Comment on "Possible observation of a glassy ferroelectric: $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_z$"

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Ferroelectricity in multicomponent $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_\delta$ (BG) glass with ferroelectric (FE) transition around $T_{fc} = 530$ K has been reported recently by Bahgat *et al.* [Phys. Rev. B **63**, 012101 (2001)]. Our microstructural, electrical transport and dielectric studies on similar BG glass prepared under similar conditions confirmed the presence of nanocrystalline phases embedded in this glass. This is actually a glass-nanocrystal composite (GNC) system. It is concluded that these nanocrystals/clusters (~10–30 nm grain size) are responsible for the ferroelectric character of the BG glass or the GNC system.

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Recently, Bahgat *et al.*[1] reported ferroelectricity in a multicomponent $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_\delta$ (BG) glass with ferroelectric (FE) transition around $T_{fc} = 530$ K. They reported the BG glass as a homogeneous single-phase glass. We prepared a similar BG glass under similar conditions. The similar glass prepared by us and Bahgat *et al.*[1] also showed identical properties. Our recent microstructural study, however, indicates that the BG type glasses prepared by us are not pure and homogeneous single-phase glasses as claimed by Bahgat *et al.*[1] (for their prepared glass) but they are glass-nanocrystal composites. Ferroelectric behavior reported by Bahgat *et al.*[1] and also observed in our prepared glass is considered by us to be due to the presence of nanocrystalline particles/clusters (~10–30 nm size), confirmed from the transmission electron microscopic study. So ferroelectricity in pure single-phase oxide glass, we believe, has not yet been discovered.

The K-free BG-type multicomponent precursor glasses (referred to as MP) viz. $Bi_4Sr_3Ca_3Cu_4O_x$, $(Bi,Pb)_4Sr_3Ca_3Cu_4O_x$, etc.,[2–6] had been reported earlier to be superconductors in their annealed phases. As-quenched MP glasses are, however, not superconducting or ferroelectric. Elaborate transport and dielectric properties of the MP glasses studied earlier[2–3,6] did not show FE transition. Transmission electron microscopic (TEM) study of the MP glasses, however, indicated[2,3] the presence of nanocrystalline phase precipitated during glass formation. Interestingly, from TEM study we noticed that BG type glasses prepared by us with different concentration of K and showing FE behavior are not pure homogeneous single-phase glass, but they are all glass-nanocrystal composites (GNC). Therefore, the ferroelectric transition has not been observed in pure glass contradicting the result reported by Bahgat *et al.*[1] who reported ferroelectricity in a similar glass considered to be a pure homogeneous glass. Moreover, for appearing ferroelectricity in pure glass, the question of appropriate symmetry also remains unaddressed.

In the present comment our objective is to show that the K-doped BG glass prepared by us and showing FE behavior is not pure homogeneous glass as considered by Bahgat *et al.*[1] but this is a GNC. As the micro structural behavior of the BG-type glasses prepared by us with different Pb and K concentrations are found to be almost similar, in the present comment, we report the microstructural and dielectric behavior of a typical BG glass viz. $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_\delta$ similar to that prepared and reported by Bahgat *et al.*[1]

We prepared the K-doped BG glass viz. $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_\delta$ by quick quenching[2–3,6] from the high temperature melt (liquid phase) at 1150 °C in air. A similar method was also used by Bahgat *et al.*[1] to prepare the same glass but we believe the glass melting temperature 950 °C, reported by them, is very low (since 950 °C is much lower than the liquid phase temperature for making this glass). X-ray diffraction (XRD) analysis using CuK_α radiation confirmed the amorphous state of our glass obtained by melt quenching. The glass transition ($T_g \sim 673$ K), and crystallization ($T_x \sim 710$ K) temperatures observed from the DTA trace agree quite well, respectively, with those (667 and 717 K) reported by Bahgat *et al.*[1] for their prepared BG glass. An endothermic peak was observed around 526 K which indicated ferroelectric transition confirmed from the dielectric study [Fig. 3(a) discussed below]. All these features indicate that the network structure and composition of the BG glass prepared by us is similar to that of the glass prepared and studied by Bahgat *et al.*[1] showing ferroelectric transitions almost around the same temperature by both the glasses. Transmission electron microscopic study (with Model 1500, Hitachi, Japan) of the finely powdered glass sample on carbon grid clearly indicated the presence of microcrystals/clusters (10–30 nm size) shown in Figs. 1(a),1(b). Hence BG glass prepared by us is a glass-nanocomposite. Similar behavior is also shown by other BG-type glasses prepared and studied by us (not reported in this comment). As usual, these nanocrystals/clusters are not clearly detected from the XRD patterns due to their small size and low concentrations (low for x-ray detection) embedded in the glass matrix. These nanoclusters are not clustered in one portion of the glass but scattered all over the glass matrix covered by glassy phase.

