

Electroinduction of Peculiar Space-Charge Regions in Fully-Glassy Lead Oxyfluoroborate Materials Discerned from Impedance Spectroscopy

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Abstract Lead oxyfluoroborate ($\text{BO}_{1.5}\text{-PbO-PbF}_2$) glasses were prepared and studied in this work in terms of dielectric response. By applying impedance spectroscopy, this study shows that electric field-induced peculiar space-charge regions form in these glasses, in the bulk adjacent to the glass–electrode interfaces. In addition, submission of these glasses to the action of a long-term electric field results in development of surface crystallization, even below the glass transition temperature. Evidence has been given in the literature that such a phenomenon involves electric field-induced redox-type electrochemical reactions that develop, simultaneously, at both glass–electrode interfaces, promoting $\beta\text{-PbF}_2$ crystallites nucleation toward the cathode side. Accordingly, it is here concluded that the above mentioned space-charge regions should incorporate those electroactive species that look forward to participate in the redox reactions that subsequently promote incidence of this non-spontaneous crystallization phenomenon.

Keywords Lead oxyfluoroborate glasses · Electrocrystallization · Dielectric properties · Space-charge effects

1 Introduction

Glassy materials with high ionic conductivity have been so far extensively investigated due to their wide applicability in the manufacture of electrochemical devices such as batteries, fuel cells, sensorial elements, etc. [1, 2]. When compared to ion-conducting ceramics, the interest on glasses arises from the simplicity and low cost of their production and the particular fact that, owing to their high homogeneity, fully-glassy materials are expected to show higher conductivities than ceramics of comparable bulk ionic transport strength. This is because semiblocking-like grain-grain contacts in ceramics have, in general, the effect of limiting strongly the overall ionic current across such polycrystalline materials [3, 4]. Prevalence of this deleterious effect may be verified via application of impedance spectroscopy during the electrical characterization of materials, a technique which makes possible the identification and separation of bulk versus interfacial dielectric processes in materials [3, 4]. The present study was focused on assessing the dielectric response of lead oxyfluoroborate ($\text{BO}_{1.5}\text{-PbO-PbF}_2$) glasses by considering the application of this technique. These materials have been treated in recent works [5–7], showing incidence of non-spontaneous crystallization phenomena, even below the glass transition temperature (T_g), when subjected to the action of a long-term electric field. These works have shown that these singular crystallization events involve, indeed, occurrence of electric field-induced redox-type electrochemical reactions that develop at both the cathode and anode electrodes, resulting in $\beta\text{-PbF}_2$ crystallization finally toward the cathode side [6, 7]. The purpose of this work was to investigate how these glasses dielectrically act in response to the action of the electric field in the stage preceding the electrocrystallization manifestation. Here, evidence is given on the formation,

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in this very early stage, of peculiar space-charge regions in these glasses, close to the electrodes. These space-charge regions show a dynamic nature under strength or polarity variation of the poling electric field.

2 Experimental Procedure

This work was conducted on melt-quenched glasses with the $50\text{BO}_{1.5}\text{--}35\text{PbO}\text{--}15\text{PbF}_2$ composition, hereafter abbreviated as BPP15, showing glass transition and crystallization temperatures of $T_g \cong 258\text{ }^\circ\text{C}$ and $T_x \cong 380\text{ }^\circ\text{C}$, respectively, as was previously reported [5, 7]. Crystallization tests and dielectric measurements were performed on Pt,Ag/BPP15/Ag,Pt-type cells subjected to different conditions of annealing time and electric field strength (see text), over temperatures ranging between 150 and 240 °C. In the above cell configuration, Ag refers to the electrodes directly fabricated out on the samples, while Pt represents thin plate electrodes from the external set-up. For the analysis of the (micro)structural and dielectric evolution of the samples during and/or after annealing, this work considered application of optical microscopy (Leica MZ12.5) and impedance spectroscopy (IS) (Solartron SI 1260) analysis techniques, this latter involving impedance measurements conducted over a wide frequency range, from 1 Hz to 1 MHz. In the following, the impedance data, $Z^*(\omega) = Z'(\omega) - jZ''(\omega)$, were graphically analyzed by using complex Z'' versus Z' plane plots, converted here into resistivity (ρ'' versus ρ') for comparison purposes, where $\rho^*(\omega) = Z^*(\omega) \cdot L$ ($L = A/h$: samples' geometrical factor; A : surface area and h : thickness).

