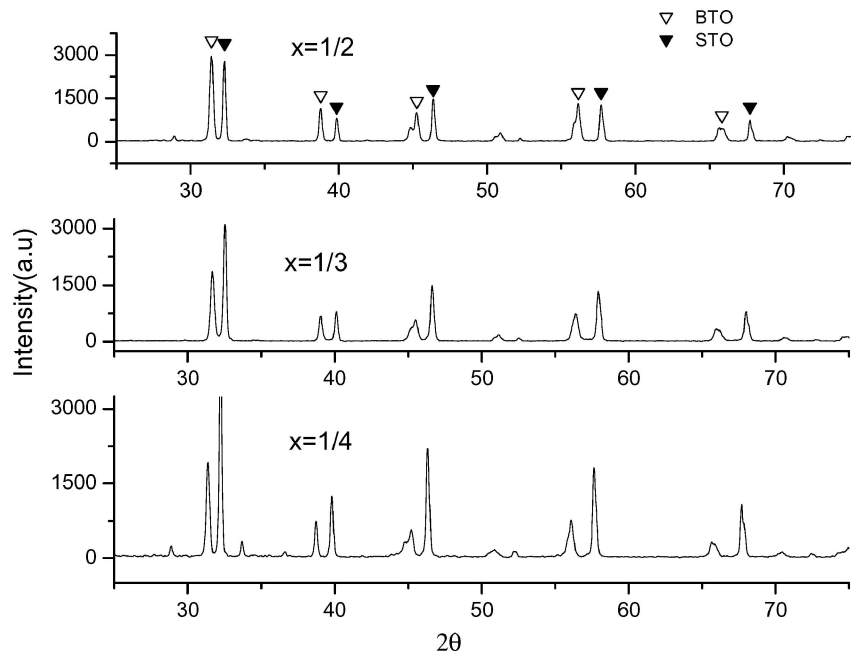


Figure 1 X-ray diffraction pattern of  $x$ BTO/(1 -  $x$ )STO composites.

