



Molecular dynamics simulation and crystal field calculations of the $\text{Eu}_2\text{O}_3\text{-PbO-SiO}_2$ glassy system submitted to long annealing time

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ARTICLE INFO

Article history:

Received 7 March 2016

Received in revised form 9 June 2016

Accepted 25 June 2016

Available online xxxx

Keywords:

Molecular dynamics

Glasses

Europium ion

Crystal field parameters

Simple overlap model

Method of equivalent nearest neighbours

ABSTRACT

The $\text{Eu}_2\text{O}_3\text{-PbO-SiO}_2$ glassy system submitted to a long annealing time (100 ps) has been obtained by molecular dynamics calculations. The average of 87/86 sites of the Eu^{3+} ion with six/seven nearest neighbours are used to discuss the number of lines and the local symmetry of the luminescent site through the crystal field parameters, using the simple overlap model in the frame of the method of equivalent nearest neighbours. The magnitude of the $B_q^2(q = 0, 1, 2)$ and the non-negligible B_4^4 and $B_4^6(B_3^4, B_3^6$ and $B_6^6)$ lead to the indication of distorted C_{4h} and C_{3i} site symmetries of the six and seven nearest neighbours, respectively. We have then compared very satisfactorily our ${}^7\text{F}_1$ sublevels calculations with those observed in the emission spectra of an Eu-borate glass annealed for 30 min and 17 h. This comparison is justified because the emission behaviour of europium ions in different glassy systems are honestly very similar. Further, the decrease observed in the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2/{}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition intensity ratio is a clear indication that the Eu^{3+} ion are nucleating a crystalline phase. Such satisfactory comparisons indicate that we have obtained a transparent glass-ceramics.

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1. Introduction

Theoretical and simulation procedures are nowadays imperative tools to provide support to scientific experimental studies [1–3]. This clearly prevents wasting time and money. From the material science point of view, lanthanide (Ln^{3+}) ions doped glasses, crystals and Ln-complexes have important applications in photonics [4–9].

Molecular dynamics (MD) has been largely employed to simulate structures, nanostructures and properties of glasses and rare-earth doped glasses. By typing and keeping the potentials of interaction within physically acceptable ranges, predictions can be made and one tries to envisage non evident local structural features and physical properties [10–14].

Recently, by using an average local structure of the Eu^{3+} ion over 187 luminescent sites in an aluminosilicate glass, the ${}^7\text{F}_1$ level splitting has been predicted and satisfactorily compared to the Eu^{3+} ion doped M_2O_3 ($\text{M} = \text{In, Sc, Lu, Y, Gd}$) series [15].

In 2004 emission spectra of Eu-borate glassy samples annealed for 30 min and 17 h at 1200°C were recorded (not published; see the experimental section) and the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (0-2) transition became less intense than the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (0-1) transition after the longer annealing time. This is a clear indication that the Eu^{3+} ions are nucleating centrosymmetric sites as a function of the annealing time. Such thermally-induced crystallization has been already observed in fluorozirconate and oxyfluoride glassy systems containing europium [16, 17]. In 2012 we have developed calculations for the $\text{Eu}_2\text{O}_3\text{-PbO-SiO}_2$ glassy system simulated by MD procedure. The system was submitted to a long annealing time from the MD point of view, namely, 100 ps (see the MD section just below). 173 sites were investigated, 87 with 6 nearest neighbours (6NN) and 86 with 7NN of the Eu^{3+} ion. This set of sites were used to obtain two average local structures (not published), and the Eu^{3+} ions are revealed in an approximate centrosymmetric site, mainly the 6NN. Thus, in this work, we are presenting MD and crystal field parameters (CFP) calculations, together with the experimental data and trying to conciliate all informations. The CFP are predicted by the simple overlap model (SOM) through the method of equivalent nearest neighbour (MENN) [18–21], with the aim of discussing the local symmetry of the luminescent ion. The analysed quantities are the sublevel positions and the splitting (ΔE) of the ${}^7\text{F}_1$ level.

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2. Molecular dynamics simulation

Using the MD technique, a set of ten different numerical samples has been simulated. Each of them is composed of about 2500 atoms respecting an equimolar $\text{SiO}_2\text{-PbO}$ composition and doped with 2% of Eu_2O_3 . The interatomic potential is the one developed by Feuston and Garofalini [22] which consists of a modified form of the Born-Mayer-Huggins ionic potential. It is composed of a two- and three-body terms. The former describes the interaction between atomic pairs while the latter is employed to take into account the covalence of Si–O and Pb–O bonds. Details on the parameters used to define these interatomic potentials can be found in the paper of Peres et al. [23].

