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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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A glass sample of composition $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_z$ was prepared by the conventional quenched-melt technique. The as-quenched sample has been confirmed to be amorphous by x-ray diffraction measurements. The scanning electron microscopy shows no sign of crystalline grain precipitation. Differential thermal analysis indicates a prominent endotherm at 530 K in addition to the glass transition at 607 K and crystallization at 717 K and melting at 1043 K. This extra endothermic peak could possibly be identified as due to a ferroelectric to paraelectric phase transition. This possibility was explored by performing electrical measurements, which include dielectric constant trace, polarization, and hysteresis loops measurements as a function of temperature. It was also found that the transition is irreversible if the glass-transition temperature was reached.

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In recent papers, Zhang and Widom[1,2] proposed a mean-field theory that predicts ferroelectric phases in dipolar systems that lacked any specific spatial correlations, provided that the density of the particles was above a critical value. They considered an amorphous solid of dipolar hard spheres where the particles were free to rotate, but were frozen at random sites. Their prediction of ferroelectric phases in dipolar systems that lack any specific spatial correlations suggests that well-tuned short-range structure may not be necessary for ferroelectric phase formation. However, applying molecular dynamics and Monte Carlo computer simulations predicted that it is possible to have ferroelectric states without fine-tuned positional correlations.[3] It was predicted also that if a ferroelectric phase is to exist in a positionally random system, the long-range spatially independent correlations arising through the reaction field must dominate the short-range position sensitive correlations, which generally act to frustrate ferroelectric order.

In an older study, ferroelectric glass concept was studied with no objections found.[4] A simple microscopic model was set up, describing the possible occurrence of a ferroelectric instability in an insulating glassy matrix. In studying dielectric soft glasses such as $Pb_5Ge_3O_{11}$, $LiTaO_3$, and $LiNbO_3$ different behavior on approaching the crystallization temperature T_x is observed.[5,6] The first $Pb_5Ge_3O_{11}$ appears to be paraelectric throughout and the dielectric constant rises monotonically with increasing temperature to exhibit a sharp cusp at T_x. While $LiTaO_3$ has a similar response as a function of T except that the magnitude of the dielectric constant is much larger and anomaly at T_x is observed and may peak below the crystallization instability. If so, this could indicate the existence of a polar glassy phase. The $LiNbO_3$ glass, on the other hand, exhibits a double peaked anomaly with extremely high values ($>10^5$) for the dielectric constant. This indicates not only a polar glassy phase but also a polar glassy phase transition.[6] The possibility that the lower-temperature peak does indeed mark a ferroelectric Curie temperature T_c remains an intriguing possibility. However, the role of short-ranged spatial correlations on ferroelectric phase formation is still not well understood. Accordingly, the possibility of ferroelectric ordering in glassy state that has not been realized experimentally might not be impossible.

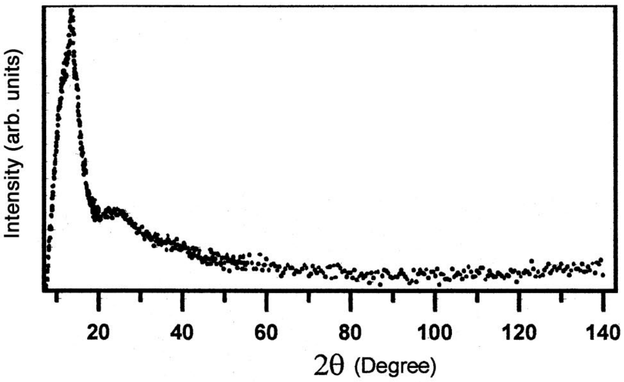
Although theoretical and experimental studies have been extended concerning the possibility of glassy ferroelectric, to our knowledge a bulky melt quenched glassy ferroelectric material was not made. Ferroelectricity reports on thin films, ball milled nanocrystalline powder, heat-treated glass ceramic, and sol gel can be found.[6–10]

