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Fluoride-modified electrical properties of lead borate glasses and electrochemically induced crystallization in the glassy state

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Lead fluoroborate glasses were prepared by the melt-quenching technique and characterized in terms of (micro)structural and electrical properties. The study was conducted on as prepared as well as temperature- and/or electric field–treated glass samples. The results show that, in the as-prepared glassy-state materials, electrical conductivity improved with increasing the PbF2 glass content. This result involves both an increase of the fluoride charge carrier density and, especially, a decrease of the activation energy from a glass structure expansion improving charge carrier mobility. Moreover, for the electric field–treated glass samples, surface crystallization was observed even below the glass transition temperature. As previously proposed in literature, and shown here, the occurrence of this phenomenon arose from an electrochemically induced redox reaction at the electrodes, followed by crystallite nucleation. Once nucleated, growth of β-PbF2 crystallites, with the indication of incorporating reduced lead ions (Pb+), was both (micro)structurally and electrically detectable and analyzed. The overall crystallization-associated features observed here adapt well with the floppy-rigid model that has been proposed to further complete the original continuous-random-network model by Zachariasen for closely addressing not only glasses’ structure but also crystallization mechanism. Finally, the crystallization-modified kinetic picture of the glasses’ electrical properties, through application of polarization/depolarization measurements originally combined with impedance spectroscopy, was extensively explored. © 2008 American Institute of Physics. [DOI: 10.1063/1.2885342]

I. INTRODUCTION

Solid materials such as glasses, polymers, and oxide ceramics with high ionic conductivity have always attracted the attention of researchers due to their wide applicability in electrochemical devices such as batteries, fuel cells, sensorial elements, and displays.1,2 In particular, when compared to ceramic materials, for instance, the interest in glassy materials also arises from the simplicity and low cost of their production. In this way, the study of ionic conductivity of fluoroborate glasses has been considered,3–5 showing the fluoride ions to be the highly mobile and main charge carriers.4,5 For executing the above-ensised application functions, any way, the materials have to be subjected to electric fields or atmosphere ambient gradients to induce electromigration through ion transport. However, nonspontaneous, electrochemically stimulated crystallization of glasses has been observed elsewhere. This is the case of surface crystallization observed in fresnoite (Ba2TiSi2O8) containing BaO-TiO2-SiO2-B2O3 and lithium niobate (LiNbO3) containing Li2O-Nb2O5-SiO2 glass ceramics.6–8 When looking for glassy materials with high conductivity properties, as may be expected and will be shown here, posterior crystallization may be inconvenient as it may reduce the materials’ ability for electrical transport owing to the development of ion blocking effects. In general, as is well known, two distinct physical processes contribute to the crystallization of glasses, namely, crystal nucleation and growth. The suppression of either may be sufficient to render glassy a supercooled liquid.1,2

In both the above-mentioned cases of nonsprontaneous crystallization in fresnoite and lithium niobate containing glass ceramics,6–8 the experiments have been conducted at high temperatures, close to their respective glass melting points, where crystallite growth rate is high but crystallites nucleation rate is low, implying no crystallization under usual conditions. In both cases, occurrence of surface crystallization has been supposed to involve a field-activated cation reduction (Ti4+ to Ti3+ and Nb5+ to Nb4+, respectively) at the cathode electrode as the main driving force promoting crystallite nucleation. Experimental evidence has been given for Ti4+ to Ti3+ reduction.7 In the present work, we report the (micro)structural and electrical properties of lead fluoroborate (BO1.5–PbO–PbF2) glasses, with a special attention paid on the fluoride ion–associated effects. Also, occurrence of nonsprontaneous crystallization and corresponding driving force were explored. Different from the above works dealing with nonsprontaneous crystallization at high temperatures, the experiments were here conducted below the glass transition temperature where crystallization phenomena (especially nucleation and thus crystal growth) are, in practice, normally unlikely.1,2 That is, as is well known from classical literature, when decreasing the temperature of a glass from its melting point to below, nucleation starts and increases reaching a
maximum at a given temperature below which the increase in rigid glass network–associated material viscosity freezes out further nucleation. Even though, interestingly, crystallization developing initially at the samples’ surface was in this work observed toward the glassy state whatever an alternating or direct current (ac or dc) voltage was applied, a very few results of which we have recently presented in Ref. 9 as an informative letter. Here, extensive discussion on the overall mechanism most likely involved in crystallization development in glasses is considered in light of existing approaches on the structural model of glassy materials.2

