Molecular dynamics simulation study of erbium induced devitrification in vitreous PbF$_2$

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Molecular dynamics simulations of the devitrification process of a lead fluoride glass doped with Er$^{3+}$ ions were carried out. This technique appears to be a relevant way to perform systematic analysis of the system structure and to study the influence of defects on PbF$_2$ crystallization. We modeled the total enthalpy, the radial distribution functions, and the diffracted intensities of systems containing different amounts of Er$^{3+}$ ions. We demonstrated by means of different simulations that Er$^{3+}$ ions lowered the devitrification temperature of PbF$_2$, in good agreement with the experimental results. The genuine role of Er$^{3+}$ ions in the devitrification process of PbF$_2$ has been investigated. Er$^{3+}$ ions have an unquestionable influence of the crystallization of PbF$_2$. Although the latter does not start in the nearest neighborhood of Er$^{3+}$ ions, the presence of Er$^{3+}$ ions in a close environment may favor the lead fluoride crystallization. © 2007 American Institute of Physics. [DOI: 10.1063/1.2771546]

I. INTRODUCTION

Nanosized crystals dispersed throughout a glassy phase form transparent glass ceramics.1 Doped with luminescent ions, these materials can be good candidates for optical applications and could be seen as an alternative to the currently used materials (glasses and single crystals). To develop active optical fibers for telecommunications, we examined the properties of erbium-doped GeO$_2$–PbO–PbF$_2$ glass ceramics obtained after the devitrification of germinate glasses. These glass ceramics are made by an oxide glassy phase with fluoride nanocrystals incorporating strongly erbium ions.2 Thanks to the crystalline environment provided to Er$^{3+}$ ions, they possess good optical properties similar to single crystals but with the advantage of a much easier synthesis. The composition of the parent glass has a great influence on the synthesis and the transparency of the glass ceramic. The content of ErF$_3$ with respect to the PbF$_2$ concentration is particularly important as it has been experimentally shown by differential thermal analysis (DTA) and x-ray diffraction (XRD) studies that ErF$_3$ was acting as a nucleating agent for the heterogeneous nucleation of PbF$_2$ crystals.3 On one hand, if the ErF$_3$ concentration is too low, PbF$_2$ crystallizes at the same temperature as the oxide compounds (PbGeO$_3$, PbGe$_2$O$_6$) and it is impossible to elaborate an oxyfluoride glass ceramic. On the other hand, if the ErF$_3$ content is too high, the glass crystallizes spontaneously and randomly during pouring and the obtained glass ceramic is opaque. Typical glass ceramics are obtained with the molar composition 50GeO$_2$:40PbO:10PbF$_2$ + xErF$_3$, with x=2, 3, and lead to highly transparent glass ceramics with Pb$_{1-x}$Er$_x$F$_{2+x}$ crystallites.

The synthesis of these materials is now well controlled but the first steps of the nanocrystal nucleation, although crucial for the transparency of the materials, are still not really well understood. There are only few experimental techniques which could be used to study the first steps of the devitrification. Among them, small angle x-ray scattering could allow establishing of the early stages of phase separation in glass systems while being heated.4 However, the 50GeO$_2$:40PbO:10PbF$_2$ system, because of its high content of Pb, strongly absorbs x-ray radiations, preventing such a method from being used. Aside from the experimental techniques, computer simulations could be a good alternative to get some information of the devitrification process. However, to limit the calculation time and the number of parameters, the system must be simplified and only the phase undergoing the thermal transformations will be simulated.

In this paper, we examine the first steps of the formation of Pb$_{1-x}$Er$_x$F$_{2+x}$ crystallites using molecular dynamics (MD) simulations. MD has been extensively used to probe the structure of silicate glasses and to determine atomic distances.5,6 It has more scarcely been used to study the devitrification process of glasses. However, the simulation by MD of structural transformations of undoped PbF$_2$ during devitrification has been recently published.7,8 In regard to...
II. MOLECULAR DYNAMICS CALCULATIONS

The MD simulations, performed using DL_POLY program, were based on a classical model, where the interactions between two ions \( i \) and \( j \) were described by the Buckingham potential \( U(r) \) as follows:

\[
U(r) = \exp(-r_j/p_i) - C_{ij}/r_j^6 - A_{ij} \exp(-r_j/p_i) - (C_{ij}/r_j^6)
\]

where \( r_j \) represents the distance between the ions \( i \) and \( j \), \( A_{ij} \) stands for the short-range repulsive coefficient, \( C_{ij} \) is an interaction parameter, and \( p_i \) is an adjustable constant. The first term of \( U(r) \) corresponds to the Coulomb interaction, the second term takes into account the short-range repulsion, and the third term corresponds to the van der Waals interaction.