Transport and dielectric studies of the K free BG type oxide glasses (termed as MP glass) viz. $Bi_4Sr_3Ca_3Cu_4O_x + Ag_2O$, $(Bi,Pb)_4Sr_3Ca_3(Cu,A)_4O_x$ (A = Cr,Mn,Fe), have been elaborately studied earlier.[2,3,7-10] These glasses showed (i) semiconducting behavior and no FE behavior was exhibited,[2,3,7-10] (ii) in the high-temperature region ($T > 285$ K $= \theta_D/2$, θ_D is the Debye temperature), the conduction process is dominated by thermally activated nearest

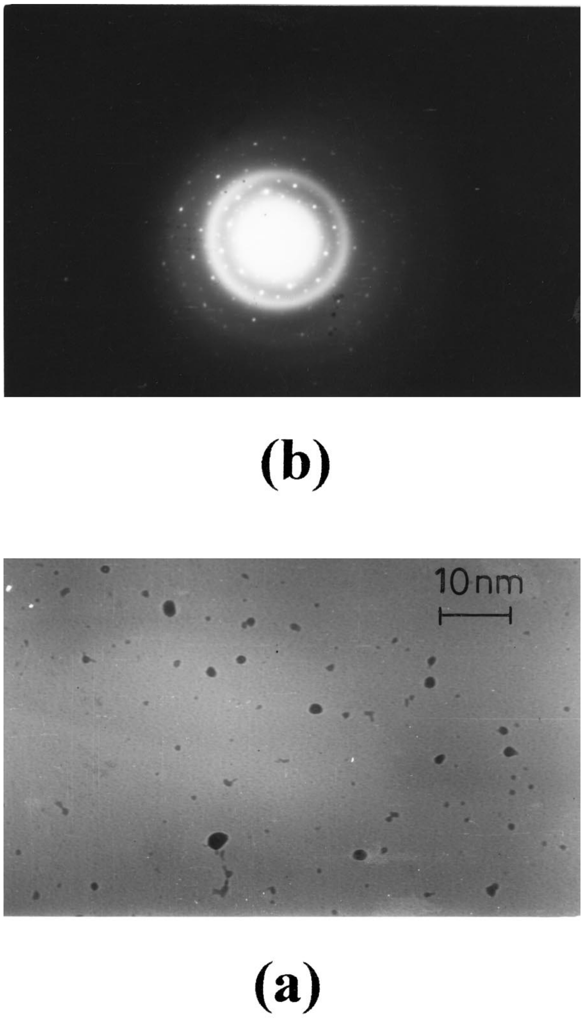

FIG. 1. (a) Transmission electron micrograph and (b) electron diffraction pattern of the BG glass $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_\delta$ (*prepared by us*) showing the presence of nanocrystalline structure.