3 Results and Discussion

Figure 1(a) illustrates a photographic image of an as-prepared BPP15 glassy sample, showing a totally transparent appearance, as expected. In the following, an IS study was conducted on such fully-glassy samples. Figure 2 shows IS data measured on a glassy sample in two different situations, while being annealed at 180 °C. That is, Fig. 2(a) refers to a spectrum recorded at a given time of dielectric measurements, by applying an alternating current (ac) electric field of $E \cong 1.0\text{ V/mm}$. Thereafter, the plan was to apply an additional direct current (dc) electric field (i.e., bias) of +5.0 V (giving $E \cong +5.0\text{ V/mm}$), for just 1 s, before performing the subsequent data record (i.e., without the bias) whose results are presented in Fig. 2(b). In terms of impedance data interpretation, we just recall, according to the ideal Debye model (that was found to be here applicable as a good approximation), that occurrence of a semicircle in complex Z'' versus Z' -like plots is characteristic of a parallel resistance-capacitance ($R_o\text{--}C_o$) network,

Fig. 1 Photographic images of (a) an as-prepared BPP15 glassy sample, and (b) a BPP15 sample after annealing at 150 °C with a dc electric field of $E \cong 3.8\text{ V/mm}$ applied, for 48 h

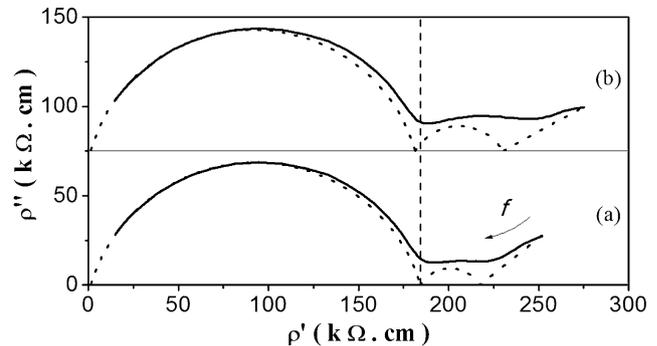
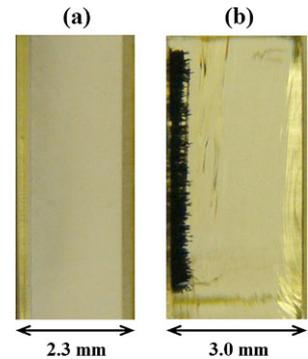


Fig. 2 Complex resistivity spectra (ρ'' vs. ρ') measured on a BPP15 glass sample at 180 °C, with an ac field of $E = 1.0\text{ V/mm}$ (a) before and (b) just after submission of the sample to a constant (dc) bias of +5 V/mm, for 1 s

to which corresponds an impedance expression of the type: $Z^*(\omega) = [R_o/(1 + \omega^2\tau^2)] - j[\omega\tau R_o/(1 + \omega^2\tau^2)]$, where $\omega = 2\pi f$, $\tau = R_o C_o = 1/2\pi f_o$ is the relaxation time and f_o the relaxation frequency (frequency at the semicircle maximum) [3, 4].

