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Dielectric Relaxation Behavior of Bismuth Doped $(Ba_{0.2}Sr_{0.8})\ TiO_3$ Ceramics

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The dielectric properties of bismuth doped $(Ba_{0.2}Sr_{0.8})TiO_3$ ceramics are investigated. The temperature dependence of the dielectric permittivity and loss factor were measured from 10^2 to 10^6Hz in the temperature range 12-320K. As the amount of Bi increases, the ferroelectric-paraelectric phase transition gets diffused and relaxed. In addition to this ferroelectric-paraelectric phase transition, other two sets of dielectric anomalies, located at 50-100K and 200-300K respectively, are also found. The possible relaxation mechanisms are briefly discussed.

Key words: barium strontium titanate, dielectric relaxation

Comportamiento de relajacion dieléctrica en cerámicas $(Ba_{0.2}Sr_{0.8})TiO_3$ dopadas con bismuto

Las propiedades dieléctricas de cerámicos dopados con bismuto son investigadas. La dependencia con la temperatura de la permitividad dieléctrica y el factor de pérdidas se midieron entre 0^2 y 10^6Hz en el rango de temperatura 12-320K. Con el aumento del contenido en Bi, la transición de fase ferroeléctrica-paraléctrica se hace difusa y reloja. Junto a esta transición de fase los conjuntos de anomalias dieléctricas, localizados a 50-100k y 200-300k respectivamente, también se encontraron. Se discute brevemente los posibles mecanismos de relajación.

Palabras clave: titanato de bario y estrancio, relajación dieléctrica

1. INTRODUCTION

$BaTiO_3$ is a typical ferroelectric with a Curie temperature around 130ºC. $BaTiO_3$ based solid solutions have been a subject of extensive study. It is known that $Ba_{1-x}Sr_xTiO_3$ can form solid solutions in the whole x range and $SrTiO_3$ shifts the Curie temperature of $BaTiO_3$ to low temperatures (1,2). Previous studies on the dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions have shown that the compositions with $x \leq 0.8$ exhibited normal ferroelectric behavior while a relaxor characteristic was observed in the $SrTiO_3$ rich side ($x>0.8$) (3,4). Relaxor behavior has been observed in many of $BaTiO_3$ based solid solutions with substitution of titanium, such as $Ba(Ti,Sn)O_3$ (5), $Ba(Ti,Zr)O_3$ (6) and $Ba(Ti,Hf)O_3$ (7).

Strontium titanate ($SrTiO_3$) is a quantum paraelectric which shows high dielectric permittivity at low temperature with no ferroelectric phase transition occuring down to near 0K (8). However, ferroelectricity was reported to be induced by Bi doping and a relaxor behavior was observed in heavily Bi doped $SrTiO_3$ (9). Such relaxor characteristics were also found in Ca doped $SrTiO_3$ (10). Although some explanations were proposed, the relaxation mechanism in these materials is still unclear. A dielectric study about the effects of Bi doping on $BaTiO_3$ (typical ferroelectric) and $SrTiO_3$ (quantum paraelectric) solid solutions may help to understand the complex relaxation behaviour.

2. EXPERIMENTAL

Ceramic samples were prepared by the conventional mixed oxide method. Reagent grade $BaCO_3$, $SrCO_3$, TiO_2 and Bi_2O_3 were weighed according to the composition $(Ba_{0.2}Sr_{0.8})_{1-1.5x}Bi_xTiO_3$ where x=0, 0.005, 0.05 and 0.1, respectively. After ball-milled in alcohol for 6 hours using agate pots and agate balls in a planetary mill, the powders were dried, and then calcined between 1100ºC and 1200ºC for 6 hours; the higher the Bi content, the lower the calcination temperature. The calcined powders were milled again for 8-10h, to obtain powders of less than 5µm of particle size. Pellets of 10mm in diameter and 2-3mm in thickness were uniaxially pressed at 100MPa and then isostatically pressed at 250MPa. The sintering was conducted between 1250 and 1350ºC for 4 hours with the lower temperature for the higher Bi content. Post-sintering annealing was carried out for x=0.005 composition at 800ºC for 30 hours in oxygen at 1atm.

Some of the sintered samples were ground into powder and the phases were identified by X-ray diffraction (XRD) analysis. The scanning electron microscopy (SEM) microstructures of the samples were observed in polished sections using a Hitachi S4100 microscope. Grain size measurements were made on SEM photographs using the intercept method.