The authors modeled the experimental Pb \( L_{III} \) edge extended x-ray-absorption fine structure (EXAFS) spectrum of a cubic \( \beta \)-PbF\(_2\) sample with two different sets of parameters and showed that the thermodynamic properties of PbF\(_2\) were very well reproduced by one of them, the Walker model. This set of parameters has also been chosen here to model the Er–F interactions between the ions, the Ewald sum technique was used.

We also examine the diffraction intensity simulation on an undoped crystalline PbF\(_2\) cell. In Sec. IV, the evolution of the total enthalpy of the cells, the radial distribution functions, and the diffusion coefficients for each system PF, PFE1, and PFE4. We also examine the diffraction intensity simulation on an undoped crystalline PbF\(_2\) cell. In Sec. IV, the evolution of the total enthalpy of the cells, the radial distribution functions, and the diffusion coefficients for each system PF, PFE1, and PFE4.

III. CHARACTERIZATION OF PURE \( \beta \)-PbF\(_2\) BY DIFFRACTION

In addition to some classical modeling which have been already performed on pure lead fluoride crystal, a new way

\[
\begin{align*}
2\text{Pb}^{2+} + \text{F}^- & \rightarrow \text{Er}^{3+} + 2\Box_{\text{p}} + 4\square_{\text{i}}:\text{PFE1}, \\
6\text{Pb}^{2+} & \rightarrow 4\text{Er}^{3+} + 2\Box_{\text{p}}:\text{PFE4}.
\end{align*}
\]

In all cases, the cells are electrically neutral but they can contain some lead or fluoride vacancies, respectively, labeled \( \Box_{\text{p}} \) and \( \square_{\text{i}} \). Table II sums up the composition of the different systems which have been studied in this work.

Once the different crystalline cells were generated, they underwent a thermal process, as illustrated in Fig. 1. First, they were heated at 3000 K, at a heating rate of +20 K/ps. Second, they were maintained at 3000 K for 50 ps to assure a complete amorphous behavior. Afterward, the cells were cooled down to 300 K at the rate of −20 K/ps in order to fix their high temperature state. Then, they were maintained at 300 K for 50 ps. At this stage, the cells were amorphous. We modeled their crystallization, also called devitrification process, by heating them from 300 up to 490 K at a slow heating rate (0.2 K/ps). As the influence of the heating rate on the glass formation and the devitrification has already been studied, they will remain constant in this study.

During the devitrification, the position and speed of each ion were recorded, enabling the calculation of the total enthalpy of the cells, the radial distribution functions, and the diffusion coefficients for each system PF, PFE1, and PFE4.

In Sec. III, we examine the validity of the diffraction intensity simulation on an undoped crystalline PbF\(_2\) cell. In Sec. IV, the evolution of the total enthalpy of PF, PFE1, and PFE4 during the devitrification will be studied. In Sec. V, we will follow the local structure of the cells during the crystallization process. This study will be completed in Sec. VI by a more accurate analysis of the systems, localizing the impurities (Er\(^{3+}\)) inside the cells. These results will be discussed in Sec. VII and the conclusions will be finally drawn in Sec. VIII.

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6\text{Pb}^{2+} & \rightarrow 4\text{Er}^{3+} + 2\Box_{\text{p}}:\text{PFE4}.
\end{align*}
\]

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### Table I. Parameters used in the simulation of the devitrification of Er:PbF\(_2\) glass.

