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Ferroelectricity in the glassy material of the composition Bi_2O_3–Pb_3O_4–CuO–K_2O

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ABSTRACT

Glass sample of the composition 31.4 Bi_2O_3–2.33 Pb_3O_4–64.53 CuO–1.74 K_2O in mol% was prepared by the conventional quenching melt technique. The as-quenched single phase glass shows interesting ferroelectric properties which is not known in the field of glass science. If the as-quenched glass is heat treated above the glass transition temperature all signs of ferroelectricity disappears completely. X-ray diffraction and transmission electron microscopy as well as differential thermal analysis were used to recognize the glassy nature of the as-quenched sample. Ac dielectric measurements were performed as a function of temperature and frequency and showing ferroelectric to paraelectric phase transition at Curie's temperature of 540 K. Non-linear polarization as a function of temperature and applied electric field as well as pyroelectricity were also studied. The conduction mechanism was confirmed to obey the adiabatic small polaron hopping (SPH) and was mainly due to electronic transport between Cu ions. The dominant factor determining conductivity was the hopping carrier mobility in this glass. From the best fits, reasonable values of various SPH and VRH parameters are obtained.

1. Introduction

Since the development made by Duwez [1] and the following success on magnetic metallic [2] and oxide glasses [3], it was a challenge to the scientific community to achieve an equivalent achievement in the field of ferroelectric glassy material. This is due to, on one hand, to the novelty of the problem and the opportunity of manufacturing new materials with unusual properties. On the other hand, by the potentiality of their application in science and engineering. However, basically in ferromagnetic glassy material the magnetic moments can interact within a short range to develop spontaneous alignment and the overall interaction shows ferromagnetic properties. On the other hand, this criterion does not apply to ferroelectric interaction, where a long-range electrical dipoles interaction is necessary; such condition is not fulfilled in a glassy network. Along the years major questions stimulating the study of this type of material were considered, firstly: Does the spontaneous ferroelectric state in homogeneous glass materials is possible? Secondly: How disturbance of the long-range, average-range and short-range order in the arrangement of atoms have an influence on the physical properties of this class of materials? It is necessary to emphasize on that; glassy materials are those amorphous materials showing a glass transition temperature T_g with random distribution of atomic arrangement and short-range order, SRO [4].

Lines [5,6] put forward the first microscopic model, describing the possible occurrence of a ferroelectric instability in an insulating glassy matrix. Using the effective-field theory of statistical mechanics which describe the physical mechanism whereby a dielectric instability might be produced in a glass. This possibility of spontaneous dipolar ordering in bulk amorphous materials prepared on the bases of polar dielectrics was theoretically predicted. According to his model, with great probability one could expect a transition to the macroscopic polar state in those amorphous materials that were prepared by rapid melt quenching of many-axes ferroelectrics, having a high value of spontaneous polarization, for example in $PbTiO_3$. Finally it was noted that in view of the presence of the frozen-in dipoles, these dielectrically soft glasses, whether ferroelectric or not, will show a strong dielectric anomaly at the crystallization temperature. This is due to the decreasingly “frozen” character of the local dipoles as the crystallization instability is approached from below. However, till recently there were no experimental works, in which Lines theory would be reliably enough and explicitly confirmed [5–7].

In a more recent papers, Zhang and Widom [8,9] 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

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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, Ayton et al. [10,11] applied molecular dynamics and Monte Carlo computer simulations predicted that it is possible to have ferroelectric states without fine-tuned positional correlations. 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.

Recently in our series of publications [12–14] it was possible for the first time to demonstrate ferroelectricity in a single phase metastable glassy material namely $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{3-x}K_xO_z$ (x = 0.1–0.4) having spontaneous polarized state. In these publications we put forward another hypothesis [12–14]. According to our original assumptions a ferroelectric state in the investigated glassy materials arises during the manufacture of the bulk glassy samples by ultrarapid melt quenching. Therefore, a polar texture is under anisotropic mechanical stresses induced by melt quenching. This stress induced poling process ought to strain which aligns the internal dipoles within the glass network in a long-range interacting manner and causes it to act very similar as in a crystal, even so the atomic arrangement in the glass structure remains random. This stress-strain induced poling cease completely if the glass sample was annealed at or above the glass transition temperature [12–14] where the glass network is completely relaxed and all microstresses are released. As a result of the ultrarapid quenching a displacement of alkaline cations due to induced strain, e.g., K^+ and probably Ca^{2+}, to off center positions within the glassy network would takes place. This behavior will lead to the ferroelectric performance of the studied material. On the basis of the above and according to the microscopic theory of glasses the quenched state of the glass structure cannot be regarded simply as an arbitrary relaxed glassy random state. This state has very special properties because it is produced by a glass forming quench. The state of the glass is in a metastable phase of equilibrium that is produced by the rapid quenching of a liquid, which suppresses single particle rearrangements. We may therefore state that the main restructuring process which creates this state of the glass is a hierarchy of solid-like structural buckling processes controlled by the internal stress fields in the glass [15].