For the dielectric measurements, sintered samples were polished and gold electrodes were sputtered on both sides.

Impedance was measured, at different frequencies between 100Hz and 1MHz, as a function of temperature, using a Solartron 1260 Impedance / Gain-Phase Analyzer and a Displex APD-Cryogenics cryostat during heating up at a rate of 1K/min in the temperature range of 12-320K. The hysteresis loops were measured using a standard Sawyer and Tower circuit.

3. RESULTS

The XRD patterns of all the studied compositions showed a single cubic perovskite phase. Figure 1 shows the XRD patterns of $(Ba_{0.2}Sr_{0.8})_{1-1.5x}Bi_xTiO_3$ for x=0.10 composition.

The SEM micrographs of all the samples showed a dense microstructure. The grain size varies between 1.8 and 4.0mm with lower values for compositions with higher x values.

Evident hysteresis loops were observed in all the compositions, indicative of a ferroelectric state. Figure 2 shows the hysteresis loops of $(Ba_{0.2}Sr_{0.8})_{1-1.5x}Bi_xTiO_3$ for x=0 and 0.10 compositions. As the amount of Bi doping increases, the hysteresis loop becomes slimmer.

Figure 3 shows the temperature dependence of the dielectric permittivity and loss factor at various frequencies for the studied compositions. $Ba_{0.2}Sr_{0.8}TiO_3$ solid solution exhibits a sharp ferroelectric / paraelectric phase transition. As the Bi content increases, the transition gradually becomes diffused and relaxed.

In addition to the ferroelectric / paraelectric phase transition, a set of dielectric anomalies, more obvious in loss-temperature curves, is also observed between 50 and 100K for the samples with low bismuth content. Moreover, a relaxation located at 200-300K is found for the x=0.005 composition.

The dielectric permittivity maximum values (ε_{max}) at 1kHz for all the compositions as well as the maximum temperatures (T_{max}) are shown in table 1. ε_{max} decreases with increase in the Bi content. The compositional dependence of T_{max} is plotted in figure 4 where it can be seen that T_{max} increases linearly up to x=0.10.

The diffuseness of the ferroelectric-paraelectric phase transition can be empirically described by the parameter $\Delta T_1=T_{0.9\varepsilon max(100Hz)}-T_{\varepsilon max(100Hz)}$, i.e., the difference between the temperature corresponing to 90% of the permittivity maximum ε_{max} in the high temperature side and $T_{\varepsilon max(100Hz)}$. The ΔT_1 values are shown in table 1. ΔT_1 increases as x increases.

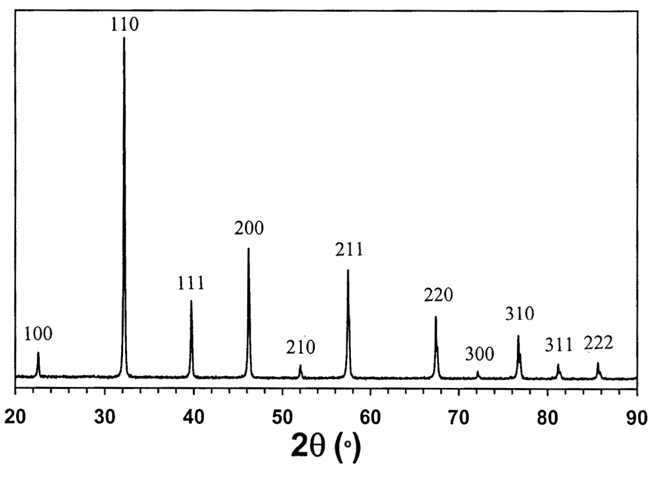

Figure 1. X-ray diffraction patterns of $(Ba_{0.2}Sr_{0.8})_{1-1.5x}Bi_xTiO_3$ (x=0.10) ceramics.

TABLE 1. DIELECTRIC PERMITTIVITY MAXIMUM (ε_{max}) (1KHZ), PERMITTIVITY MAXIMUM TEMPERATURE (T_{max}) (1KHZ), $\Delta T_1=T_{0.9\varepsilon max(100Hz)}-T_{\varepsilon max(100Hz)}$ and $\Delta T_2=T_{max(1MHz)}-T_{max(100Hz)}$ for $(Ba_{0.2}Sr_{0.8})_{1-1.5x}Bi_xTiO_3$ CERAMICS.

x	ε_{max} (at 1kHz)	T_{max} (K) (at 1kHz)	ΔT_1 (K)	ΔT_2 (K)
0	23310	127	_	_
0.005	14500	130	13	3
0.05	3480	154	31	33
0.1	2960	178	50	48

In order to quantify the frequency dispersion of T_{max}, i.e., the relaxation degree, a parameter ΔT_2 defined as $\Delta T_2=T_{max(1MHz)}-T_{max(100Hz)}$ was used. ΔT_2 for the different compositions are also shown in table 1. ΔT_2 also increases as x increases.