<table>
<thead>
<tr>
<th>Interactions</th>
<th>( A_{ij} ) (eV)</th>
<th>( C_{ij} ) (eV Å(^6))</th>
<th>( \rho_{ij} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb–F [10]</td>
<td>122.7</td>
<td>0</td>
<td>0.516</td>
</tr>
<tr>
<td>F–F [10]</td>
<td>10 225</td>
<td>107.3</td>
<td>0.225</td>
</tr>
<tr>
<td>Er–F [11]</td>
<td>1880.44</td>
<td>0</td>
<td>0.292</td>
</tr>
</tbody>
</table>

### Table II. Composition of the different systems under study.

<table>
<thead>
<tr>
<th>System</th>
<th>Number of Pb(^{2+}) ions</th>
<th>Number of F(^{−}) ions</th>
<th>Number of Er(^{3+}) ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF</td>
<td>864</td>
<td>1728</td>
<td>0</td>
</tr>
<tr>
<td>PFE1</td>
<td>862</td>
<td>1727</td>
<td>1</td>
</tr>
<tr>
<td>PFE4</td>
<td>858</td>
<td>1728</td>
<td>4</td>
</tr>
</tbody>
</table>

FIG. 1. Different steps of the thermal process: (1) heating (+20 K/ps), (2) thermalization at 3000 K, (3) cooling (−20 K/ps), (4) thermalization at 300 K, and (5) devitrification (+0.2 K/ps).
of modeling the crystallization of the lead fluoride system has been developed here using the diffracted intensity. The modeling has been first undertaken on a pure and perfect crystalline PbF$_2$ system (composed of 160 000 atoms forming a cube of 14.2 nm side). Figure 2 shows the modeled spectrum of the PbF$_2$ single crystal at room temperature. This spectrum could be compared to the experimental diagram obtained with the same anticathode wavelength (1.54 Å) published by Portella et al. The position and relative intensity of the diffraction peaks of the modeled structure are in good agreement with the position and intensity of those obtained experimentally. However, the peaks obtained by modeling present a non-negligible linewidth, whereas the experimental peaks are much thinner. This difference comes from the number of atoms used in the simulation and the size of the cell. In fact, the linewidth of the simulated peaks is in good agreement with what Scherrer’s formula would give for a cell of that size. For instance, a linewidth of 0.65° can be calculated by Scherrer’s formula for the (111) Bragg peak of a 14.2 nm side crystallite. The same simulation, driven on a bigger system, results in a diagram with narrower peaks (linewidth converging toward the experimental value) but no other changes are observed. The simulation of the diffracted intensity could be used to study the crystallization of PbF$_2$ systems.

IV. EVOLUTION OF THE CRYSTALLIZATION TEMPERATURE OF PbF$_2$ AS A FUNCTION OF ErF$_3$ CONTENT

The evolution of total enthalpy of the systems PF, PFE1, and PFE4 during the devitrification is plotted in Fig. 3. For each cell, the enthalpy linearly increases with the temperature up to a certain temperature (440 K for PF, 410 K for PFE1, and 380 K for PFE4). At these temperatures, the enthalpy roughly drops. It is related to an exothermic event, which is the crystallization of the cells. The crystallization temperature, labeled $T_c$, depends on the number of Er$^{3+}$ incorporated inside the cells: that higher the Er$^{3+}$ number, the smaller the $T_c$. The presence of Er$^{3+}$ ions seems to ease the lead fluoride crystallization.

From the modeling, one can also observe that the crystallization temperatures found via MD simulations are underestimated compared to the experimental values which are situated around 400 °C. This discrepancy is due to the nature of the model and, in particular, to the interaction potentials and the system size.

V. STRUCTURAL EVOLUTION DURING THE DEVITRIFICATION

The radial distribution functions for the pairs Pb–Pb, Pb–F, F–F, and Pb–Er have been calculated for the three cells PF, PFE1, and PFE4. For the sake of conciseness, we will only discuss the results obtained for the pair Pb–F, knowing that similar conclusions could be drawn from the Pb–Pb, F–F, and Pb–Er radial distribution curves.

Figures 4(a) and 4(b) show the radial distribution curves $g(r)$ for the pair Pb–F in, respectively, the systems PF and PFE4 during the devitrification process. In both cases, at low temperature (300 K), the peaks are rather broad. As the temperature increases, they narrow and become more intense, reflecting an ordering in the cells. After a certain temperature, the curve shape does not change anymore, assuring that the crystallization is completed. For both cells, the first peak is centered at 2.55 Å, indicating the average distance between Pb$^{2+}$ and F$.\textsuperscript{-}$ This result is in good agreement with the EXAFS data of lead fluoride crystals. For PF, the crystallization occurs between 440 and 450 K. By following the evolution of the radial distribution curves between these two temperatures, one can observe the progressive crystallization of the system [Figs. 4(a) and 4(b)]. The crystallization of PFE4 occurs between 380 and 390 K, at lower temperatures than the one of PF. In both cases, significant evolutions can be observed just before $T_c$.