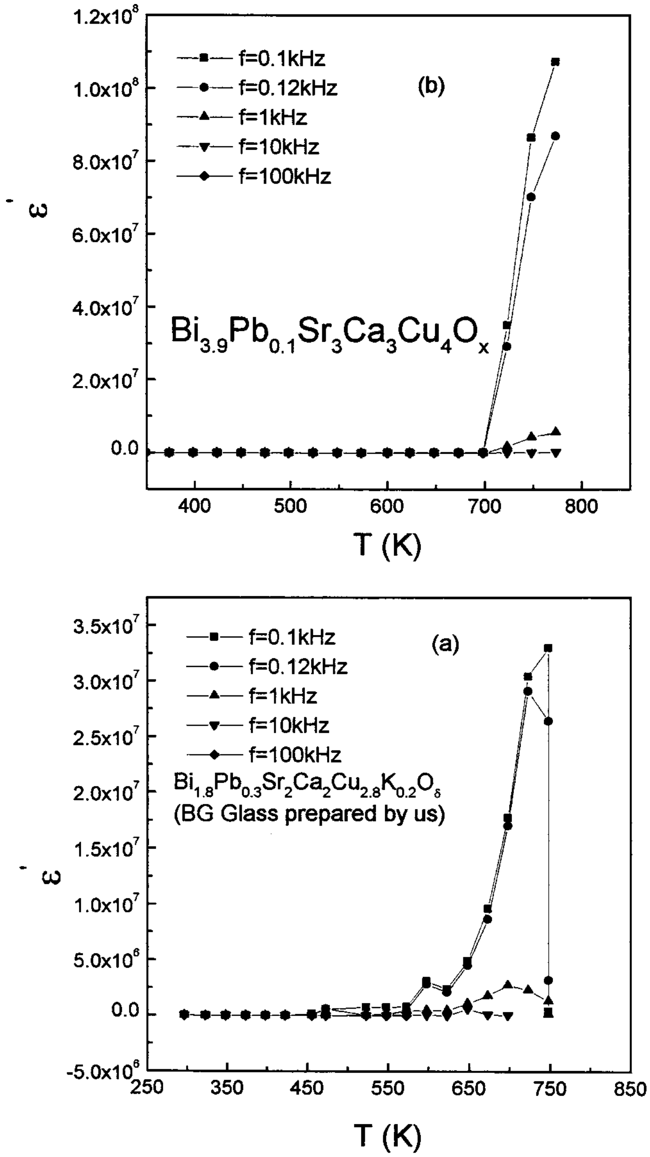

FIG. 2. Variation of the real part of dielectric constant ε' vs T of (a) our BG glass viz. $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_\delta$ and (b) a typical MP glass viz. $Bi_{3.9}Pb_{0.1}Sr_3Ca_3Cu_4O_x$ for different frequencies.

neighbor hopping of small polarons, (iii) below $\theta_D/2$, the variable range hopping conduction is valid, and (iv) these glasses are precursors for high T_c superconductors (i.e., become superconductors by annealing around 840 °C). Except the superconducting behavior in the annealed phase, the BG glass prepared by us is also found to exhibit all the above features (i)–(iii) as observed from the electrical transport property measurement (not shown in this comment and to be shown elsewhere).

Figure 2(a) shows the variation of dielectric constant of the BG glass, prepared by us, dispersed with nanocrystalline particles/clusters as a function of temperature for different frequencies 0.1, 0.12, 1.0, 10, 100 kHz. Dielectric behavior of a typical K free MP glass (viz. $Bi_{3.9}Pb_{0.1}Sr_3Ca_3Cu_4O_x$) which becomes superconductor by annealing is also shown in Fig. 2(b) for comparison. Interestingly, the maximum value of the peak temperature ($\sim$725–730 K) [shown in Fig. 2(a) for the BG glass prepared by us] matches with that obtained from the DTA curve by Bahgat *et al.*[1] The dielectric constant ε' (real part) values of our BG glasses are little larger than those of the multicomponent Bi-based MP glasses.[2,6] This is considered to be due to the presence of nanocrystalline phases embedded in the BG glasses with higher dielectric constants (lower conductivity). The dielectric constant data also follow the Curie-Weiss relation $\varepsilon' = C/(T-T_0)$, where C is the Curie Constant. T_0 is the extrapolated intersection of the high temperature part of the plot with the temperature axis as shown in Fig. 3(a). The value of $T_0(=467\,\mathrm{K})$ is also close to the value (470 K) observed by Bahgat *et al.*[1] for their prepared glass. The order of the transition is identified by finding the ratio of the slopes $\partial(1/\varepsilon)/\partial T$ below and above $T_c \sim 526\,\mathrm{K}$. The value of this ratio ($=-2.63$) indicates that the transition is of the first order type. This value of the slope in our sample is little smaller in magnitude from that of the glass prepared by Bahgat *et al.*[1] because of the slightly different network structure and density which is also reflected from the little different values of T_g and T_x from those obtained by Bahgat and