Figure 5 shows the temperature dependence of the dielectric permittivity and loss factor for x=0.005 composition after post-annealed at 800ºC for 30 hours in oxygen. The 200-300K dielectric peaks vanish by oxygen annealing.

4. DISCUSSION

No second phase containing Bi could be detected by X-ray or SEM up to x=0.01, suggesting that all the Bi was incorporated into the perovskite lattice of $(Ba_{0.2}Sr_{0.8})TiO_3$. The compositional dependence of T_{max} (figure 4) seems to confirm this suggestion.

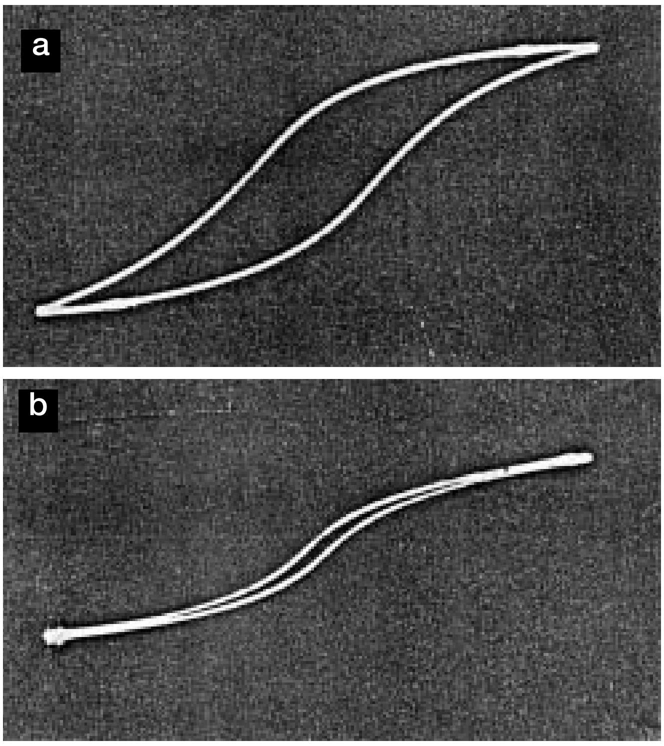

Figure 2. Hysteresis loops at 50Hz for $(Ba_{0.2}Sr_{0.8})_{1-1.5x}Bi_xTiO_3$ ceramics: x=0 at 15K (a) and x=0.10 at 120K (b). Tips of loops are 4.2μC/cm^2 and 7.8kV/cm^2 for (a), 2.5μC/cm^2 and 7.8kV/cm^2 for (b).

As can be seen in figure 3, undoped $(Ba_{0.2}Sr_{0.8})TiO_3$ ceramics exhibits a normal ferroelectric behavior: a sharp permittivity peak independent of frequency. However, an evident relaxor behavior is observed in Bi doped samples. The diffuseness of the phase transition (characterized by ΔT_1) and the frequency dispersion of the T_{max} (characterized by ΔT_2) significantly increase as the Bi content increases (table 1).

Previous study on Bi doped $BaTiO_3$ showed that no dielectric diffuseness and frequency dispersion was observed within the solubility limit (11). However, a round dielectric permittivity peak with frequency dependence was reported in Bi doped $SrTiO_3$ ceramics (9). This led us to consider that the relaxor behavior of Bi doped $(Ba_{0.2}Sr_{0.8})TiO_3$ has a similar nature to that of Bi doped $SrTiO_3$. It was suggested that Bi ions were located at off center positions of Sr^{2+} sites and that strontium vacancies (V_{Sr}'') may occur in Bi doped $SrTiO_3$ in order to balance the charge misfit caused by trivalent Bi^{3+} ions substituting divalent Sr^{2+} ions (9). Off-center Bi^{3+} ions and Bi^{3+}-V_{Sr}'' centers form dipoles and thus set up local electric fields. The ferroelectric relaxor behavior of Bi doped $SrTiO_3$ was then attributed to the random field induced domain state (9).