Figure 5 represents the evolution of the diffracted intensity for PFE4 during the devitrification. At 300 K, one can observe several broadbands centered at $2\theta = 27^\circ$, 47$^\circ$, and 74$^\circ$. These bands are characteristic of the amorphous matter. As the temperature increases, they disappear and narrower peaks rise in intensity. These peaks correspond to the diffraction peaks of the lead fluoride phase, as seen in Fig. 2. For PFE4 at 370 K, the diffraction peaks appear, whereas the same simulation performed on the PF cell does not exhibit any Bragg peaks at this temperature. For PF, the apparition...
of the diffraction peaks occurs at higher temperature. At 380 K, in PFE4, the peaks are well defined, evidencing the good crystallization of PbF$_2$. At higher temperatures, the peaks keep on narrowing, reflecting the disappearance of the structural defects with the temperature.

The diffusion coefficients of Pb$^{2+}$, F$^-$, and Er$^{3+}$ have also been calculated for the modeled devitrification. Their evolution is represented for PF and PFE4 in Fig. 6. From these plots, we can observe that fluorine ions start moving as soon as the temperature increases. These light ions have usually a great mobility, whereas the mobility of heavier ions (Pb$^{2+}$ and Er$^{3+}$) is much more limited. From those graphs, drastic changes appear in the diffusion coefficients within the temperature range corresponding to the thermodynamic transition. Indeed, when the temperature reaches 440 K for PF and 380 K for PFE4, the F$^-$ mobility drastically falls down. Meanwhile, Pb$^{2+}$ and Er$^{3+}$ ions start moving. One can consider that the devitrification is set off by a sudden increase of the lead and the erbium diffusion. Moreover, it is well known that the fluorine ion diffusion reveals an important characteristic of this superionic conductor compound. As pointed out by Kosacki et al., PbF$_2$ is, among all the superionic fluorite crystals, the one with the lowest transition temperature to the superionic state and the highest degree of fluorine sublattice disorder. Also, the degree of anion sublattice disordering determines the parameters of the transition to the superionic state. In our simulations, the amorphous character of the glassy PbF$_2$, with high concentration of defects, promotes the high mobility of the fluoride ions, which drops abruptly with the decrease of defect concentration due to devitrification. These results are supported experimentally by measurements of the electrical conductivity of lead germanate oxyfluoride glasses and glass ceramics, in which with the crystallization, decreasing conductivities have been observed, despite the fact that the crystalline phase so obtained ($\beta$-PbF$_2$) is a good ionic conductor. The authors attributed the decreasing of conductivity to the fact that conducting regions with smaller conductivities are present in the interface region between the $\beta$-PbF$_2$ crystals, which are dispersed and isolated from each other in the glass ceramics. However, our simulation results go beyond, showing that inside the PbF$_2$ glass, fluorine ions have higher mobility than they do in crystals.

**VI. INFLUENCE OF Er$^{3+}$ ON THE CRYSTALLIZATION**

The three cells (PF, PFE1, and PFE4) were divided in smaller cells, called subcells. Each subcell is labeled by means of three plus or minus index (+++), (++−), (+−+),…, etc., depending on their position with respect to the origin of the cell, as illustrated in Fig. 7(a). The intensity diffracted at 390 K by each subcell of PFE4 has been plotted separately and reported in Fig. 7(b). One can notice that each plot presents the diffraction peaks, indicating that each subcell is at least partly crystallized. This is consistent with the previous results as we showed that 390 K is the temperature where the crystallization of PFE4 occurs. However, the diffracted intensity varies from one subcell to another, which reflects the inhomogeneous crystallization inside the system. The location of Er$^{3+}$ ions inside the subcells has been performed. We can observe that the subcells containing Er$^{3+}$ ions are those with less order and regions without erbium are more ordered than the others.

![FIG. 4. Evolution of the radial distribution function Pb–F during the devitrification process for the systems (a) PF and (b) PFE4.](image-url)

![FIG. 5. Evolution of the diffracted intensity during the devitrification process for PFE4.](image-url)
The calculation of the total enthalpy of the systems PF, PFE1, and PFE4 showed that the crystallization temperature of PbF₂ decreases with the increase of Er³⁺ ions. It is consistent with the experimental DTA and XRD measurements obtained in GeO₂:PbO:PbF₂ glass ceramics, showing that the increase of ErF₃ content inside the material induces the lowering of $T_c$. From the experiments, it has been concluded that ErF₃ acts as a nucleating agent for the heterogeneous devitrification of PbF₂. MD simulations show that Er³⁺ ions have an overall influence of the crystallization temperature of PbF₂ and that the model used reproduces this experimental effect. The effect of Er³⁺ on the structure of PbF₂ during the devitrification was then of great interest.

