

## Anomalous dielectric relaxation behavior of K-doped amorphous $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ ( $x=0-0.75$ ) oxides

S. Mollah, A. K. Bera, S. Chakraborty, and B. K. Chaudhuri

*Solid State Physics Department, Indian Association for the Cultivation of Science, Calcutta-700032, India*

(Received 26 July 1993; revised manuscript received 22 November 1993)

In this paper we report the dielectric properties of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$  ( $x=0, 0.2, 0.4, 0.625, \text{ and } 0.75$ ) glasses at different temperatures (80–450 K) and frequencies (1–10 kHz). Distinct anomalies (large increases) in the dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) are observed for all the glasses between 297 and 320 K. A similar anomaly showing a change from semiconducting to metallic behavior is also observed in the electrical conductivities around the same temperature region. The anomalies observed around this temperature are considered to be associated with the orientational motion of the  $\text{BiO}_3$  or  $\text{BiO}_6$  structural units present in the glasses. Such motions might give rise to structural instability and different kinds of phase transitions including a superconducting transition in the crystalline phases.

### I. INTRODUCTION

The  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$  (BKB) and  $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_{3-\delta}$  (BBP) type noncopper oxides have been greatly studied<sup>1-3</sup> because of their superconducting behavior at relatively higher temperatures<sup>3</sup> (at 30 K for BKB with  $x=0.4$ ). Recently, several other oxide glasses like  $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_y$  (Bi-4:3:3:4) etc., have been found<sup>4</sup> to be good precursors for high- $T_c$  superconductors. While making an attempt to prepare BKB and BBP superconductors from their respective glassy phases, we noticed that only BKB forms glasses with different concentrations of potassium (K) or other alkali metals. Since BKB and BBP oxides show both metal-insulator and superconducting transitions<sup>5,6</sup> in their respective ceramic phases, it is interesting to study and compare the semiconducting behavior of the BKB glasses with that of the Bi-4:3:3:4 type glasses, which also show superconducting transitions in their respective glass-ceramic (crystalline) phases.

In the present paper we report the interesting anomalous nature of the dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) observed in the BKB and  $\text{BaBiO}_{3-\delta}$  (without K) glasses. The said anomaly, also observed in the dc conductivity, is considered to be associated with the motion of  $\text{BiO}_3$  or  $\text{BiO}_6$ -type structural units already existing in the glasses. It is also pointed out that such an ionic or molecular motion is responsible for lattice distortion leading to interesting ferroelectric, metal-insulator, or even superconducting behavior.

### II. EXPERIMENTAL

The  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$  glasses ( $\text{BaBiO}_{3-\delta}$ ,  $\text{Ba}_{0.8}\text{K}_{0.2}\text{BiO}_{3-\delta}$ ,  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$ ,  $\text{Ba}_{0.375}\text{K}_{0.625}\text{BiO}_{3-\delta}$ , and  $\text{Ba}_{0.25}\text{K}_{0.75}\text{BiO}_{3-\delta}$ ) were prepared by the quick-quenching method discussed earlier.<sup>7</sup> Appropriate amounts of  $\text{BaCO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{Bi}_2\text{O}_3$ , all of purity 99.99% (or better), were well mixed for each composition and then first sintered at 500 °C for 10 h. The sintered sample was melted at 1200 °C for 1 h (for each sample).

The melt thus obtained was quickly quenched between two steel blocks at room temperature. The amorphous character of all the dark brown glasses (except the  $\text{BaBiO}_{3-\delta}$  glass which is light yellow) was tested by x-ray-diffraction (XRD) (Philips model PW 1710) and scanning electron microscopic (Hitachi model 415A) studies. The XRD patterns of some of the glasses, indicating their amorphous character, are shown in Fig. 1(a). The infrared (ir) absorption spectra [Fig. 1(b)] with KBr indicate almost identical features with those of the Bi-4:3:3:4-type glasses<sup>8</sup> containing Bi as discussed earlier, along with some new peaks.<sup>9</sup> The most prominent ir absorption peaks are indicated in Fig. 1(b). The fundamental peaks around 540–620 and 470  $\text{cm}^{-1}$  correspond to