Verification of these results of ferroelectricity in glasses of the same composition were published recently [16–20]. However, according to transmission electrons micrographs, TEM, Mukherjee et al. [16–18] interpreted the confirmed ferroelectricity as due to nanocrystalline clusters 10–50 nm in size [16–18] containing particles of size less than 10 nm precipitated in their own samples. This interpretation was put forward without any definite theoretical or experimental prove that these nanocrystals are the origin of the observed ferroelectricity. According to these studies [16–18] it is interesting to note that the obtained devitrified state do not show any sign of ferroelectricity or superconductivity. However, it may show superconducting properties under special conditions of crystallization [21,22]. Furthermore, by applying Maxwell–Wagner polarization of heterogeneous components [14] on Mukherjee et al. micrograph results [16–18], it was predicted that the observed ferroelectricity is duo to the glassy part of their sample [14]. In other publications by Geridnev and Repnikov [19,20] ferroelectricity was confirmed further in a similar set of samples, $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_{3-x}K_xO_z$ (x = 0.1–0.4), by applying nonlinear dielectric measurements. It was revealed that the value of the dielectric constant decreased by a quadratic law as biased dc field strength is increased. Such behavior of the dielectric permittivity under external bias electric field speaks in favor of a dielectric nonlinearity, which can be described in frames of a thermodynamic theory of ferroelectricity [19,20].

On the other hand, the hypothesis put forward by us [12–14] concerning the effect of the residual microstresses as due thermal quashing on the local dipolar ordering was examined and explicitly confirmed on thin Quasi-amorphous films of $BaTiO_3$ [23,24]. Nevertheless, the generation of electric polarization in an insulating crystalline solid by an elastic strain gradient is referred to as the flexoelectric effect [25].

Alternatively, the dc conductivity of transition metal oxide (TMO) glasses has been targeted for extensive studies [18,26–32] because of their interesting semiconducting properties as well as for their probable technological applications. The conduction mechanism in these glasses was understood by the small polaron hopping (SPH) model [33–35] based on strong electron–lattice interaction. The experimental results of conductivity and other transport properties of many borate glasses containing transition metal ions supported the SPH model [31–36]. At low or intermediate temperatures (below $\theta_D/2$, θ_D: the Debye temperature) where polaron binding energy is less than kT (k is the Boltzmann constant and T is the absolute temperature), the three-dimensional (3D) variable-range hopping (VRH) [33,36] with $T^{1/4}$ dependence of conductivity σ takes place. The VRH was reported for V_2O_5–NiO–TeO_2 [25] and V_2O_5–BaO–B_2O_3 glasses [30]. VRH was reported in BaO–CaO–Fe_2O_3–P_2O_5 glasses [31] as well. However, we reported recently the nature of polaron hopping mechanism (adiabatic or non-adiabatic) in a series of glasses and glass–ceramic nanocrystals of V_2O_5–$BaTiO_3$ series [37]. It should be mentioned that the above two models were based, in common, on a single phonon approach.

In the present work the electrical and ferroelectric properties of a single phase glass sample with the composition 31.4 Bi_2O_3–2.33 Pb_3O_4–64.53 CuO–1.74 K_2O in mol% is examined with the least number of chemical components and showing the ferroelectric properties.

2. Experimental

In the present work a glass sample of the compositions 31.4 Bi_2O_3–2.33 Pb_3O_4–64.53 CuO–1.74 K_2O in mol.% was prepared by the quenched melt technique from reagent grade Bi_2O_3, Pb_3O_4, CuO and K_2CO_3, respectively. The batch was mixed and melted in a platinum crucible at 1000–1050 °C for 30 min during which the melt was stirred to improve the homogeneity. Further increase of the melting temperature above 1050 °C may cause a loss of Bi_2O_3 as due to volatilization. The melt was then poured and rapidly quenched between two copper plates; hammer and anvil. Sheets of opaque black glass samples of 0.5 mm thick were obtained. X-ray diffraction, transmission electron microscopy (TEM) and differential thermal analysis (DTA) were applied to identify the glassy nature of the sample. Dielectric constant, dc and ac electrical conductivity, polarization (P), hysteresis loops ($E-P$) and pyroelectricity measurements were used to identify the electrical properties of the sample as a function of frequency and temperature.

Grounded powder of the as-quenched glass sample was examined by X-ray powder diffraction (XRD) using Cu Kα radiation. Optical microscopy of the polished surface of the sample as well as TEM, using a JOEL-JEM-1010 transmission electron microscope (600,000×) were used to examine the glass sample for possible crystallization. Dc electrical conductivity, σ_{dc}, was measured by the two probe technique as well. Silver painted electrodes were pasted on the two faces of a polished sample. On the other hand, real ε' and imaginary ε'' components of the dielectric constant were performed in the frequency range 0.12–100 kHz and in the temperature range 300–700 K. The ac measurements were obtained using CRL Bridge, Stanford Res. Model SR-720 which is computer controlled. On the other hand the dc conductivity was measured with the aid of HP-425A electrometer. 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 at temperatures up to 600 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 300–600 K. In all these experiments the heating rate was 2 K/min. 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 15 kV/cm. Pyroelectric current was measured on a previously poled sample (24 V) which was cooled from 570 K to room temperature. The specimen was heated again from room temperature up to 570 K