In a number of recent systematic studies,[11–14] glass systems of the main former Bi_2O_3 were considered and applied to prepare melt quenched glasses as precursor to superconducting glass-ceramics. Glasses of compositions $Bi_4Sr_3Ca_3Cu_4O_{16}$ and $Bi_2Pb_{0.5}Sr_2Ca_2Cu_3O_y$ doped with Na shows many interesting dielectric properties, although without any anomalies.[13,14]

In the present work x-ray diffraction, scanning electron microscopy (SEM) and differential thermal analysis (DTA) were applied to identify the glassy nature of the sample. Dielectric constant ε, polarization P, and hysteresis loops (E-P) measurements were used to identify the electrical properties of the sample as a function of frequency and temperature.

A glass sample of the composition $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_z$ was prepared by the quenched melt technique from reagent grade Bi_2O_3, Pb_3O_4, $SrCO_3$, $CaCO_3$, CuO, and K_2CO_3. The batch was melted at 950 °C for 30 min during which the melt was stirred to improving the homogeneity. The melt was then poured and rapidly quenched between two copper plates; hammer and anvil. Sheets of opaque black glass samples (0.5 mm thick) were obtained. Grounded powder of the as-quenched glass sample was examined by x-ray powder diffraction using Mo-K_α radiation. Optical microscope of the polished surface of the sample, as well as scanning electron microscopy, using a JOEL-JSM-5400 scanning microscope were used to examine the surface of the glass sample for possible crystallization.

On the other hand, real ε' and imaginary ε'' components of the dielectric constant $\varepsilon^* = \varepsilon' + j\varepsilon''$ measurements were performed at the frequency range 0.12–100 kHz, and in the temperature range 300–700 K. Silver painted electrodes were pasted on the two faces of a polished sample. The di-



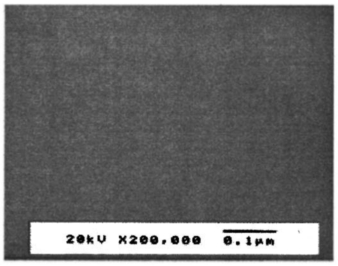


Plate 1

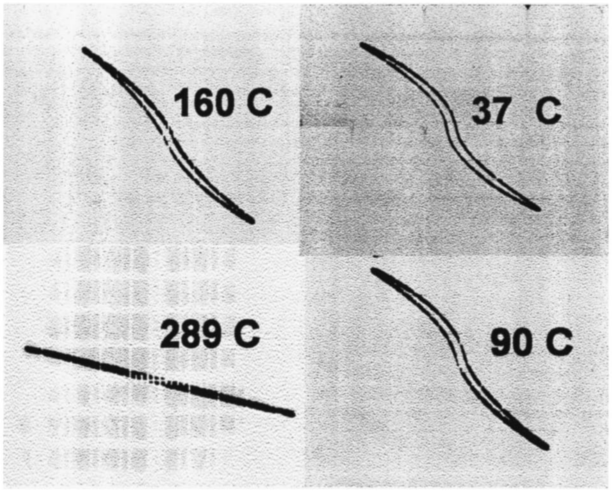


Plate 2

FIG. 1. X-ray diffraction pattern of the as quenched glass sample, using Mo-K_α radiation. Plate 1: SEM micrograph of the quenched glass sample. Plate 2: Representative hysteresis loops of the as-quenched glass sample at different temperatures indicated in °C, up to $T>T_c$. Applied frequency is 70 Hz and applied electric field is 1.5 kV/cm.

TABLE I. Important transition temperatures as obtained from the DTA thermogram for the as quenched glass sample. T_c is the Curie point, T_g is the glass transition, T_x is the crystallization, and T_m is the melting temperature, respectively.