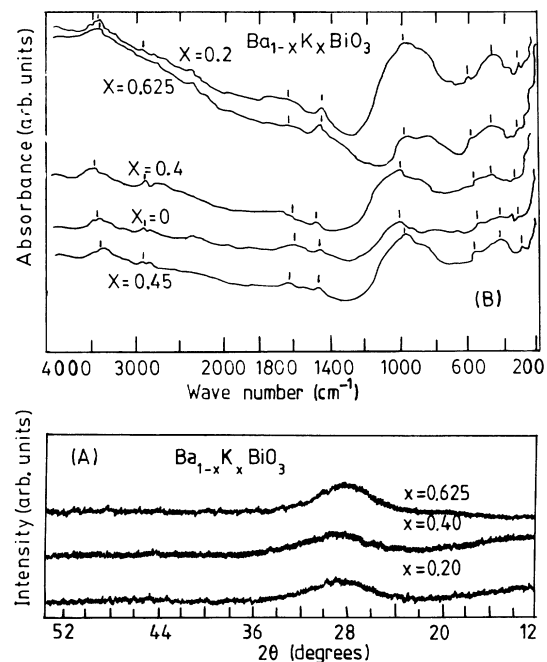


FIG. 1. X-ray powder diffraction patterns (a) and infrared absorption spectra (b) of some  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$  glasses.

TABLE I. Some important parameters for the  $Ba_{1-x}K_xBiO_{3-\delta}$  glasses.

Samples	$BaBiO_{3-\delta}$	$Ba_{0.8}K_{0.2}BiO_{3-\delta}$	$Ba_{0.6}K_{0.4}BiO_{3-\delta}$	$Ba_{0.375}K_{0.625}BiO_{3-\delta}$	$Ba_{0.25}Bi_{0.75}BiO_{3-\delta}$
Values of $x$	0.0	0.20	0.40	0.625	0.75
Density ( $g/cm^3$ ) <sup>a</sup>	8.55	6.95	4.65	5.28	6.30
$T_g$ ( $^{\circ}C$ )	344 $\pm$ 2	342 $\pm$ 2	341 $\pm$ 2	338 $\pm$ 2	335 $\pm$ 2
$T_p$ (K)	313 $\pm$ 1	312 $\pm$ 1	309 $\pm$ 1	297 $\pm$ 1	( $\sim$ 300)

<sup>a</sup>Error in the determination of density lies within  $\pm 5\%$ .

the presence of  $BiO_3$  and  $BiO_6$  structural units as discussed earlier.<sup>8</sup> Densities ( $\rho$ ) of the glasses (measured by Archimedes' method with carbon tetrachloride as an immersion liquid) first decrease with increase of K content show a minimum around  $x=0.4$  (Table I) and then increase with further increase of K content. This behavior is analogous to the "germanate anomaly" observed in the  $Na_2O-GeO_2$  glasses.<sup>10</sup> An estimation of the glass transition temperature ( $T_g$ ) and oxygen content are made, respectively, from differential thermal analysis and thermogravimetric analysis. The oxygen content of the glasses are found to be 2–3% less than the corresponding theoretical values. Some important parameters of the glasses are shown in Table I. The chemically estimated metal compositions, as shown in Table II, are found to be a little less than the corresponding theoretical values. This is primarily due to evaporation losses. The properties of the BKB glasses are assumed to be not affected by this small loss of metal ions. The dielectric constants of the well-shaped glass plates with sputtered gold electrodes were measured by a bridge (GR model 1615A) as in our earlier work.<sup>7</sup> The gold-plated samples were annealed at 200 $^{\circ}C$  for 2 h for good contact of the electrodes as well as for the removal of voids and microcracks, if any. To confirm the anomaly observed in the temperature-dependent dielectric constant curve (Fig. 2), we also measured dc conductivity ( $\sigma_{dc}$ ) of the BKB glasses (Figs. 2 and 3) as a function of temperature, following the procedure discussed earlier.<sup>7</sup> The Ohmic character was confirmed from the  $I-V$  characteristic curves for all the glasses.

### III. EXPERIMENTAL RESULTS

The thermal variations of dielectric constant ( $\epsilon'$ ) at different frequencies for the  $BaBiO_{3-\delta}$  and  $Ba_{0.375}K_{0.625}KBiO_{3-\delta}$  glasses [shown in Figs. 2(a) and 2(b)] exhibit sharp peaks around 300 K. The peak tem-

perature ( $T_p$  say) slightly varies with K concentrations as shown in Table I. Other glass compositions also show similar behavior. It is interesting to note that a similar anomaly has also been observed in the temperature-dependent dc conductivity ( $\sigma_{dc}$ ) as shown in Figs. 2(c) and 3 for some of the glasses in our investigation. Below the peak temperature  $T_p$ ,  $\epsilon'$  increases with increase of temperature whereas above  $T_p$  it decreases first and then again increases linearly with increase of temperature. In many transition-metal oxide (TMO) glasses<sup>11,12</sup> and also in the Bi-4:3:3:4-type glassy<sup>8</sup> precursors for high- $T_c$  superconductors,  $\epsilon'$  increases very slowly with temperature in the low-temperature region; but above a certain temperature it increases very sharply with increase of temperature, which is not observed in the BKB and  $BaBiO_{3-\delta}$  glasses. Furthermore, the peaks observed in  $\epsilon'-T$  plots of some TMO glasses<sup>11,12</sup> mentioned above indicate Debye-type dielectric relaxation behavior. But unlike BKB glasses the TMO glasses, in general, do not show any peak in dc conductivity. As shown in Figs. 2(c) and 3(a) the thermal variation of dc conductivity indicates metallic behavior above  $T_p$  (decrease of conductivity with increase of temperature), which is similar to a metal-insulator-like transition. At lower temperature (below  $T_p$ ),  $\sigma_{dc}$  remains almost temperature independent [Fig. 3(a)]. These are the very special features of the BKB-type glasses.