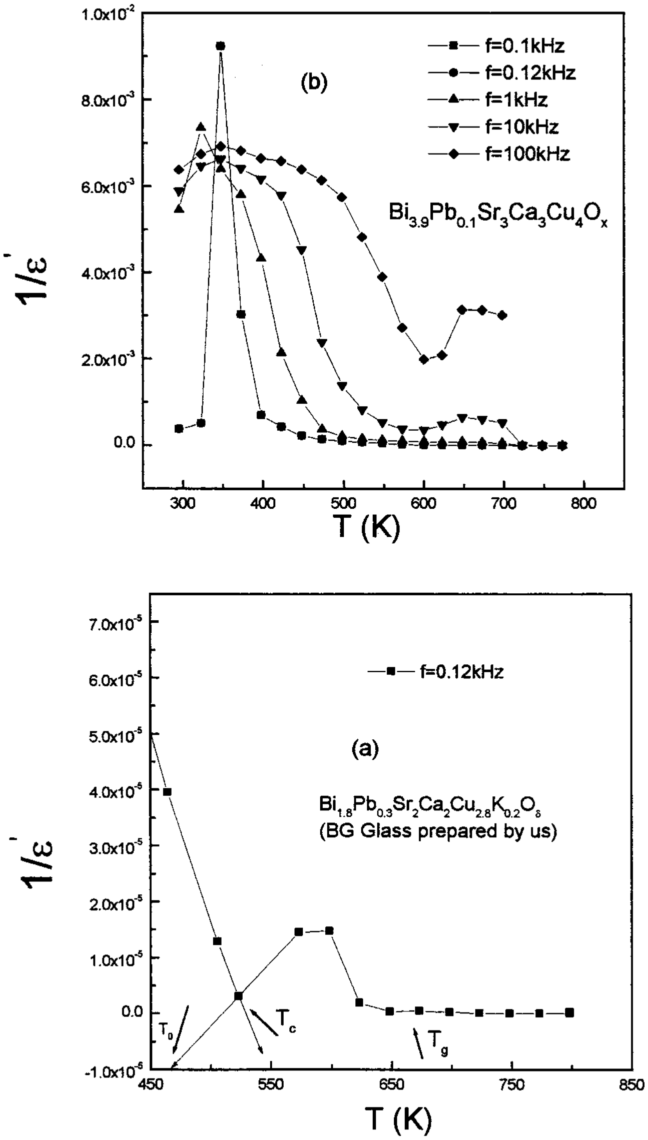

FIG. 3. Thermal variation of inverse of the real part of dielectric constant (ϵ') of (a) the BG glass viz. $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_\delta$ prepared by us and showing ferroelectric transition around 526 K *similar to that of the same glass prepared by Bahgat et al.* and (b) a typical K free MP glass viz. $Bi_{3.9}Pb_{0.1}Sr_3Ca_3Cu_4O_x$ which is not ferroelectric but becomes superconductor by annealing at 840 °C. The K containing glass does not become superconductor by annealing around 840 °C (unlike the corresponding K free glass).

co-workers. This type of difference is always observed in the two glasses of identical compositions prepared by the same or different groups, because of metastable glass structure and difference in size of the nanoclusters in the glasses. In the present FE system, slight difference of nanostructure and their concentration might also cause large difference in the FE behavior and hence the magnitude of the slope. Ferroelectric behavior of nanocrystals and dependence of ferroelectricity on the nanostructures have already been reported[11,12] in the literature. Regarding the order of transition, we should mention that in case of second order phase transition, T_0 is practically the same as the transition temperature or the Curie point T_c, while in case of a first order transition T_0 is lower than the Curie temperature T_c (=526 K) observed by us [Fig. 3(a)]. A similar result was also obtained by Bahgat *et al.*[1] for the same glass prepared and studied by them.

It is also interesting to mention here that the K-free glasses prepared by us are precursors for high-T_C superconductor (becoming superconductor by annealing, not discussed in this paper). The plot of $1/\epsilon'$ vs T for a typical K-free MP glass viz. $Bi_{3.9}Pb_{0.1}Sr_3Ca_3Cu_4O_x$ shown in Fig. 3(b), however, does not at all match with that of BG glass showing FE behavior [Fig. 3(a)] in its as-quenched glassy phases.

The following is finally concluded. (i) The glass prepared and studied by Bahgat *et al.*[1] which showed FE transition (first reported by Bahgat *et al.*[1]) is similar to that prepared and studied by us exhibiting similar FE properties. (ii) The BG glass prepared by us is a GNC and it is not a pure homogeneous and single-phase glass. In our opinion, the BG glass prepared by Bahgat *et al.*[1] should have similar nanostructural character. (iii) We consider that the presence of nanocrystalline phases embedded in the glass is responsible for the ferroelectricity in these GNC's. (iv) Because of the presence of nanocrystals in the glass, appropriate symmetry condition necessary for the appearance of ferroelectricity is satisfied in the nanoclusters embedded in the glass matrix. As mentioned above, the ferroelectric behavior in $PbTiO_3$ nanocrystals etc. has already been observed.[11,12] Each nanocluster acts as FE domain. Moreover, in the BG glass studied by us (similar to that prepared by Bahgat *et al.*[1]), superconducting behavior is suppressed (in their annealed phase such as MP glass) due to alkali metal (K) doping in the Cu site because of modification of the glass network structure. More elaborate microstructural and other studies on such glass-nanocrystal composites would be interesting.

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