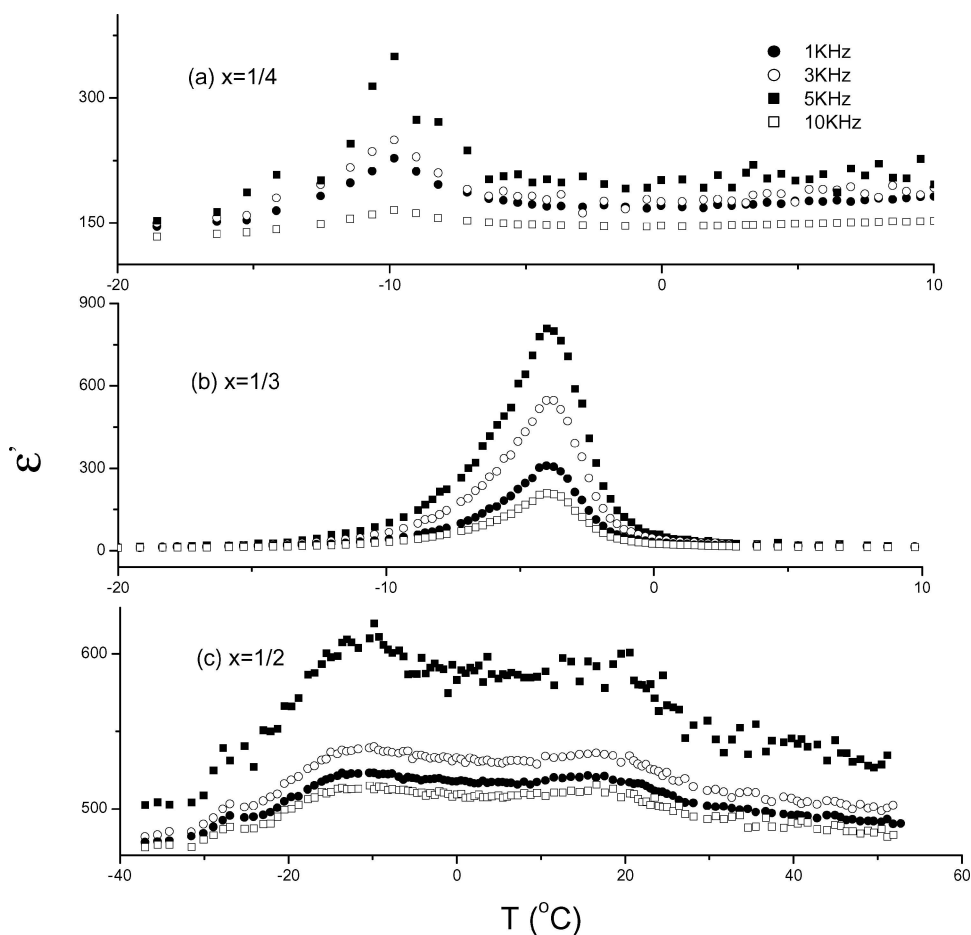


Figure 2 Temperature and frequency dependence of dielectric constants of  $x$ BTO/(1 -  $x$ )STO composites.

TEM even at 5 K. 7 with PT content  $x\%$  of PMN- $x\%$ PT increasing, the distribution of PR's becomes scarce and the relaxor behavior will gradually weaken and finally disappear when  $x\%$  reaches 40%.

The tetragonal phase BTO embedded into the surrounding cubic phase STO in BTO/STO composites is similar as the structural characterization of relaxor fer-

roelectrics. When the PR's concentration  $x < 1/3$ , they are too scarce to form polarization order between PR's, and the non-PR's will easily establish longrange order with decreasing temperature. It will become the normal ferroelectric phase transition gradually with the PR decreasing. Dielectric measurements show that when the BTO concentration is  $x = 1/3$ , the BTO/STO

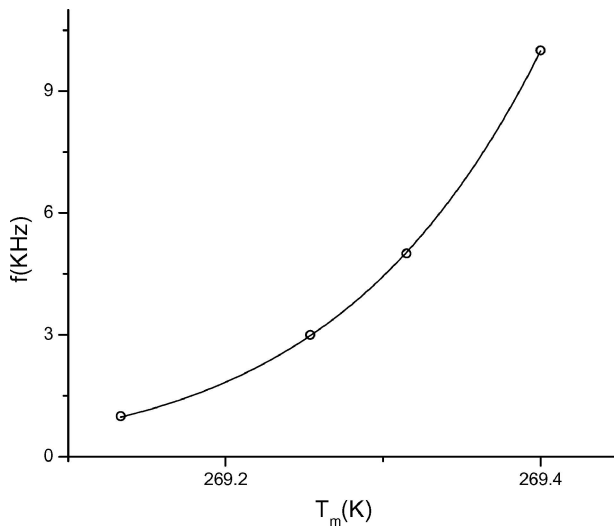


Figure 3 Frequency dependence of  $T_m$  for (1/3)BTO/(2/3)STO. The symbols indicate data points and the solid line indicates the fit to Vogel-Fulcher relationship.

composite displays the typical relaxation behavior. The relaxor ferroelectric behavior is believed to be the result of local polar order of PR's [21]. The most obvious relaxation behavior for BTO/STO composite system is that the concentration of BTO equals 1/3.

One of the most promising frontiers in ultrasonic imaging technology is the development of ultrasonic transducers and arrays [22]. The design of ultrasonic array requires higher dielectric constant of piezoelectric materials at room temperature and lower acoustic impedance is desirable for matching with human body for medical imaging transducers. The dielectric relaxation behavior of the composites provides the flexibility of relaxor ferroelectrics. The material properties can be varied in order to satisfy the need of various ultrasonic transducers and arrays.