Figure 4(a) shows the nonlinear variation of  $\epsilon'$  with frequency for a typical  $Ba_{0.375}K_{0.625}BiO_{3-\delta}$  glass. The corresponding variations of  $\epsilon'$  for different glasses at a fixed temperature of 343 K are shown in Fig. 4(b). This type of nonlinear variation of dielectric constant with frequency is also uncommon in many TMO glasses studied earlier.<sup>8,11,12</sup>

The dielectric loss ( $\epsilon''$ ) of the BKB glass was calculated from the ac conductivity  $\sigma_{ac}(\omega)$  data, as discussed earlier,<sup>8</sup> using the relation  $\epsilon''(\omega) = \sigma_{ac}(\omega) / (\epsilon_0 \omega)$  (where  $\epsilon_0$  is the permittivity in vacuum and  $\omega$  is the measuring angu-

TABLE II. Theoretically and chemically (in parentheses) determined wt % of K, Bi, and Ba.

Sample	K (wt %) <sup>a</sup>	Bi (wt %) <sup>a</sup>	Ba (wt %) <sup>a</sup>
$BaBiO_{3-\delta}$	0.0 (0.0)	52.99 (49.76)	34.83 (33.00)
$Ba_{0.8}K_{0.2}BiO_{3-\delta}$	2.08 (2.01)	55.77 (53.69)	29.32 (30.30)
$Ba_{0.6}K_{0.4}BiO_{3-\delta}$	4.40 (3.08)	58.86 (56.99)	23.21 (22.10)
$Ba_{0.375}K_{0.625}BiO_{3-\delta}$	6.99 (6.77)	62.31 (61.00)	16.38 (15.47)
$Ba_{0.25}Bi_{0.75}BiO_{3-\delta}$	8.78 (8.22)	67.04 (65.18)	13.21 (10.70)

<sup>a</sup>Error in the determination of wt % lies within  $\pm 5\%$ .

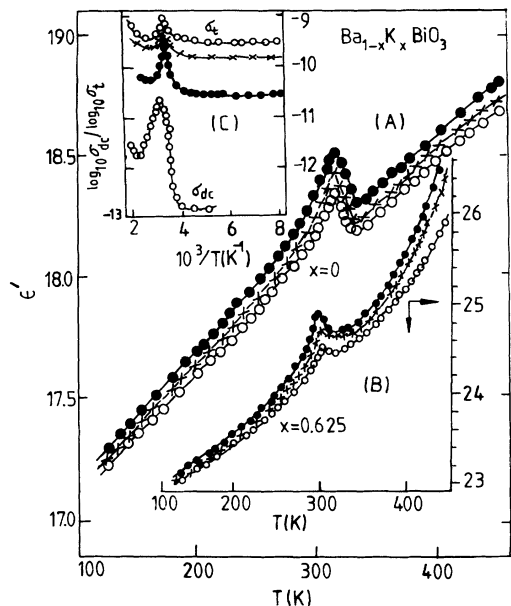


FIG. 2. Thermal variations of the dielectric constant ( $\epsilon'$ ) of some  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$  glasses with  $x=0$  (a) and  $x=0.625$  (b) at different frequencies 10 (○), 5 (×), and 1 (●) kHz, respectively. (c) Variations of  $\log_{10}(\sigma_{dc})$  and  $\log_{10}(\sigma_t)$  as a function of inverse temperature (where  $\sigma_{dc}$ =dc conductivity and  $\sigma_t$ =total frequency-dependent conductivity) of the typical  $\text{BaBiO}_{3-\delta}$  glass at 10 (○), 5 (×), and 1 (●) kHz.