T_c (K)	T_g (K)	T_x (K)	T_m (K)
530	607	717	1043

electric constant was obtained using a (RLC) bridge; Stanford Res. Model SR-720. The sample temperature was measured by a (chromal-alumal) type K thermocouple which is placed as close as possible to the sample. Ferroelectric hysteresis loops were observed using a Sawyer-Tower circuit[15] at temperatures up to 700 K and at a frequency of 70 Hz. The same circuit was used as well for the measurement of the temperature dependence of the polarization over the temperature range 300–700 K. The polarization as a function of electric field (E-P) characteristic was measured at room temperature under ac electric field of frequency 70 Hz with amplitude reaching 1.6 kV/cm.

Figure 1 shows the x-ray diffraction of the as-quenched glass sample. It can be seen that there are only the broad diffraction peaks characteristic of glassy structure. Similar patterns were obtained for glasses of comparable constituents.[11,12,14] On the other hand, a SEM micrograph is shown in plate 1. It is seen that there is no crystalline precipitation. A similar result was observed on comparable glass.[16]

The glassy state of the as-quenched sample was monitored also by DTA. The sample was heated from room temperature up to 900 °C with a rate of 20 °C/min. The DTA thermogram shows three different endothermic and one exothermic transitions. These where identified as a glass transition temperature (T_g), melting temperature (T_m), and an extra peak which is usually not observed with conventional glasses. This endothermic peak is at a temperature lower than T_g and is designated from the results of the present work as due to a ferroelectric to paraelectric phase transition (i.e., Curie's point T_c). A fourth peak that is exothermic indicates the crystallization temperature T_x of the glass. Table I summarize the results of the DTA measurement shown in Fig. 2(a). The DTA thermogram indicate that the endothermic peak at $T_c=530\pm2$ K, is due to a first-order phase transition while the sample is still in its glassy state, where $T_c \ll T_g < T_x$, as shown. Similar observation is familiar in the field of ferromagnetic metallic glasses.[17]

Usually a ferroelectric to paraelectric endothermic peak is observed in DTA thermograms only after devitrifying the amorphous samples.[9,10] It was also evident that the ferroelectric behavior depends on the size of the precipitating crystallites following heat treatment, where the transition at the Curie temperature T_c becomes increasingly diffuse and may vanishes with decreasing the grain size within the nanometer scale.[9,18,19] A comparable behavior is familiar in the field of superparamagnetic materials.

Figure 2(b) shows the variation of the dielectric constant as a function of temperature at different applied frequencies. It can be seen that there are mainly two different maximums with dielectric constant ranging from 6.3×10^4 to 1.6×10^5. The maximum at 525 ± 5 K is evidently an indication that the sample is not only in a polar phase but actually it is in a polar glassy phase transition. While the maximum at 606 K coincide with the inflection point of the DTA thermogram, Fig. 2(a) indicating the glass transition temperature. This observation may be explained on the basis of the microscopic model proposed by Glass *et al.*[6]