II. EXPERIMENTAL PROCEDURE

Glass compositions of 50 BO1.5−(50−x) PbO−xPbF2 [i.e., 33.3 B2O3−(66.7−x) PbO−xPbF2] with x=0, 5, 10, 15, 20, and 30 cationic % (hereafter referred to as BPP00, BPP05, BPP10, BPP15, BPP20, and BPP30, respectively) were prepared by the melt-quenching technique. Well-homogenized mixtures of oxide reagent grades were melted in a platinum crucible at a temperature of 780 °C. The melting was observed after 5 min of heat treatment, after which melt homogenization by stirring for a further 30 min and then quenching to room temperature were achieved. Polished flat as well as disk-shaped samples were prepared for subsequent study. The glass products were characterized in terms of density from applying the Archimedes method, differential scanning calorimetry (DSC) (2090 calorimeter, TA), x-ray diffraction (XRD) (Rigaku-Rotaflex RU-200B), and optical microscopy (Olympus BHA-751-p-ls). Electrical characterizations involved impedance spectroscopy (Solartron SI 1260) in the 1 Hz–13 MHz frequency range, from room temperature to ~240 °C, and using silver electrodes. The study was completed with some dc measurements (Keithley 610C electrometer) conducted at 240 °C on the BPP15 sample in the time domain (polarization and depolarization responses). The measured impedance and dc resistance data were converted into resistivity taking into consideration the samples’ dimensions.

III. RESULTS AND DISCUSSION

A. PbF2-modified properties of the synthesized lead oxiborate glasses

Figure 1(a) illustrates optical microscope images summarizing the picture of the produced glasses after quenching. The products are transparent and yellow-to uncoloredlike as the PbF2 glass content increased. Figure 2 shows the results

FIG. 2. DSC curves recorded for all the prepared BPP glass compositions while rising temperature.

FIG. 3. Room temperature XRD patterns of the as-quenched samples. These show a glassy state, except for the BPP30 composition that shows crystallization corresponding to β-PbF2 formation.

FIG. 1. (Color online) (a) Photographic images showing a general picture of as-produced BPP flat-shaped glass samples. (b) Morphological aspects of a BPP15 disk-shaped glass sample after remaining 10 h subjected to a 1.25 V dc voltage at 240 °C. In this case, surface crystallization was observed and identified to correspond to a β-PbF2 phase formation.
obtained from the DSC analysis for all the BPP glass compositions, the main features of which are summarized in Table I in terms of glass transition and crystallization temperatures \( T_g \) and \( T_c \), respectively. While a flat DSC curve is observed for the BPP00 composition, except for the occurrence of the glass transition at \( T_g \), the other BPP compositions show a clear exothermic peak associated with the crystallization process. The nonobservation of crystallization in the BPP00 glass sample is a clear indication that PbF\(_2\) acts here as the crystal forming component. The endothermic peaks observed above the crystallization temperature correspond to glass melting as clearly detected in the BPP05 composition plus, most likely, fusion of other minor crystallized phases. Glass melting in the BPP00 sample should occur at a higher temperature. The overall behavior of the DSC curves thus suggests that the glass melting point decreases with increasing PbF\(_2\) glass component.

The typical results observed from impedance spectroscopy (IS) are summarized in Fig. 5 for as-prepared BPP00, BPP05, and BPP10 glass samples, according to measurements conducted with an ac voltage of 0.75 V (a field of \(-0.44 \text{ V/mm}\)), just after stabilizing the measuring temperature at 225 °C. As expected, a single semicircle was observed in all the studied cases. In terms of IS, such an electrical response may be ideally simulated by using a simple parallel resistance-capacitance (\( R\)-\( C \)) circuit. Our experimental data were in practice fitted using the professional ZVIEW software that includes consideration of frequency-dependent capacitances, namely, constant phase element (CPE), instead of the ideal capacitance (\( C \)) ones, for better data fitting. Nevertheless, deviations of the parallel \( R\)-CPE circuit from the ideal \( R\)-\( C \) one were indeed insignificant. In addition, as summarized in Table II, the large quantity of experimental IS results found elsewhere have established the capacitance order of magnitude of generic species or processes. Accordingly, the values of capacitance supply a simple but well-accepted criterion for identifying the origin of dielectric processes. In the present case, the estimated semicircle-associated capacitance remained in the order of \( 10^{-11} \text{ F} \), which is typical of bulk electrical processes.
TABLE II. Capacitance values and their possible interpretation in terms of origin.

<table>
<thead>
<tr>
<th>Capacitance (F)</th>
<th>Responsible phenomenon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-12}$–$10^{-11}$</td>
<td>Bulk</td>
</tr>
<tr>
<td>$10^{-11}$–$10^{-8}$</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>$10^{-9}$–$10^{-7}$</td>
<td>Surface layer</td>
</tr>
<tr>
<td>$10^{-7}$–$10^{-5}$</td>
<td>Sample-electrode interface</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>Electrochemical reactions</td>
</tr>
</tbody>
</table>