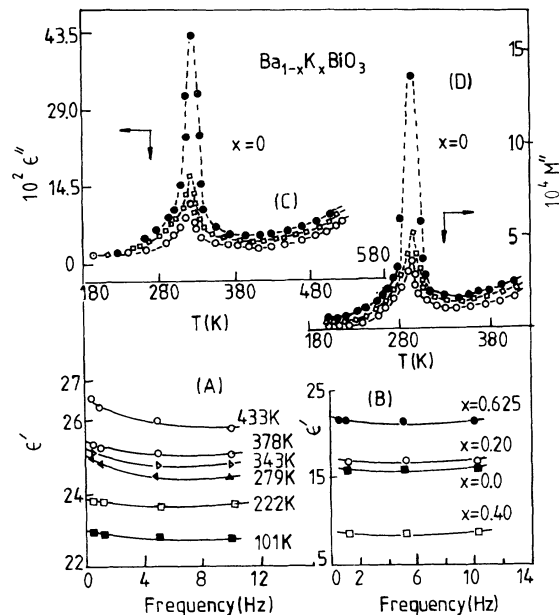


FIG. 4. (a) Frequency-dependent dielectric constant ( $\epsilon'$ ) at different temperatures of the  $\text{Ba}_{0.375}\text{K}_{0.675}\text{BiO}_{3-\delta}$  glass and (b) at different potassium concentrations (for a fixed temperature of 343 K) of the  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$  glasses. (c) Thermal variation of the imaginary part of the dielectric constant ( $\epsilon''$ ) and (d) dielectric modulus ( $M''$ ) of the  $\text{BaBiO}_{3-\delta}$  glass at 10 (○), 5 (□), and 1 (●) kHz.

lar frequency). For the  $\text{BaBiO}_{3-\delta}$  glass, the temperature variation of  $\epsilon''$  [Fig. 4(c)] indicates the presence of a sharp peak around  $T_p$  where  $\epsilon'$  and the dc conductivity also showed peaks [Figs. 2(c) and 3(a)]. A similar plot for another glass  $\text{Ba}_{0.375}\text{K}_{0.625}\text{BiO}_{3-\delta}$  shown in Fig. 5(a) indicates two sharp peaks; the first peak around  $T_p$  resembles

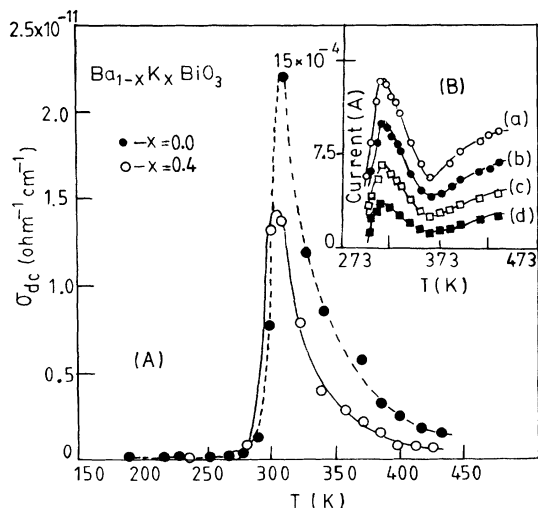


FIG. 3. (a) Thermal variations of dc conductivity of the  $\text{BaBiO}_{3-\delta}$  and  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$  glasses; (b) Variation of the thermally stimulated depolarization current (TSDC) of the  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$  glass for different applied voltages a 250, b 200, c 150, and d 100 V.

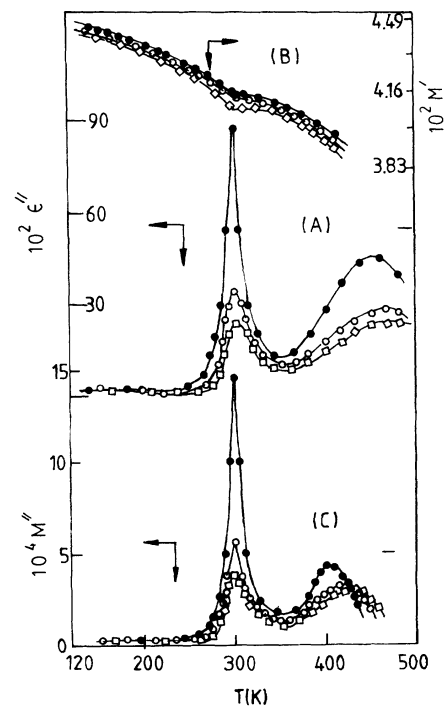


FIG. 5. Thermal variation of the imaginary part of the (a) the dielectric constant ( $\epsilon''$ ), (b) the real part of the dielectric modulus ( $M'$ ) and (c) the imaginary part of the dielectric modulus ( $M''$ ) at 10 (□), 5 (○), and 1 (●) kHz of the  $\text{Ba}_{0.375}\text{K}_{0.675}\text{BiO}_{3-\delta}$  glass.