A glass structure has been obtained for each numerical sample in applying a melt and quench procedure, with an integration time step of 1 fs. Starting from a crystalline structure, the samples have been melt at 8000 K for 40 ps to ensure a perfect mixing. Then, they have been cooled to room temperature in successive temperature steps at 7000, 6000, 5000 K, then from 4000 K down to 2000 K in steps of 200 K, and finally at 1500, 1000, 500 and 300 K. Throughout cooling, at each temperature step, the velocities were rescaled to control the temperature for 2 ps and then continued at constant energy for an equilibration period of 8 ps. In such a way, the total quench time was 180 ps for an average quench rate of $4.3 \times 10^{13} \text{ K} \cdot \text{s}^{-1}$. However, between 4000 and 2000 K, the quench rate was slowed in order to allow for further structural relaxation in a temperature domain in which the glass transition occurs. Finally, the glass structure at room temperature was annealed at 4000 K for 100 ps before a last cooling stage to room temperature. One has to note that the glass transition temperature of a MD sample is always much higher than the experimental one. This is a well known issue (see e.g. Vollmayr et al. [24] and Soules et al. [25]) that can be explained by a simulated quenching procedure that is necessary much faster than the experimental one. This annealing stage has been applied to investigate how it can affect the local structure around the doping ion and, as a result, can modify the luminescence features.

The analysis of the local structure around Eu^{3+} has shown that its second coordination shell is mainly composed of lead oxide, confirming that the luminescent ions are preferentially located in lead-rich domains [23]. The annealing stage do not affect significantly this trend. In contrast, considering a radial cutoff of 2.8 Å, the average number of oxygen in the first coordination shell of Eu^{3+} is increased from 6.40 to 6.62 with the annealing stage. Actually, from Fig. 1, it can be observed a shift of the first peak of the Eu–O Radial Distribution Function (RDF), as well as a rising of the plateau of the associated Cumulative Distribution Function (CDF). This is the evidence that the annealing stage involves a lengthening of the average Eu–O bond length and an increase of the Eu^{3+} average coordination number. From Fig. 2, the statistical occurrence of the Eu sites as a function of its coordination shows that the increase of the mean coordination number is due to a decrease of the number of 5-coordinated sites, along with an increase of the number of 7-coordinated sites. Among the 200 sites extracted from the ten numerical samples after the annealing treatment, 87 and 86 sites have been referred to as 6NN (site 1) and 7NN (site 2) sites, respectively. These 173 sites were stored for further analysis and more particularly for crystal field calculations.

3. Experimental

3.1. I-Glass preparation

The Eu-borate sample was prepared by dissolving boric acid (H_3BO_3 , 99.99 % Aldrich) 99 mol% and europium chloride (EuCl_3 , 99.99 % Aldrich) 1 mol% in filtered coconut water. This is an interesting procedure to produce nanosized powder samples [26]. This

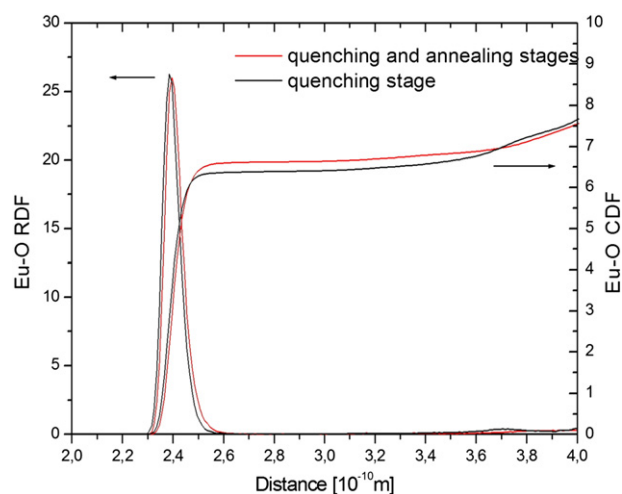


Fig. 1. Eu–O Radial Distribution Function (RDF, on the left axis) and associated Eu–O Cumulative Distribution Function (CDF, on the right axis), in the simulated sample after the quenching stage (black lines), and after the annealing stage (red lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