$(Ba_{0.2}Sr_{0.8})TiO_3$, differently from $SrTiO_3$, is a ferroelectric. Similarly as suggested for Bi doped $SrTiO_3$ (9), the Bi^{3+} ions substituting for Sr^{2+} ions in $(Ba_{0.2}Sr_{0.8})TiO_3$ solid solution can also be located at off-center positions and A site (strontium and/or barium) vacancies (V_A'') may also appear to compensate the charge imbalance arising from the substitution of A sites by Bi^{3+} ions. A random electric field formed by off-center

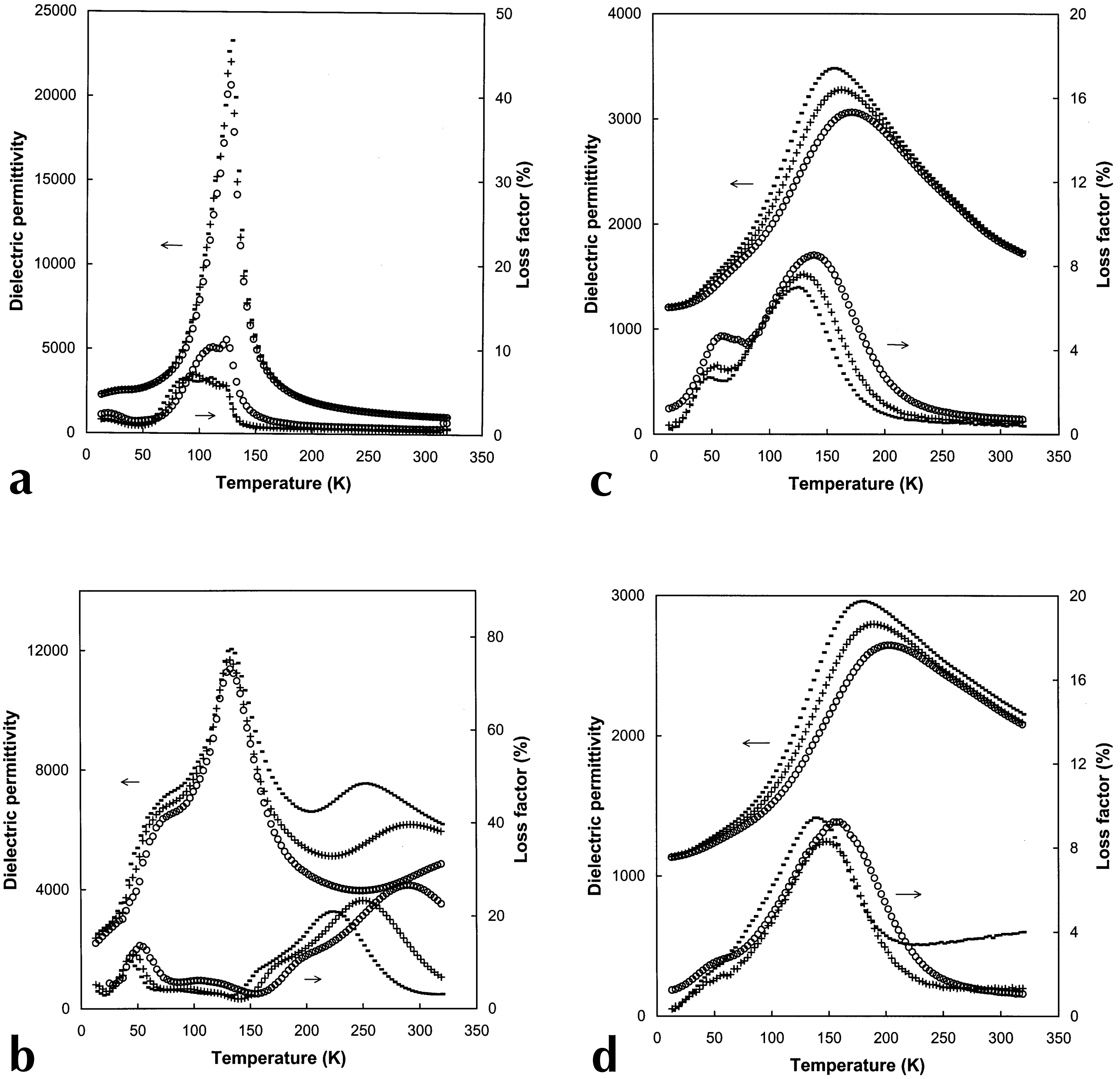

Figure 3. Temperature dependence of dielectric permittivity and loss factor at various frequencies for $(Ba_{0.2}Sr_{0.8})_{1-1.5x}Bi_xTiO_3$ ceramics where x=0 (a), 0.005 (b), 0.05 (c) and 0.1 (d). (-1kHz, + 10kHz, o 100kHz)