All the complex resistivity spectra presented in this work were analyzed on the basis of near-Debye model (including consideration of the constant-phase element [3], fairly reducible here to the ordinary capacitor), together with the well-established criterion of magnitude order of capacitance for identifying origin of dielectric responses from materials [3, 4]. In both Fig. 2(a) and (b), concretely, a semicircle is resolved toward the highest frequencies, and involved C_o values of $\sim 10^{-11}\text{ F}$, being attributable to the dielectric response from the glass bulk [3, 4]. From the expression given above, moreover, one deduces that the diameter of an impedance semicircle basically reduces to R_o . Accordingly, the bulk resistivity in both the situations shown in Fig. 2 remains unchanged ($\rho_o \cong 183.9\text{ k}\Omega\text{ cm}$). This result and, especially, the fact of observing also an unaffected value of the intrinsic relaxation frequency ($f_o \cong 133\text{ kHz} \Rightarrow \tau_o \cong 1.2\text{ }\mu\text{s}$ in both situations) are to be expected in cases of basically unchanged physico-chemical properties of the glass bulk during annealing.

Still with respect to Fig. 2(a) and (b), an impedance spike-like response (theoretically interpretable as a semicir-

cle with a very high diameter and, thus, high associated resistance or resistivity) is resolved toward the lowest frequencies, and involved C_o values of $\sim 10^{-5}$ F, typical of material-electrode interface contribution [3, 4]. In this work, we were especially concerned with the second semicircle appearing toward the intermediate frequencies, for which C_o values of $\sim 10^{-8}$ F were estimated, attributable to surface layer-like effects [3, 4]. In dielectric studies of glasses, observation of impedance spectra consisting of two [6, 8, 9] rather than a single [10, 11] semicircles is normally attributed to a partially-crystallized state of the glasses. This is not here the case, provided that the IS experiments were in this work conducted on fully-glassy BPP15 samples. In other words, there is in principle no reason to link this intermediate-frequency semicircle to either glass-crystal or grain-boundary interfaces, as may apply for glass-ceramics. In fact, different from [5], we rather verified here, after repeated experiments, that BPP15 samples showing Fig. 2-like spectra did not always manifest detectable sign of crystallization (according to microscopy and XRD observations), depending on the annealing time before switching off the electric field. Note in this Fig. 2, moreover, that while the characteristics of the high-frequency bulk semicircle remain independent on application or not of an additional dc bias, the diameter of the semicircle located toward the intermediate frequencies increases after application of an enhanced dc electric field.

To advance this discussion, we chose to also examine how the impedance response of these materials behaves after application of an identical but inverted additional dc bias of -5.0 V (giving $E \cong -5$ V/mm), also for just 1 s. The results are shown in Fig. 3, noting that the present experiment was performed sequentially after that whose results were shown in Fig. 2. Once again, there is no variation of the high frequency-semicircle (resistivity and relaxation time) characteristics, while the diameter of the intermediate frequency-semicircle shows initially a decrease, followed by an increase after subsequent application of the same dc bias. These results, involving variable quantitative characteristics (diameter) of an impedance semicircle, depending on bias strength and polarity (Figs. 2 and 3), are indicative that this second semicircle should involve electric field-induced dynamic space-charge regions that form in such materials, close to the electrodes. In particular, a competition between space-charge formation and enhancement, after application of an improved dc electric field, versus charge redistribution from one to another electrode, according to the direction of the applied electric bias, should account for the complex quantitative behavior of this semicircle. We note that despite these variations, the relaxation time associated to this semicircle also remained basically unaffected ($\tau_o \cong 0.9 \pm 0.2$ ms in most cases, i.e., a discrepancy of about 22%, which remains within the measuring error margins fittingly expectable in IS), indicating as well an