The simulations of the radial distribution functions, of the diffracted intensity, and of the diffusion coefficients were all able to show and follow the crystallization process. The results coming from the different approaches (x-ray diffraction, simulation of the enthalpy, etc.) are consistent and lead to the conclusion that the addition of Er³⁺ induces a decrease of the crystallization temperature of PbF₂ and the crystallization is progressive within the cell. As it has been demonstrated with the modeling of the enthalpy, the more erbium ions are added to the cell, the lower is the crystallization temperature of PbF₂. These simulations are complementary from each other and show different means of detecting the crystallization of a glass. In particular, the simulation of the diffracted intensity appears to be relevant in this work as it is a straightforward evaluation of the completeness of the crystallization. However, all these calculations give an average evaluation of the crystallization of the cells and in any way allow determining whether the devitrification starts in the neighborhood of Er³⁺.

To get more information about the early stages of the crystallization and, in particular, to understand what happens around Er³⁺, the study has been led further. Figure 8 represents the position of the each ion inside the PFE4 cell at different temperatures during the devitrification process. These snapshots reflect the progressive order appearing in the cells while heating. Crystalline plans are visible at a temperature of 370 K, and the crystallization is achieved after 390 K. So the process is accomplished within a wider range of temperature and presents an intermediate state where an amorphous phase is compressed between two growing crys-
talline phases. Important information that can be derived from those snapshots is the fact that the crystalline planes begin to grow in regions without Er ions.

Moreover, to confirm this observation, we did some modeling of the diffracted intensity of the cell depending on the position of Er\(^{3+}\). Cutting the cell in eight subcells and then treating them separately enable to locate the Er\(^{3+}\) ions inside the cell (Fig. 7). These simulations reveal that the different regions of a cell are not crystallized with the same efficiency and that the regions containing Er\(^{3+}\) are less crystallized. The devitrification seems to be less efficient in the subcells containing the doping ions. Therefore, it proves that the crystallization of PbF\(_2\) does not start at the nearest neighbor distance of Er\(^{3+}\) ions. However, because of the periodic boundary conditions used in MD simulations, there may be some Er\(^{3+}\) ions at close distance to the subcells where the crystallization is more significant. Hence, PbF\(_2\) crystallization does not begin directly around Er\(^{3+}\) ions but probably at a close distance from them.

VIII. CONCLUSION

MD simulations of the total enthalpy of erbium-doped PbF\(_2\) glasses successfully reproduce the experimental results, showing that the introduction of erbium ions in a PbF\(_2\) system has a major influence on the crystallization of the lead fluoride phase. The introduction of only one trivalent erbium ion in a cell comprising about 860 Pb\(^{2+}\) ions has a huge influence as it decreases the crystallization temperature of PbF\(_2\) by 30 K. In agreement with the experiments, MD simulations prove that Er\(^{3+}\) ions ease the crystallization of PbF\(_2\).

Radial distribution functions, diffracted intensities, and diffusion coefficient variations have been simulated as well to follow the early stage of crystallization. The evolution of radial distribution functions and of diffracted intensities during the devitrification process indicate the progressive crystallization of PbF\(_2\) and doped-PbF\(_2\) systems. It also reveals, in agreement with the simulations of the total enthalpy, that the presence of Er\(^{3+}\) ions favors the crystallization of PbF\(_2\).

The analysis of the diffusion coefficients shows that the mobility of the fluorine ions is much higher in glassy PbF\(_2\), which comprises a higher concentration on defects, than in the crystal. Finally, to get more information about the local role of Er\(^{3+}\) ions onto the crystallization process of PbF\(_2\), we performed some MD simulations while localizing the Er\(^{3+}\) ions inside the cells. It demonstrates that the crystallization does not take place directly around Er\(^{3+}\) ions but it probably starts at short distances from Er\(^{3+}\).

Further investigations on the influence of Er\(^{3+}\) onto the devitrification of PbF\(_2\) could involve the study of other systems. For example, other cells could be built up, without respecting the charge balance but without comprising any vacancies.