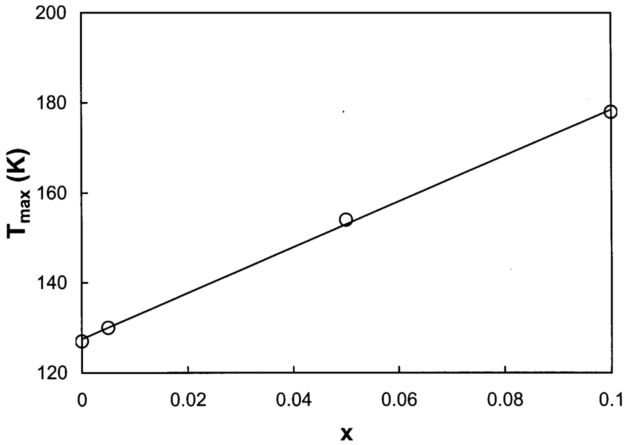

Figure 4. Compositional dependence of T_{max} at 1kHz.

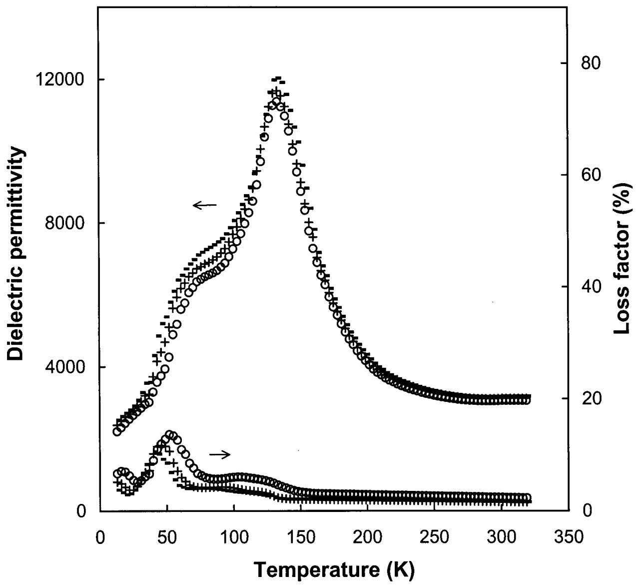

Figure 5. Temperature dependence of dielectric permittivity and loss factor at various frequencies for $(Ba_{0.2}Sr_{0.8})_{1-1.5x}Bi_xTiO_3$ (x=0.005) ceramics after post-sintering annealed at 800ºC for 30 hours in oxygen. (-1kHz, + 10kHz, o 100kHz)

Bi^{3+} ions and Bi^{3+}-V_A'' dipoles would then suppress ferroelectricity, accounting for the relaxor behavior of Bi doped $(Ba_{0.2}Sr_{0.8})TiO_3$ ceramics.

Annealing the x=0.005 sample in oxygen eliminates the dielectric peaks located at 200-300K (figure 5). In addition, the as-sintered x=0.005 sample shows a lightly grey colour, changing to white one by oxygen annealing, suggesting that the 200-300K dielectric peaks are related to the oxygen vacancies.

The nature of the 50-100K peaks is not certain at the moment. A low temperature X-ray diffraction analysis is being carried out to see if there is any new phase transition in this temperature range.

5. CONCLUSIONS

The ferroelectric-paraelectric phase transition of $(Ba_{0.2}Sr_{0.8})TiO_3$ solid solution becomes diffused and relaxed by Bi doping. The degree of the diffuseness and relaxation increases as the Bi contnet increases. In addition to the ferroelectric-paraelectric phase transition, other two sets of dielectric peaks, located at 50-100K and 200-300K respectively, were also found. It is suggested that Bi^{3+} ions located at off-center Sr^{2+} positions and Bi^{3+}-V_A'' dipoles set up a random electric field, originating the relaxor behavior of Bi doped $(Ba_{0.2}Sr_{0.8})TiO_3$. The 200-300K dielectric peaks are suggested to be related to the oxygen vacancies.

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