the first anomaly observed in the  $\epsilon'$  versus  $T$  plot [Fig. 2(b)], and the other relatively broad peak appearing at a higher temperature is the dielectric anomaly associated with Debye-type relaxation with a relaxation frequency  $f_c = 1/2\pi\tau$  (where  $\tau$  is the relaxation time). All the other BKB glasses show the second peak. For the  $\text{BaBiO}_{3-\delta}$  glass, the second peak is not prominent [Fig. 4(c)] and it might appear at a higher temperature beyond the temperature range of our investigations. Both  $\epsilon'$  and  $\epsilon''$  increase with increase of K content in the glasses. The peaks observed in the  $\epsilon'-T$ ,  $\epsilon''-T$ , and  $\sigma_{dc}-T$  curves for the BKB glasses are considered to be associated with origins other than the Debye characteristic peak observed in many TMO glasses. To show the Debye-type relaxation behavior, it is sometimes (where  $\epsilon''$  vs  $T$  curves do not show the Debye peak) important to study the temperature-dependent dielectric modulus, as discussed below.

Using the experimental values of  $\epsilon'$  and  $\epsilon''$ , the real  $[M' = \epsilon' / \{(\epsilon')^2 + (\epsilon'')^2\}]$  and the imaginary  $[M'' = \epsilon'' / \{(\epsilon')^2 + (\epsilon'')^2\}]$  parts of the dielectric modulus ( $M^*$ ) are calculated.<sup>13</sup> The thermal variation of  $M'$  for a typical  $\text{Ba}_{0.375}\text{K}_{0.675}\text{BiO}_{3-\delta}$  glass shown in Fig. 5(b) indicates a small anomaly around  $T_p$ . The corresponding variations of  $M''$  with temperature for the  $\text{BaBiO}_{3-\delta}$  and  $\text{Ba}_{0.375}\text{K}_{0.675}\text{BiO}_{3-\delta}$  glasses are shown, respectively, in Figs. 4(d) and 5(c) both of which indicate sharp peaks around the respective  $T_p$  values (Table I). Other glasses also show similar behavior. Except for the  $\text{BaBiO}_{3-\delta}$  glass [Fig. 4(d)], a second maximum is also observed in the  $M''-T$  plots [Fig. 5(c)]. The peak position of the second maximum shifts to the higher-temperature region with increase of frequency [Fig. 5(c)]; this is a characteristic feature of Debye-type relaxation behavior of the BKB glasses in the regions for  $T > T_p$ . For the  $\text{BaBiO}_{3-\delta}$  glass, the second maximum in the  $M''-T$  curve is not observed within the temperature range of our investigation. The first peak height in the  $\epsilon''-T$  and  $M''-T$  plots is also found to decrease with increase of measuring frequency. The second higher-temperature peak position of the  $M''$  versus  $T$  curves gives the temperature at which the measuring frequency is equal to the relaxation frequency  $f_c$  [ $= \nu_c \exp(-W_c/k_B T)$ , where  $W_c$  is the activation energy for conductivity relaxation, and  $k_B$  is the Boltzmann constant]. Since the behavior of  $f_c$  plotted as a function of  $1/T$  (for  $T > T_p$ ) is almost similar to the temperature-dependent dc conductivity ( $\sigma_{dc}$ ), a thermally activated dielectric relaxation mechanism is indicated above  $T_p$ .

To find information about the relaxation times, we also plotted  $\epsilon''(\omega)$  versus  $\epsilon'(\omega)$  (known as a Cole-Cole plot<sup>14</sup>) at a fixed temperature of 255 K, as shown in Fig. 6 for some typical glass compositions. The semicircular nature of the curves as suggested by Cole and Cole<sup>14</sup> is not very prominent for these glasses. This is also true for the Bi-4:3:3:4 glasses studied earlier.<sup>8</sup> As suggested by Grant<sup>15</sup> this might be due to the large value of the high-frequency capacitance or dc conductivity of these glasses. A similar nature of the Cole-Cole plot has recently been observed in polymeric semiconductors.<sup>16</sup> Due to the lack of a fit of

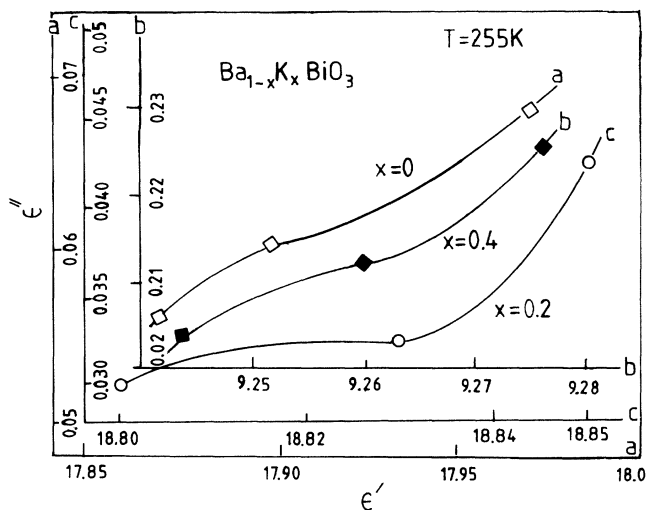


FIG. 6. Variation of the imaginary part ( $\epsilon''$ ) as a function of the real part ( $\epsilon'$ ) of the dielectric constant for three different BKB glasses at a fixed temperature (255 K).