Comparing between all the synthesized glass compositions, the most important observation from Fig. 5 was that the bulk glass resistivity ($\rho_{BG}$—which nearly reduces to the semi-circle diameter) $^{10,11}$ decreases with increasing PbF$_2$ glass content. Values of $\rho_{BG}$ finally extracted from the IS data analysis are included in Table III for all the compositions, and their overall behavior is shown in Fig. 6 as a function of PbF$_2$ glass content. Interpreting the resulting behavior of $\rho_{BG}$ requires considering firstly that resistivity satisfies

$$\rho = [Nq\mu]^{-1},$$

where $N$ represents the charge carrier concentration, while $q$ and $\mu$ refer to the charge value and mobility, respectively. Consequently, provided that the fluoride ions are the main conduction charge carriers in fluoroborate-based glasses, the final result according to which $\rho_{BG}$ decreases with increasing PbF$_2$ glass content (see Table III) is then to be theoretically expected ($\rho_{BG} = 1/N\mu$).

At this point, quantitatively speaking, however, the electrical transport process merits a further attention. Notice that while there is a resistivity difference of almost two magnitude orders from $x=0$ to $x=5$, the difference strongly drops tending to only one magnitude order or less between the samples with $x \gg 5$. Considering the thermally activated character of mobility ($\mu$), resistivity data extracted from IS may be processed using, for instance, a simple Arrhenius relation,

$$\rho = \rho' \exp(E/kT),$$

where $\rho'$ is the preexponential factor, $E$ the activation energy associated with charge mobility, $k$ the Boltzmann’s constant, and $T$ the absolute temperature. Results from such a data treatment are illustrated in Fig. 7 in terms of $\log \rho$ versus $1/T$. They show linear behaviors from which values of the activation energy ($E_{BG}$) involved were estimated and are given in Table III. In addition, values of the molar volume ($V$) of all the prepared glass samples were also calculated from the respective molar mass ($M$) and measured density ($d$) as $V=M/d$. The behaviors of both $E_{BG}$ and $V$ are illustrated in the Fig. 6 inset. A PbF$_2$-induced decrease of activation energy is observed. This result is congruent with an increase of the glass molar volume that implies a glass network expansion and, thus, an increase of the free volume for fluoride ion migration. Even though, notice that while an almost linear variation of $E_{BG}$ is observed for $x \gg 5$, a much more steep $E_{BG}$ variation characterizes the transition from $x=0$ to $x=5$, that is, irrespective of the insignificant PbF$_2$-induced variation of the material molar volume between these two lower glass compositions. To account for this result, one should reasonably assume a change of dominating charge carriers in the systems, in good agreement with a previous such statement in literature when comparing electrical transport features in fluoride-free and fluoride-containing lead borate glasses. That is, while the electric current in lead fluoroborate glasses is carried by the fluoride ions, the one in lead borate glasses has been invoked to rather be of protonic type owing to the presence of hydrogen impurities that are not completely eliminated from the glass structure. The $E_{BG}$ values estimated here compare well with those values previously reported in the literature for lead fluoroborate glasses.

B. Nonspontaneous crystallization of the lead oxifluoroborate glasses toward low temperatures

Returning to the IS experiments we conducted, Fig. 8 now shows the electrical results observed in those glass

TABLE III. Resistivity values (measured at 240 °C) and activation energy values of the glasses and crystallization-associated component ($\rho_{BG}$, $\rho_{GC}$, $E_{BG}$, and $E_{GC}$) extracted from the electrical analysis (see text). Included also are the values of crystallization-associated versus bulk glass resistivity.

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>$\rho_{BG}$ (Ω cm)</th>
<th>$E_{BG}$ (eV)</th>
<th>$\rho_{GC}$ (Ω cm)</th>
<th>$E_{GC}$ (eV)</th>
<th>$\rho_{GC}/\rho_{BG}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPP00</td>
<td>$8.3 \times 10^6$</td>
<td>1.39</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>BPP05</td>
<td>$5.7 \times 10^7$</td>
<td>1.03</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>BPP10</td>
<td>$2.3 \times 10^5$</td>
<td>0.90</td>
<td>$3.5 \times 10^5$</td>
<td>1.15</td>
<td>0.15</td>
</tr>
<tr>
<td>BPP15</td>
<td>$2.9 \times 10^5$</td>
<td>0.80</td>
<td>$1.2 \times 10^5$</td>
<td>1.08</td>
<td>0.41</td>
</tr>
<tr>
<td>BPP20</td>
<td>$4.2 \times 10^4$</td>
<td>0.69</td>
<td>$3.2 \times 10^4$</td>
<td>0.91</td>
<td>0.76</td>
</tr>
</tbody>
</table>
samples with $x>5$ (BPP10, BPP15, and BPP20) after subsequent electrical measurements at the same temperature of 225 °C. With time, interestingly, a second semicircle appeared at the intermediate frequencies, besides the spikelike electrical response manifesting toward the lowest frequencies. In terms of IS, the equivalent circuit to be considered as representing the whole system would now consist of the series combination of three parallel $R$-$C$ circuits (or $R$-CPE-type circuits for better data fitting, as was pointed out above).