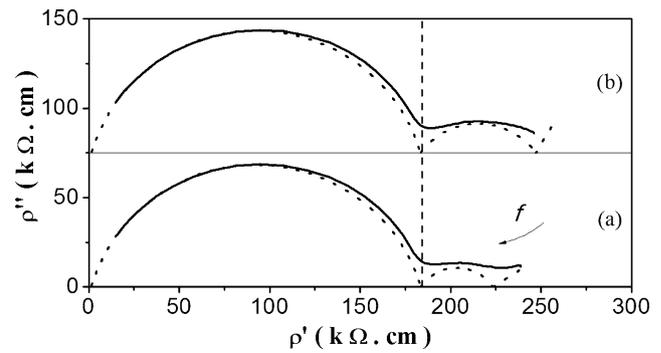


Fig. 3 (a)–(b) Complex resistivity spectra (ρ'' vs. ρ') subsequently measured on a BPP15 glass sample as a continuation of Fig. 2 experiment. That is, these data were sequentially recorded at 180°C , with an ac field of $E = 1.0$ V/mm, just after submission of the sample to a constant (dc) bias of -5 V/mm, for 1 s

unchanged intrinsic nature of these postulated space-charge regions, as would be in fact supposed.

It is important to emphasize here, as well discerned in literature [6, 8, 9] and commented above, that manifestation of such a second semicircle turns to be normally real only when dealing with partially-crystallized glasses. We should, however, point out that occurrence of this semicircle in totally-glassy systems has been usually noted, in our laboratory, only in those systems showing a trend to electrocrystallization. (This excludes, for instance, the case of fluoride-free lead borate glasses.) For the BPP15 glass materials studied in this work, Fig. 1(b) illustrates a photographic image of a sample after electrical treatment at 150°C (relatively far below T_g) with a direct current (dc) electric field of $E \cong 3.8$ V/mm, for 48 h. This shows that electric field-induced crystallization developed at the sample surface that remained in contact with the cathode electrode. In recent works [5–7], the crystalline phase appearing in this material has been identified as $\beta\text{-PbF}_2$, while being demonstrated that incidence of this nonspontaneous crystallization involves indeed the following simultaneous redox-type electrochemical reactions [6, 7]: $\text{Pb}^{2+} + e^- \rightarrow \text{Pb}^+$ (followed by $\text{Pb}^+ + e^- \rightarrow \text{Pb}^0$) at the cathode and $2\text{F}^- \rightarrow \text{F}_2(\text{g}) + 2e^-$ at the anode. The subsequent formation of nuclei at the sample surface is believed to most likely arise from a glass viscosity decrease toward the cathode side due to ion reduction [12–14].

All the above results allow concluding that the intermediate frequency-semicircle-related dynamic space-charge regions identified in this work from impedance spectroscopy (Figs. 2 and 3) should incorporate those electrical species compromised with incidence of the redox-type electrochemical reactions that are finally responsible for the development of electrocrystallization in these glasses. Considering that the fluoride ions are the main charge carriers during electrical transport in oxyfluoroborate-based glasses [15–17], therefore, the suggestion is that these space-charge

arrangements should be rich in fluoride ions toward the anode, these species looking forward the opportunity to oxidize, a reaction that is expected to be simultaneously compensated, at the cathode, with the lead cation reduction that induces directly the surface crystallization. Complementary dielectric studies are in progress in order to get further insights into this issue. At present, in particular, it is reasonable to observe that the relocation of the space charge from one to another electrode after electric field inversion, as deduced from analyzing Figs. 2 and 3, is concomitant with development of this non-spontaneous crystallization at finally both glass surfaces for a long-term ac experiment, as was advised in [5].

4 Conclusions

In summary, this work has verified that when subjected to the action of a long-term electric field, surface crystallization truly occurs in lead oxyfluoroborate ($\text{BO}_{1.5}\text{-PbO-PbF}_2$) glasses toward the cathode side. Moreover, application of impedance spectroscopy allowed identifying the formation of peculiar space-charge regions extending into the fully-glassy bulk material toward the electrodes, that is, in the stage preceding crystallization development. These space-charge arrangements show to be dynamic in nature, and should incorporate those electroactive species that are expected to participate in the redox reactions invoked elsewhere to finally electroinduce crystallization. Accordingly, impedance spectroscopy experiments reveal to be, therefore, an excellent procedure that may help monitoring real-time evolution of such glassy systems to electrocrystallization.

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