the experimental data to a pure semicircular Cole-Cole plot and because of the limited frequency range of our measurements, it is difficult to determine accurately the value for  $\beta$  [the slope of the Cole-Cole plot at  $\epsilon''=0$  gives the value of  $(1-\beta)\pi/2$ ]. However, from Fig. 6 it is clear that the values of  $\beta$  for different BKB glasses are greater than zero but less than 1. This indicates that the BKB glasses have a distribution of relaxation times similar to the Bi-4:3:3:4 glasses,<sup>8</sup> becoming superconducting in their glass-ceramic phases.

#### IV. DISCUSSION

The large dielectric peak observed in the BKB glasses between 300 and 320 K is found to be not due to the appearance of spontaneous polarization, as in the case of ferroelectric materials.<sup>17</sup> There are examples<sup>18</sup> of large dielectric anomalies in crystals without ferroelectric or antiferroelectric transitions. The large anomalies in the dielectric constants, and loss factors as well as in the dc conductivity of the  $\text{BaBiO}_{3-\delta}$  and BKB glasses are considered to be associated with the orientations of the  $\text{BiO}_6$  octahedra or the  $\text{BiO}_3$  tetrahedral units<sup>8</sup> around  $T_p$ . The presence of such structural units has already been indicated from the ir spectra [Fig. 1(b)] of these glasses. Since Bi can exist in two valence states  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$ , a change from the low-valence state to the higher-valence state is also possible. However, it is also observed<sup>10</sup> from thermally stimulated depolarization measurements that thermally stimulated depolarization currents (TSDC) plotted as a function of temperature show peaks around  $T_p$ . This type of anomaly in the TSDC versus temperature curves, as shown in Fig. 3(b) for a typical  $\text{Ba}_{0.6}\text{K}_{0.4}\text{O}_{3-\delta}$  glass, also indicates the probable dipolar orientation in these glasses.<sup>19</sup>

It should be pointed out that such an anomaly around  $T_p$  has not been observed in the ceramic BKB or

BaBiO<sub>3-δ</sub> samples. At higher temperatures both BaBi<sub>1-x</sub>, Pb<sub>x</sub>Pb<sub>x</sub>O<sub>3-δ</sub> and Ba<sub>1-x</sub>K<sub>x</sub>BiO<sub>3-δ</sub> exhibit, for all  $x$ , the ideal cubic perovskite structure.<sup>20,21</sup> They also undergo a variety of structural phase transitions as a function of  $x$ . The various low-temperature phases represent only small distortions from the ideal phase. For  $x=1$ , a charge-density-wave instability of Pb or K leads to semiconducting behavior.<sup>22,23</sup> With increase of Pb or K concentration,<sup>23</sup> the semiconducting energy gap decreases and semimetallic behavior results for  $x < 0.4$ . It is seen from Fig. 3(a) that, even in the glassy phase, a decrease of dc conductivity with increase of temperature (metallic or semimetallic behavior above  $T_p$ ) is observed. We believe that the rotational or orientational motion of the BiO<sub>3</sub> structural units mentioned above gives rise to structural instability in the glass network (as in ferroelectric crystals) in the presence of strong electron-phonon interaction in such a system.

As for BKB glasses, large dielectric constants have also been reported in La<sub>2</sub>CuO<sub>4</sub>,<sup>24</sup> and in the high-temperature phase of polycrystalline YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>,<sup>25</sup> associated with structural instability. Ferroelectrics generally exhibit a large dielectric constant ( $\epsilon'$ ) both above and below (but near) their Curie point  $T_f$ . It was shown by Testardi *et al.*<sup>25</sup> that the large dielectric constants observed in La<sub>2</sub>CuO<sub>4</sub> or in the high-temperature phase of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> are not precisely due to true ferroelectricity, but to incipient ferroelectricity or some other causes. Frohlich<sup>26</sup> pointed out that the conditions  $\epsilon' \rightarrow \infty$  and  $\omega_T \rightarrow 0$  for  $T > T_f$  would lead to an insulator-(semiconductor-) to-metallic transition on cooling if the system retained linear response, or a ferroelectric transition in the event of nonlinear response. Similar arguments appear to be true even for the BKB system. Recently Bussmann-Holder *et al.*<sup>21</sup> also suggested the possibility of a common origin of ferroelectricity and superconductivity for the BaBi<sub>1-x</sub>Pb<sub>x</sub>O<sub>3-δ</sub>-type oxides.