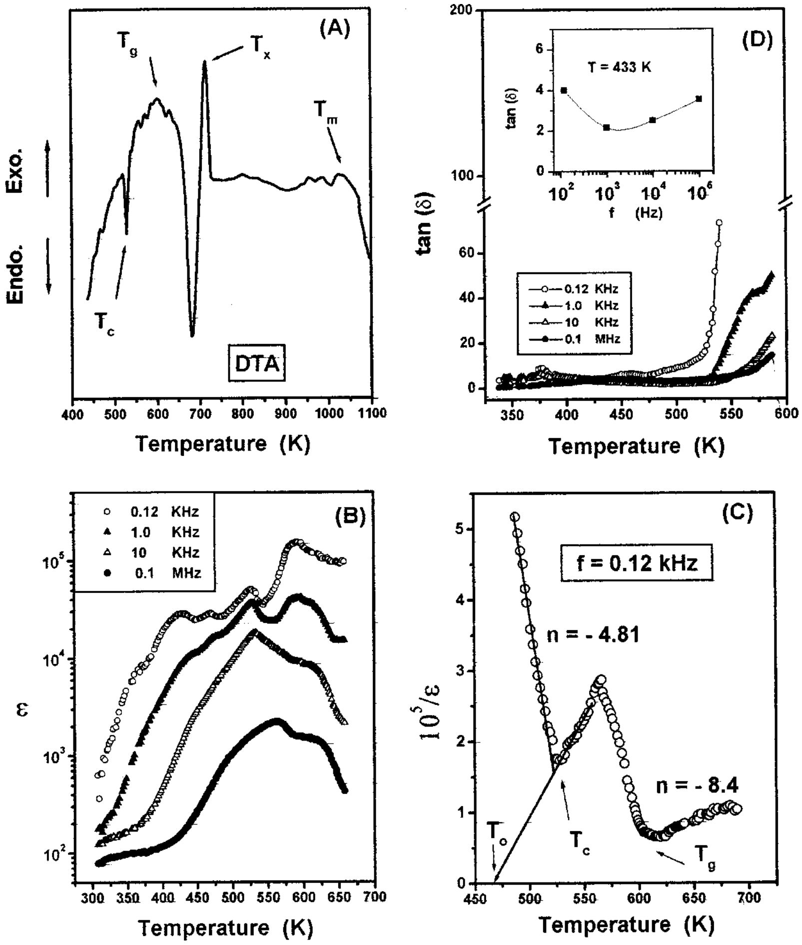


FIG. 2. Experimental results of the as quenched glass sample $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_z$. (a) The DTA thermogram, showing different transitions. (b) Dielectric constant as a function of temperature at applied frequency of 0.12–100 kHz. (c) Inverse dielectric constant as a function of temperature showing the values of n and T_0 of the Curie's Eq. (1) at frequency 0.12 kHz. (d) Loss tangent as a function of temperature, the inset shows a representative example of the variation of tan(δ) as a function of frequency.

The fact that DTA data shows an endothermic peak at this same temperature could support the conclusion that our glass sample is actually ferroelectrically ordered below 525 K, namely, the Curie point T_c. It is also evident from Fig. 2(b) that the temperature position of this dielectric peak maximum is almost frequency independent, indicating that there are insignificant relaxational effects.

On the other hand, the dielectric constant data could be treated according to the Curie-Weiss relation

$$\varepsilon = \frac{C}{T - T_0}. \tag{1}$$

Here $C = 3.87 \times 10^6$ K is the Curie constant and $T_0 = 470$ K is the extrapolated intersection of the high-temperature part of the plot with the temperature axis as shown in Fig. 2(c). However, to identify the order of this transition it is usually a general practice to find out the ratio n of the slopes $\partial(1/\varepsilon)/\partial T$ below and above T_c, which is $(n = -4.81)$, see Fig. 2(c). This value indicates according to the theory of Devonshire[20] that the observed transition is of first-order type in agreement with the above DTA results and is due to metastability at the transition. While if the same criteria is applied to the second peak at about 607 K which was identified as due to the glass transition T_g $(n = -8.4)$ indicating a clear first-order transition. It is observed that the Curie constant is one order of magnitude higher than the corresponding values of crystalline materials, e.g., $C = 1.8 \times 10^5$ K for $BaTiO_3$,[20] this may be due to the glassy nature of our sample.

Figure 2(d) shows the variation of the loss in terms of, $\tan(\delta) = \varepsilon''/\varepsilon'$. It is seen that the loss is of the same order of magnitude as observed usually in Bi-Cu glasses of comparable compositions [12,14,21]. While it increases considerably as the glass transition temperature, T_g, is approached. On the other hand as can be seen from the insert of Fig. 2(d) the loss is almost frequency independent at 434 K, indicating insignificant relaxation effects.

Plate (2) shows representing examples of the hysteresis loops as a function of temperature. It is seen that the loops collapse as the temperature is increased up to the Curie point. These loops prove the ferroelectricity nature of the present as quenched amorphous sample. It was also found that the transition is reversible if the glass transition temperature T_g was not reached.