In conclusion, The BTO/STO composites were found to exhibit relaxation behavior. The concentration of BTO affects the relaxation characteristic. When BTO concentration is 1/3, it displays typical relaxation behavior, and obeys the VF law. The existence of the polar ferroelectric phase and nonpolar paraelectric phase in the BTO/STO composites, are the direct reason of their dielectric relaxation behavior. When the concentration of the PR's is 1/3, the BTO/STO displays a typical dielectric relaxation behavior. The concentration is lower or higher than 1/3 will weak its relaxation behavior and gradually tends to typical STO and BTO ferroelectrics, respectively. Further work on the dielectric relaxation behavior of composites will be helpful to better un-

derstand the structural nature of the polar order and the mechanism of relaxor ferroelectrics. At the same time the dielectric relaxation behavior of composites provides the flexibility of varying relaxor ferroelectrics, which have the potential for applications to transducers, sensors and other modern electronic devices.

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### References

1. L. E. CROSS, *Ferroelectrics* **76** (1987) 241.
2. R. BLINC, J. DOLINSEK, A. GREGOROVIC, B. XALAR, C. FILIPIC, Z. KUTNJAK, A. LEVSTIK and R. PIRC, *Phys. Rev. Lett.* **83** (1999) 424.
3. E. V. COLLA, E. Y. KORALEVA, N. M. OKUNEVA and S. B. VAKHRUSHEV, *ibid.* **74** (1995) 1681.
4. D. VIEHLAND, S. J. JANG, L. E. CROSS and M. WUTTIG, *J. Appl. Phys.* **68** (1990) 2916.
5. E. COURTENS, *Phys. Rev. B* **33** (1986) 2975.
6. Z.-G. YE, Y. BING, J. GAO and A. A. BOKOV, *ibid.* **67** (2003) 104104.
7. N. DE MATHAN, E. HUSSON, J. R. GAVARRI, A. W. HEIWAT and A. MORELL, *J. Phys. Condens. Matter* **3** (1991) 8159.
8. H. K. GUO, G. FU, X. G. TANG, J. X. ZHANG and Z. X. CHEN, *ibid.* **10** (1998) L297.
9. P. D. LOPATH, S. E. PARK, K. K. SHUNG and T. R. SHROUT, *IEEE Ultras. Sympos.* **2** (1997) 1643.
10. A. R. JAMES, S. PRIYA, K. UCHINO and K. SRINIVAS, *J. Appl. Phys.* **90** (2001) 3504.
11. W. HEYWANG, *J. Mater. Sci.* **6** (1971) 1214.
12. A. CHEN, Z. YU and Z. JING, *Phys. Rev. B* **61** (2000) 957.
13. M. M. KUMAR, K. SRINIVAS and S. V. SURYANARAYANA, *Appl. Phys. Lett.* **76** (2000) 1330.
14. V. V. LEMANOV, E. P. SMIRNOVA, A. V. SOTNIKOV and M. WEIHACHT, *ibid.* **77** (2000) 4205.
15. C. MENORET, J. M. KIAT, B. DKHIL, M. DAMMAK and O. HERNANDEZ, *Phys. Rev. B* **65** (2002) 224104.
16. T. TSURUMI, T. ICHIKAWA, T. HARIGAI, H. KAKEMOTO and S. WADA, *J. Appl. Phys.* **91** (2002) 2284.
17. T. ZHAO, Z. H. CHEN, F. CHEN, W. S. SHI, H. B. LU and G. Z. YANG, *Phys. Rev. B* **60** (1999) 1607.
18. H. K. GUO, X. G. TANG, J. X. ZHANG, S. W. SHAN, M. M. WU and Y. J. LUO, *J. Mater. Sci. Lett.* **17** (1998) 1567.
19. C. R. RANDALL and A. S. BHALLA, *Jpn. J. Appl. Phys.* **29** (1990) 327.
20. G. BURNS and F. H. DACOL, *Phys. Rev. B* **28** (1983) 2527.
21. B. DKHIL, J. M. KIATE, G. CALVARIN, G. BALDINOZZI, S. B. VAKHRUSHEV and E. SUARD, *ibid.* **65** (2001) 24104.
22. K. K. SHUNG and M. ZIPPARO, *IEEE Eng. Med. & Biol.* **15** (1996) 20.

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