Kristoffel and Konsin<sup>27,28</sup> also showed the importance of such structural instability arising from strong electron-phonon interactions. Not only is the application of such a model to elucidate the mechanism of superconductivity justified, but their structural similarity to the ferroelectric perovskites also, shown by the fact that these systems exhibit high static dielectric constants,<sup>29</sup>

suggests that an important role is played by the electron-phonon interaction. The unusual local anisotropy of the nonlinear electron-phonon interaction (arising from such orientational motion of some of the ions or groups in the lattice) admits the reduction of a three-dimensional system to pseudo-one-dimensional systems as only one axis is lattice-dynamically relevant for the evolution of the polar state [e.g., [100] in ABO<sub>3</sub> (Ref. 30)]. The basic assumption of the underlying model is that in superconductors the same nonlinear electron-phonon coupling plays an essential role, thus again admitting the application of a one-dimensional model. It can be shown<sup>21,27</sup> that the lattice distortion and also the semiconducting energy gap decrease with increase of temperature (from low temperature) as in the theory of superconductivity and the Peierls transition.<sup>30</sup> Jorgensen *et al.*<sup>31</sup> also considered lattice instability to explain superconductivity in La<sub>2-x</sub>Ba<sub>x</sub>CuO<sub>4</sub>. The nonsuperconducting La<sub>2</sub>CuO<sub>4</sub>, which has an orthorhombic structure, exhibits semiconducting behavior. The orthorhombic distortion is proposed to result from a Peierls  $2k_F$  instability or a soft zone-boundary phonon mode. The role of Ba is to suppress the instability and stabilize a higher-symmetry tetragonal structure, which is metallic or superconducting.

Thus it appears that the strong electron-phonon interaction in BKB- or in BBP-type oxides might give rise to many types of transitions including superconducting<sup>21</sup> transitions. From knowledge of the existing theoretical models,<sup>21,26,27</sup> the nonlinear behavior of the conductivity and large dielectric constant can be phenomenologically explained. In the BKB system the rotational motion of the active ions (BiO<sub>3</sub> or BiO<sub>6</sub>) plays an important role for strong electron-phonon interaction and lattice distortion. The elaborate calculation which has already been carried out by Bussmann-Holder *et al.*<sup>21,32</sup> for the BaBi<sub>1-x</sub>Pb<sub>x</sub>O<sub>3-δ</sub>-type oxides elucidated interesting features of superconductivity and ferroelectricity.

#### ACKNOWLEDGMENTS

The authors are grateful to the Department of Science and Technology (DST) and also to the Council of Scientific and Industrial Research (CSIR), Government of India, for financial assistance to do the work.

<sup>1</sup>R. J. Cava, B. Batlogg, J. J. Krajewski, R. Farrow, L. W. Rupp, A. E. White, K. Short, W. F. Peck, and T. Kometani, *Nature* **332**, 814 (1988).

<sup>2</sup>D. G. Hinks, B. Dabrowski, J. D. Jorgensen, A. W. Michel, D. R. Richards, S. Pei, and D. Shi, *Nature* **333**, 836 (1988).

<sup>3</sup>R. Kuentzler, C. Hornick, Y. Dossmann, S. Wegner, R. El Farsi, and M. Drillon, *Physica C* **184**, 316 (1991).

<sup>4</sup>T. Kawai, T. Horiuchi, K. Mitsu, K. Ogura, S. Tanaka, and S. Kawai, *Physica C* **161**, 561 (1989); H. Zheng, M. W. Colby, and J. D. Mackenzie, *J. Non-Cryst. Solids*, **127**, 143 (1991).

<sup>5</sup>L. F. Mattheiss and D. R. Hamann, *Phys. Rev. B* **28**, 4227 (1983); L. F. Mattheiss, *Jpn. J. Appl. Phys.* **24**, Suppl. 2, 6

(1985).

<sup>6</sup>T. M. Rice and L. Sneddon, *Phys. Rev. Lett.* **47**, 681 (1981).

<sup>7</sup>S. Mollah, K. K. Som, K. Bose, A. K. Chakravorty, and B. K. Chaudhuri, *Phys. Rev. B* **46**, 11 075 (1992); S. Mollah, K. K. Som, K. Bose, and B. K. Chaudhuri, *J. Appl. Phys.* **74**, 931 (1993).