On the other hand Fig. 3(a) describe the behavior of polarization as a function of temperature according to the relation [4]

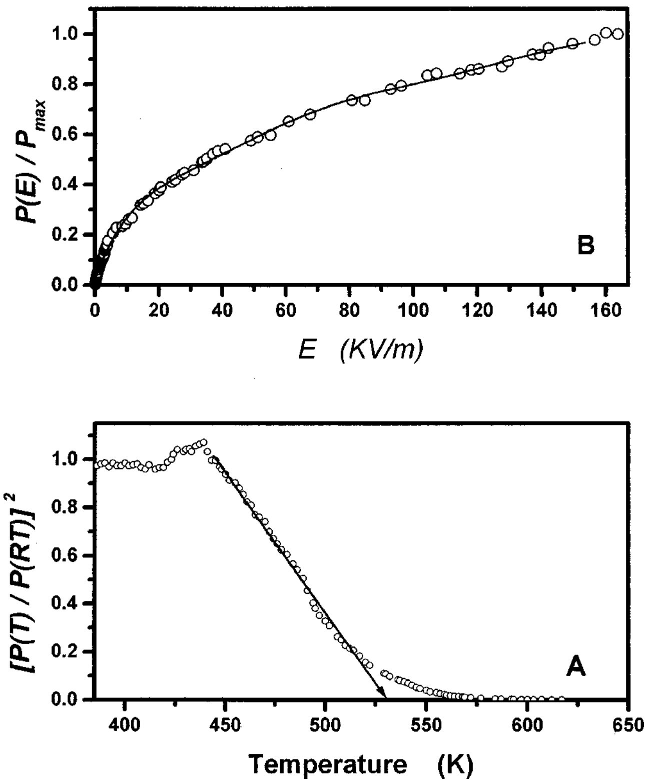


FIG. 3. (a) Reduced polarization as a function of temperature according to Eq. (2) of the as-quenched glass sample, showing the intersecting Curie's temperature with $P(RT)=0.23\,\mu\mathrm{C/cm^2}$. (b) Room temperature variation of the reduced polarization $[P(E)/P_{\max}]$ as a function of the applied ac field at 70 Hz, as obtained using the Sawyer and Tawer circuit (Ref. 15), with $P_{\max}=0.26\,\mu\mathrm{C/cm^2}$.

$$\frac{P(T)}{P(RT)}=\left[\frac{T_c-T}{T_c}\right]^{1/2}, \tag{2}$$

where $P(RT)=0.23\,\mu\mathrm{C/cm^2}$ at room temperature, the straight curve intersects with temperature axis at the Curie temperature T_c, which is almost the same as obtained following the above techniques.

Figure 3(b) however, shows the room temperature variation of the reduced polarization with $P_{\max}=0.26\,\mu\mathrm{C/cm^2}$, as a function of the applied ac field at 70 Hz. It can be seen that as the field is increased the corresponding polarization increases to saturate at much higher fields. A similar behavior characterizes clamped ferroelectric materials.[22]

In conclusion it is evident that the as-quenched glass of the chemical composition $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{2.8}K_{0.2}O_z$ prepared by the melt-quenching technique possibly shows clear ferroelectric properties. The Curie temperature at 530 K is lower than the glass-transition temperature, i.e., $T_c<T_g$, with no trace of crystallization. It was also found from the dielectric measurements that the transition (ferroelectric↔paraelectric) is reversible if T_g is not reached. This indicates that the ferroelectric ordering may have an origin due to residual microstresses developed during quenching of the glass melt. However, ferroelectrics such as ours may be explained by the presence of dipole inhomogeneity. The inhomogeneity is either ascribed, first to the composition fluctuation, which is almost macroscopic in scale. Secondly to the fluctuation in chemical ordering, which is intermediate in length scale. And thirdly to glassy dipolar frustration of the microscopic (ferroelectric or antiferroelectric) ordering of ions whose scale is of the order of the glass network.

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