While the high-frequency semicircle reproduced well the characteristics of the bulk response from Fig. 5, with capacitance values in the order of $10^{-11}$ F, the second semicircle revealed capacitance values in the order of $10^{-9}$–$10^{-8}$ F, typical of interfacial processes, and the impedance spike showed capacitance values in the order of $10^{-6}$–$10^{-5}$ F, typical of electrode effects (Table II). The appearance of the second semicircle, whose final effect is to increase the material resistivity, was attributed to the development of an electric field–induced crystallization process in these glasses below the glass transition temperature ($T_g$). To demonstrate this effect, a BPP15 glass sample was treated with a dc voltage of 1.25 V for 10 h at 240 °C. The corresponding XRD results are included in Fig. 4 (curve BPP15C) and show diffraction peaks belonging also mainly to -PbF$_2$ phase formation. The long-term and higher dc instead of ac voltage was used with the expectation of enhancing the crystallization process. Figure 1 shows the morphological aspects of the BPP15 sample after this dc electric field treatment. The -PbF$_2$ crystalline phase formed at the cathode sample surface. Changing the electric field polarity also led to -PbF$_2$ formation at the other sample surface. Values of the crystallization-associated resistivity ($\rho_{GC}$) extracted from the IS data analysis and the resulting $\rho_{GC}/\rho_{BG}$ ratio are also given in Table III. With increasing PbF$_2$ content, it is concluded that $\rho_{GC}$ decreases, while the quantity $\rho_{GC}/\rho_{BG}$ increases (as may also be visually noted from Fig. 8). To avoid any misinterpretation, it is important to realize that, as they show interfacial-type capacitance values, the crystallization-related semicircles in Fig. 8 should accordingly be associated with the glass-crystal interface density instead of the own crystal volume fraction; the consequence of which will be further shown and discussed below.

As an interesting point, we looked at any time variation of this nonspontaneous crystallization process, that is, from the IS point of view. Figure 9 summarizes results from impedance measurements conducted on the BPP15 glass sample kept at 240 °C, with the applied ac voltage of
0.75 V, at two different times. Figure 9(a) refers to the impedance dispersion measured after remaining the sample about 6 h under the constant application of the 0.75 V ac voltage. Occurrence of the two glass- and crystallization-associated semicircles is clearly detected. Subsequently, the electric field was switched off, and Fig. 9(b) presently refers to the impedance dispersion finally measured after remaining the sample 41 h without electric field applied. The graph reveals that a decrease of the crystallization-associated semicircle diameter (and, thus, corresponding resistivity $\rho_{GC}$) is noted. When trying interpreting this result, the following observations should be made. On one hand, the values of $\rho_{BG}$ and $\rho_{GC}$ so far mentioned indeed refer to macroscopic resistivities that may be individually expressed in terms of the corresponding microscopic resistivity, $\rho_{i}^{\text{mic}}$, as $\rho_i = n_i \rho_{i}^{\text{mic}}$, where $n_i$ represents the volume fraction of the component under consideration. In terms of the series combination of all the contributing components involved, the total (macroscopic) resistivity satisfies

$$\rho_{tot} = \sum_i n_i \rho_{i}^{\text{mic}},$$

with the condition that $\sum_i n_i = 1$. On the other hand, volume fraction ($n_i$) of an electric field–induced crystalline phase is not expected to decrease with time once the electric field has been switched off. The latter observation strongly supports the above conclusive statement that, as the crystallization-related semicircles (in Fig. 8 as well as Fig. 9) show interfacial-type capacitance values ($\sim 10^{-9} - 10^{-8}$ F), they should thus be associated with the glass-crystal interface density instead of the own crystal volume fraction. It is consequently here proposed that the time decreasing behavior of $\rho_{GC}$ in Fig. 9 should rather involve a crystallite coalescence effect. That is, after field-promoted nucleation, atom attachment at dispersed-like crystal nuclei-glass interfaces is expected to favor crystal growth to the point of turning crystallization electrically detectable. In the following, however, the same crystal growth process should also promote (with time) crystal-to-crystal contacts, allowing crystals to coalesce and, thus, a reduction of the overall glass-crystal interface density. This fact is expected to bring down resistivity of this interface, if being monitored. Results from Fig. 9 therefore suggest that, once the electric field–induced crystal nuclei are formed, thermally assisted crystallite growth (leading here to crystal coalescence) also occurs even at such low temperatures below the glass transition. In other words, as compared to crystal growth, lack of crystal nucleation activity far below the crystallization temperature, especially in the glassy state, should be considered the main factor usually limiting development of spontaneous crystallization. In this way, our result appears to be a proof of the idea from literature that crystal growth can be expected to occur at any temperature below the melting point so long as a nucleus is available. From a strategic viewpoint, it is important to point out that the probability of detectably realizing the above role of temperature during crystallization is expected to be high when switching off the electric field, as we did here, provided that this latter driving force would tend to occasionally promote the opposite effect in the glassy component: nucleation and, consequently, an increase of the glass-crystal interface density, thus masking the real effect from temperature.