<sup>8</sup>K. K. Som, S. Mollah, K. Bose, and B. K. Chaudhuri, *Phys. Rev. B* **45**, 1165 (1992); **47**, 534 (1993).

<sup>9</sup>S. Mollah, A. K. Bera, and B. K. Chaudhuri (unpublished).

<sup>10</sup>G. S. Henderson and M. E. Fleet, *J. Non-Cryst. Solids* **134**, 259 (1991).

<sup>11</sup>A. Mansingh, V. K. Dhawan, and M. Sayer, *Philos. Mag. B*

- 48, 215 (1983).
- <sup>12</sup>A. Mansingh, J. K. Vaid, and R. P. Tandon, *J. Phys. C* **8**, 1023 (1975).
- <sup>13</sup>P. B. Macedo, C. T. Moynighan, and R. Bose, *Phys. Chem. Glasses* **13**, 171 (1972).
- <sup>14</sup>K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).
- <sup>15</sup>F. A. Grant, *J. Appl. Phys.* **29**, 76 (1958).
- <sup>16</sup>N. Afanasev, L. V. Mukaeva, M. G. Voronkov, and T. G. Ermakova, *Dokl. Akad. Nauk SSSR* **320**, 856 (1991) [*Sov. Phys. Dokl.* **36**, 694 (1991)].
- <sup>17</sup>M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectric and Related Materials* (Clarendon, Oxford, 1977).
- <sup>18</sup>R. Pepinsky, in *Physics of Electronic Ceramics*, edited by L. L. Hench and D. B. Dove (Dekker, New York, 1972), Pt. B, p. 567.
- <sup>19</sup>J. Laudat and F. Laudat, *Z. Phys. Chem.* **178**, 211 (1991); J. van Turnhout, in *Electrets*, edited by G. M. Sessler, Topics in Applied Physics Vol. 33 (Springer-Verlag, New York, 1980), p. 81.
- <sup>20</sup>A. W. Sleight, J. J. Gibson, and P. E. Biessted, *Solid State Commun.* **17**, 27 (1975).
- <sup>21</sup>A. Bussmann-Holder, H. Buttner, A. Simon, and V. Waas, *Z. Phys. B* **79**, 445 (1990), and references therein.
- <sup>22</sup>D. E. Cox and A. W. Sleight, *Acta. Crystallogr. Sect. B* **34**, 1 (1979); A. Chaillout, A. Santoro, J. P. Remeika, A. S. Cooper, G. P. Espinosa, and M. Marezio, *Solid State Commun.* **65**, 1363 (1988).
- <sup>23</sup>T. D. Thanh, A. Koma, and S. Tanaka, *J. Appl. Phys.* **22**, 205 (1980); S. Tajima, S. Uchida, A. Kasaki, M. Takagi, K. Kitazawa, S. Takeda, and A. Katsui, *Phys. Rev. B* **32**, 6302 (1985); S. Tajima, S. Uchida, S. Masaki, H. Takaji, K. K. Tazawa, S. Tanaka, and S. Sagai, *ibid.* **36**, 1696 (1988).
- <sup>24</sup>D. Reagor, E. Abrens, S. W. Cheong, A. Migliori, and Z. Fisk, *Phys. Rev. Lett.* **62**, 2048 (1989).
- <sup>25</sup>L. R. Testardi, W. G. Moulton, H. Mathias, H. K. Ng, and C. M. Rey, *Phys. Rev. B* **37**, 2324 (1988).
- <sup>26</sup>H. Frohlich, in *Ferroelectricity*, edited by E. Weller (Elsevier, New York, 1967), p. 9.
- <sup>27</sup>N. N. Kristoffel and P. Konsin, *Phys. Status Solidi* **28**, 731 (1968).
- <sup>28</sup>P. Konsin, *Phys. Status Solidi* **76**, 487 (1976).
- <sup>29</sup>Y. N. Venetsev, V. V. Bogatko, M. V. Plotnikova, and S. J. Rieman, *Ferroelectrics* **56**, 61 (1984).
- <sup>30</sup>L. N. Bulaevskii, *Usp. Fiz. Nauk* **115**, 263 (1974) [*Sov. Phys. Usp.* **18**, 131 (1975)]; **116**, 449 (1975) [**18**, 514 (1975)].
- <sup>31</sup>J. D. Jorgensen, H. B. Schuttler, D. G. Hinks, D. W. Capone, H. K. Zhang, and M. B. Brodsky, *Phys. Rev. Lett.* **58**, 1024 (1987).
- <sup>32</sup>A. Bussmann-Holder, H. Bilz, and G. Benedek, *Phys. Rev. B* **39**, 4840 (1989).