For IS data collected under quite similar conditions of measuring time, the resistivity values from the crystallization-related semicircle ($\rho_{GC}$) were also processed using the above Arrhenius-type expression and data plotting formalisms. The results are illustrated in Fig. 10 and linear behaviors are observed as well. Average values of activation energy ($E_{GC}$) estimated after considering four to five independent temperature runs of measurements have been also included in Table III. They lie above those of the corresponding bulk glass matrix ($E_{BG}$) and below the low-temperature bulk value of $E_{BC} \approx 1.29 \pm 0.05$ eV that may be calculated from the data given in Ref. 14 for $\beta$-PbF$_2$ single crystals and polycrystals. In the crystal case, migration of the fluoride anions has been invoked to most likely also lead to conduction in $\beta$-PbF$_2$, but through the anion vacancy mechanism. Quantitatively speaking, it is believed that structural effects involving the presence of (i) Pb$^+$ ions and, especially, (ii) structure mismatch–related surface defects at the glass-crystal interface could be at the origin of the intermediate values, between bulk glass ($E_{BG}$) and crystal ($E_{BC}$), finally observed for the glass-crystal interface ($E_{GC}$). Correlation between the decreasing behavior of $E_{BG}$ and $E_{GC}$ with rising PbF$_2$ glass content is to some extent coherent with this speculation. Of course, a specific study would be needed to properly clarify this point. In any case, the fact that $E_{GC} > E_{BG}$ is to be considered the factor responsible for the partially blocking effect observed for migration of the charge carriers across the glass-crystal interface, implying a reduction of the conductive ability of the resulting glass-ceramic materials. On the other hand, as was pointed out above when comparing Figs. 5 and 8, the electrical properties of each glass matrix composition (i.e., $\rho_{BG}$ and, thus, $E_{BG}$) before and after crystallization remained almost unchanged during all the experiments conducted. This result may be understood as a consequence of the low concentration of crystalline phase definitively synthesized, as normally expected in strongly glass forming systems, especially here for such low...
annealing temperatures considered. In other words, irrespective of the resulting glass-ceramic nature of the electric field–treated lead oxifluoroborate glasses, contribution of (a few volume fraction of) the $\beta$-PbF$_2$ crystals to the IS spectra is at this time apparently irrelevant.

**C. Electrochemical origin and overall mechanism involved in the nonspontaneous crystallization of the lead oxifluoroborate glasses**

In the literature, the electric field–promoted surface crystallization observed in fresnoite containing BaO–TiO$_2$–SiO$_2$–B$_2$O$_3$ and lithium niobate containing Li$_2$O–Nb$_2$O$_5$–SiO$_2$ glass ceramics in the solid-state temperature region approaching their respective melting points, where spontaneous crystallization is unlikely, has been associated with redox-type reactions at the electrodes. In particular, reduction of Ti$^{4+}$ to Ti$^{3+}$ or Nb$^{5+}$ to Nb$^{4+}$ at the cathode is expected to decrease the material viscosity so as to stimulate nuclei formation even at such high temperatures. By analogy with these works, the following electrode reactions may also be proposed to hold in our BPP glasses: for cathode,

$$\text{Pb}^{2+} + e^- \rightarrow \text{Pb}^+,$$

and for anode,

$$2F^- \rightarrow F_2(g) + 2e^-.$$

In Fig. 4, we have also included the XRD results observed from the BPP15 glass sample after treatment with the 1.25 V dc voltage at 240 °C, but now for 30 h (curve BPP15D). Formation of metallic lead (Pb$^0$) is detected, suggesting validity of the above Pb$^{2+}$+e$-\rightarrow$Pb$^+$ reaction, followed by Pb$^+$+e$^-\rightarrow$Pb$^0$. Presently, we have no direct evidence of fluor evolution at the anode electrode. Considering, however, that no crystallization was observed in the fluoride-free lead borate glass and that the fluoride ions are the main charge carriers responsible for the electrical transport process in these BPP glasses, it seems reasonable to propose, by analogy with literature, the oxidation of most likely fluoride at the anode interface. In the case of fresnoite containing glass ceramics, reduced titanium ions (Ti$^{3+}$) incorporate into the fresnoite crystal lattice in low quantity (less than 10 at. %), after which a barium oxititanate (III) forms at sufficiently high Ti$^{3+}$ concentrations. In the present $\beta$-PbF$_2$ containing BO$_{1.5}$-PbO–PbF$_2$ glass ceramics, the curve BPP15D from Fig. 4 shows that formation of metallic lead occurred along with decomposition of the $\beta$-PbF$_2$ crystalline phase. This result suggests that reduced lead ions (Pb$^+$) should also incorporate into the crystalline phase, which may be then charge compensated with fluoride ion vacancies, i.e., PbF$_{2-x}$-\(_{x}\=\)Pb$^{2+}$F$^\text{-}_{2-x}$. Only a continuous reduction reaction of crystal-Pb$^+$ ions leading to metallic lead formation should account for the simultaneous decomposition of the $\beta$-PbF$_2$ crystalline phase.

At this stage, however, some remarks have to be made when attempting to closely address the whole mechanism governing crystallization of glasses at the microscopic level. When considering the case of classical, spontaneous crystallization developing at $T_4$ to a detectable extent, it is well known that instead of manifesting homogeneously (i.e., with equal probability throughout the bulk of a glass), nucleation normally is heterogeneous owing to the presence of external and/or internal surfaces that act as energetically favored sites for heterogeneous nucleation in glasses. That is why crystallization is expected and, in fact, usually seen to originate at a sample surface rather than bulk, in glasses free of bulk defects. Irrespective of this fact, however, what is in practice also seen is that crystallization does not really develop simultaneously (in the sense of equal probability) at all of these surface points. The reasons to be considered as accounting for this experimental observation are (1) the preexistence of not only (external) single but also multisurface points where nucleation is firstly promoted, and (2) the fact that once a surface nucleus is stably formed (i.e., with a size minimally equal to the critical one necessary to survive), its growth is automatically favored with respect to simultaneous nucleation at strictly all the surface points, depending only on the frequency of atom attachment at the new crystal nucleus-glass interface.

When considering now the specific case of the electrochemically induced crystallization phenomenon presented here, it would appear reasonable to expect that the reduction reaction of Pb$^{2+}$ to Pb$^+$, occurring at the cathode electrode and promoting crystal nucleation, would uniformly take place along the entire sample surface where the electrode-glass contact is thoroughly guaranteed. Accordingly, with the cathode electrode acting as a permanent source of electrons for reduction, crystallization would thus be supposed to occur somewhat simultaneously (again from the probabilistic viewpoint) at all the surface points. Surprisingly, however, the results we have observed, in practice, are not different from those of spontaneous surface crystallization. Besides Fig. 1(b) presented before, an example of such a remark may also be seen in Fig. 11 that shows a relatively early stage of crystallization in a BPP15 flat-shaped sample treated with a dc voltage of 1.25 V (~0.58 V/mm) for about 8 h at 240 °C. Summarizing, two observations were straightforward: crystallization originated and manifested (i) much more intensely at the multi- rather than single-surface points; (ii) without showing any simultaneous development when comparing between all the multi- or single-surface points. In
consequence, the only two reasons pointed out above (that is, consistent with classical literature) to account for the locally unequal crystallization phenomenon observed at a glass surface are apparently not enough to totally approach the question of crystallization mechanism in glasses. We, in fact, believe that this statement should also apply for homogeneous (bulk) nucleation and crystallization. Such a simple but important observation suggests that the original, well-accepted structural model first proposed by Zachariaes,\textsuperscript{15} according to which a glassy material forms a continuous-random network throughout, is perhaps somewhat incomplete.

As has been proposed in the literature,\textsuperscript{16–19} it appears much more plausible to consider the rigidity model that invokes a glassy material to be rather comprised of small floppy-like regions embedded into a rigid network. From this viewpoint, the nucleation process has been proposed to originate at the floppy regions, especially (we conclude) those located at a sample surface where this process would be energetically favored. For the electrochemically induced crystallization observed here to also develop heterogeneously (in time and local distribution), a reasonable assumption would therefore be that the floppy regions are much more sensitive to the reduction reaction, as they involve less rigid bonds. Accordingly, the reduction-associated decrease of the material viscosity, invoked above to account for occurrence of the nonspontaneous crystallization, is to be considered to manifest only quite locally. In terms of the crystallization mechanism and glass rigidity model, we believe that after reduction, the presence of Pb\textsuperscript{2+} ions should soften the strength of the surrounding network bonds and cause a growth of preexisting floppy regions until they reach the appropriate dimensions for finally enabling surface nucleation. In other words, assuming the preexistence of floppy glass regions at which the reduction-promoted nucleation process would apparently be favored, subsequent crystallization spreading outward at the surface and from surface to bulk may be viewed as resulting from a gradual conversion of vitreous networks from rigid to floppy.

D. Relaxation processes and surface crystallization development viewed from combining IS and polarization/depolarization techniques

In this work, keeping in mind that inducing crystallization by a voltage application is a real fact, we then also explored the electric field–modified picture, if any (as would be expected), of polarization/depolarization development in such glasses. It is worth mentioning that a complete characterization of dielectric processes often requires an analysis of the behavior of the involved physical/chemical magnitudes in the time domain as well.\textsuperscript{11,20} Notice, for instance, that the relaxation frequencies (frequencies lying at the impedance semicircle maxima) from the electrode processes are in this work not resolved (Figs. 8 and 9 only show electrode-associated spikes at the lowest frequencies) because of falling, if truly occurring (i.e., if assuming partially rather than totally blocking electrodes), toward quite low frequencies below the apparatus window. In consequence, estimating the electrical parameters (e.g., resistivity and/or capacitance) corresponding to the electrodes, as we did from IS and related data fitting formalism, really involved higher errors. (For reference, these showed to remain—in most cases—above 60% for the electrode, while keeping mostly below 10% for the glass as well as crystallization-associated resistances and capacitances).

Considering that the dynamic evolution of dielectric and relaxation processes in the time and the frequency domains are in opposite directions (high frequencies are associated with short times and vice versa),\textsuperscript{10,11,20} any difficulty on extracting highly accurate electrode parameters from IS can thus be experimentally overcome by conducting time-domain measurements and a sampling of the materials’ properties of interest toward larger times. The simplest but generally most applied experiment consists of the charge and discharge under a step voltage of a dielectric material inserted into a condensator. The current density from applying the above experiment obeys the following:

\[
J_\rho(t) = (E/\rho_0) + (dP/dt),
\]

and for depolarization:

\[
J_\rho(t) = -dP/dt,
\]

where \(P(t) = P_S[1 - \exp(-t/\tau)]\) for polarization and \(P(t) = P_S \exp(-t/\tau)\) for depolarization, if assuming, to a first approximation, ideal Debye-type polarization/depolarization \(P(t)\) functions.\textsuperscript{21} In the above relations, \(E\) is the applied dc electric field, \(\rho_0\) the time-independent, dc resistivity, \(P_S\) the steady-state polarization, and \(\tau\) the relaxation time. Accordingly, \(J_\rho(0) = (E/\rho_0) + (P_S/\tau)\) and \(J_\rho(\infty) = (E/\rho_0)\) for polarization, while \(J_\rho(0) = P_S/\tau\) and \(J_\rho(\infty) = 0\) for depolarization. Following the Ohm’s law, i.e., \(\rho(t) = J_\rho(t)/E\), the expected resistivity behavior associated with polarization ideally satisfies

\[
\rho(t) = [(1/\rho_0) + (P_S/E)\exp(-t/\tau)]^{-1},
\]

implying that \(\rho(0) = \rho_0/[1 + (\rho_0 P_S/E)]\) and \(\rho(\infty) = \rho_0\). Figure 12(a) shows the time behavior of the total dc resistivity \(\rho_{\text{tot}}(t)\) measured (in the dc electrometer) at 240 °C on a BPP15 sample, during 20 h, while subjected to a 1.25 V dc voltage (open symbols). As expected, the resistivity increases with a clearly reduced rate as time rises, but without showing, however, the ideal trend to saturation. As a reference for the discussion below, we just recall that the total resistivity includes at this time both the material and electrode contributions: \(\rho_{\text{tot}} = \rho_{\text{mat}} + \rho_{\text{elec}}\).

Figure 12(b) shows subsequent impedance measurements conducted on this BPP15 sample, now with a 0.75 V ac voltage, after switching off the above dc voltage. While the glass-associated semicircle remains unchanged, the crystallization-associated resistivity (second semicircle diameter) continuously reduces. At first glance, this result may (i) appear surprising and (ii) be subject to speculative interpretations. Remembering, however, that in terms of polarization/depolarization time scale, bulk processes are almost instantaneous and hard to register,\textsuperscript{21} what is really seen in Fig. 12(b) is that interfacial depolarization is manifesting while that of bulk already took place. This interesting observation makes recommendable and, in fact, original the combination of IS with polarization and/or depolarization techniques to explore the features of (di)electrical relaxation.
processes of materials at a microstructural-like (bulk versus interface) level, simultaneously in both time and frequency domains. Here, as explored below, the procedure may also help depict the development of crystallization in real time. The resistivity data corresponding to \( f = 10 \, \text{Hz} \) (i.e., reflecting basically the electrode-free dc resistivity, \( \rho_{\text{mat}} \)) in Fig. 12(b) have also been plotted in Fig. 12(a) (closed symbols). Ideally speaking, depolarization currents go to zero with time \( [J(t)]_{\infty} = 0 \), see above. This means that if resistivities \( \rho(t) \) were simultaneously measured in the presence of depolarization, as we did from IS, this would show a decrease tending to \( \rho(\infty) = E_m / J_m \), where \( E_m \) is actually the measuring field and \( J_m \) the \( E_m \)-induced current superposed to the decaying depolarization current \( J(t) \). In Fig. 12(a), for instance, \( \rho_{\text{mat}}(\infty) \) was expected to coincide with the material resistivity initially measured at \( t = 0 \), just before the dc treatment, under an equal \( E_m \) value (star symbol). Interestingly, however, resistivity tends irreversibly to a finally different stationary value after 25 h of measurements. This effect is here associated with development of the electrochemically induced crystallization in the glass. Accordingly, the nonsaturating trend of the open-symbol curve in Fig. 12(a) toward larger times should then involve the combination of both polarization and crystallization phenomena.

Moreover, the time dependences of the polarization-related resistivity data from Fig. 12(a) were fitted through expression (6) rewritten in terms of conductivity \( \sigma_{\text{tot}} \) (\( = \rho_{\text{tot}}^{-1} \)) as \( \sigma_{\text{tot}}(t) = A_1 + A_2 \exp\left(-t/t_1\right) \). The fitting was restricted to a limited range of measuring times, as justified later. Values obtained for the three parameters \( A_1(=\sigma_0), A_2(=P_0/E) \) and \( A_3(=\tau) \) were \((1.246 \pm 0.002) \times 10^{-7} \, \Omega \, \text{cm}^{-1} \), \((8.29 \pm 0.04) \times 10^{-7} \, \Omega \, \text{cm}^{-1} \), and \(3198 \pm 10 \, \text{s} \), respectively. The estimated value of \( \tau \) (approaching here 1 h) represents a relaxation frequency of \( f_0(=1/2\pi\tau) \approx 5.0 \times 10^{-5} \, \text{Hz} \), that is, far below the value of \( f = 1 \, \text{Hz} \) corresponding to our limiting low-frequency IS window. Considering the Debye approximation that \( \tau \approx RC \) (where \( R = \rho L \); \( L \): sample geometry factor), \(^{10-12,20} \) a capacitance value of \( C \approx (1.1 \pm 0.2) \times 10^{-12} \, \text{F} \) may be estimated. In terms of magnitude order, this is a much better approximate value than the \( 10^{-6} - 10^{-5} \, \text{F} \) order we predicted from IS. Notice according to Table II that the new estimated capacitance falls well into the magnitude order range expected for electrochemical reactions \(^{12} \) (to be actually generalized as going down to about \( 10^{-4} \, \text{F} \) from above), in good agreement with the mechanism proposed to account for the origin of the electrode crystallization in these glasses. In Fig. 13, treatment of the above data in terms of \( \sigma_{\text{tot}}(t) \) and \( [\sigma_{\text{tot}}(t) - \sigma_0] \) is shown in a monolog scale. Ideally speaking, as supposedly \( \sigma_{\text{tot}}(\infty) = \sigma_0 \), the logarithm values of absolute \( \sigma_{\text{tot}}(t) - \sigma\_0 \) are expected to show a linear behavior tending to \( -\infty \) for \( t \to \infty \). In practice, however, a departure from such a linear behavior is seen in the figure with increasing time, that is, above \( t_2 \approx 4.5 \, \text{h} \). (The data fitting achieved to extract the above \( A_1, A_2 \), and \( A_3 \) parameters was restricted to the time range where the linear behavior was found, i.e., \( t < t_2 \)). Actually, the logarithm values tended to \( -\infty \) just above \( t_2 \), at \( t_C \approx 5.1 \, \text{h} \) where the equality \( \sigma_{\text{tot}}(t_C) = \sigma_0 \) holds thus. The solid symbols plotted in the figure above \( t_C \) correspond to the logarithm values of absolute \( \sigma_{\text{tot}}(t > t_C) - \sigma_0 \). In terms of interpretation, the high-time data departure (from \( t_C \) above) should arise from the development of the surface crystallization, introducing additional blocking effects in the studied system.

IV. CONCLUSIONS

The present study has shown that (micro)structural and electrical properties of lead fluoroborate glasses are truly strongly dependent on the PbF<sub>2</sub> glass content. In particular, a decrease of the activation energy from an increase of the glass molar volume is responsible for an increased conductivity process observed in these glasses with increasing PbF<sub>2</sub>. In addition, it is shown that electric field–induced surface crystallization occurred in such glassy materials below the glass temperature. The phenomenon arose from a field-induced redox reaction at the electrodes, followed by crystallites nucleation and growth. The results also suggest that reduced lead ions (Pb<sup>+</sup>) incorporate into the βPbF<sub>2</sub> crystall-
line phase. This fact accounts for decomposition of this phase from a continuous crystal-lead (Pb⁺) reduction, allowing to the formation of metallic lead (Pb). From the electrical transport viewpoint, appearance of the crystallized phase had the effect of reducing the total material conductivity. Finally, this work has also shown that impedance spectroscopy and its novel combination with polarization/depolarization experiments are complementary powerful techniques that may help monitor crystallization in glassy materials and, in general, contribute to the study of (di)electrical relaxation processes of materials viewed simultaneously from both time and frequency domains.

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