solution was submitted to 100 °C for 24 h for preparing the proteic xerogel. To be free of organic traces due to the coconut water, one has melt the xerogel to 1200 °C for 30 min for calcination. The glass has been obtained with the melt quenched to room temperature. The glass was then submitted to two annealing processes, the first one at 1200 °C for 30 min and the second one for 17 h at the same temperature. The main objective of the project was the preparation of a purely borate glass, without modifiers. Thus, only a small quantity of the prepared glass was used to test the possibility of producing glass-ceramics. The indication that we have prepared a glassceramics has been made by two evidences: i) the unaided eye observation of its translucent appearance no matter whether the sample is annealed for 30 min or 17 h and ii) by UV–Vis spectroscopy measurements. Such spectra have shown the reduction of the (0-2)/(0-1) intensity ratio as a function of the annealing time.

The main argument to assert that 100 ps is a long annealing time in MD simulation, and can be compared to 17 h in the experiment,

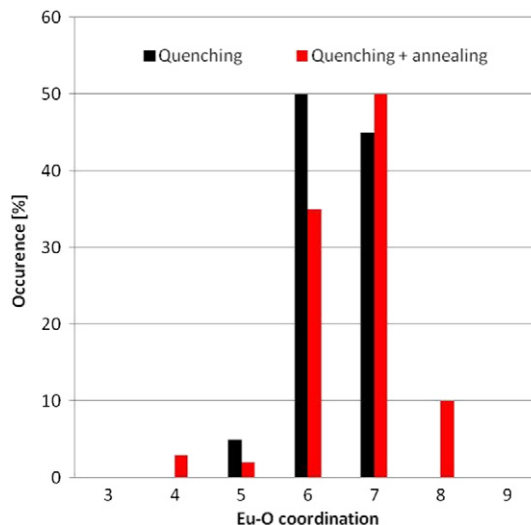


Fig. 2. Statistical occurrence of the Eu sites as a function of the coordination number, after the quenching stage (black bars), and after the annealing stage (red bars). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is related to the sample size. The experimental sample size is of the order of mm. Thermal diffusion and thermalization processes can reach minutes or hours. The simulation sample size is in the range of nm. The scale of time in thermal diffusion and thermalization processes are expected to be shorter. This is also true for quenching rates.

3.2. II-Luminescence

The fluorescence spectra were made with the samples in powder and obtained in an ISS PC1™ Spectrofluorometer, equipped with a 300 W Xe lamp for the excitation measurements at 257 nm (charge transfer band, CTB) and at 394 nm (⁵L₆ level). The emission was registered by a monochromator of 25 cm. The slit width was 0.5 mm for excitation and emission monochromators, both with 1200 grooves/mm.

One of the authors (H.C.C.O.) has developed this experimental procedure a long time ago in our group. Thus, the experimental part of this paper is both to pay tribute to our colleague and to use the luminescence measurements to validate our predictions, because the profile of the emission lines strongly suggests that the Eu ions occupy a high symmetry site, due to the fact that the (0-2)/(0-1) transition intensity ratio decreases with the annealing time.

4. Crystal field parameters

The Ln-NN interaction has been described by the electrostatic interaction between the 4f electrons and effective charges of the NN [27], assuming that the Ln-NN bonds are purely ionic. This has been recently discussed elsewhere [21]. The total hamiltonian which describes the energy level positions includes the free ion and crystal field Hamiltonians, H_{FI} and H_{CF} , respectively. The diagonalisation of the H_{FI} leads to the determination of the J eigenvalues, which states the energy level barycenter. By taking the barycenters as reference for our calculations, we have to take into account only the diagonalisation of H_{CF} , whose expression is given by

$$H_{CF} = \sum_{k,q,i} B_q^k C_q^k(\Omega_i) \quad (1)$$

C_q^k is the Racah spherical tensor and B_q^k is given by

$$B_q^k = \sum_j \sqrt{\frac{4\pi}{2k+1}} e^2 g_j \langle r^k \rangle \frac{Y_{k,q}^*(\Omega_j)}{R_j^{k+1}} \quad (2)$$

$-g_j e$ is the NN effective charge, R_j is the Ln-NN distance with respect to a coordinate system centered at the nucleus of the lanthanide ion, $Y_{k,q}^*$ is the spherical harmonic, and $\langle r^k \rangle$ are the radial integrals associated to the 4f electrons.

The first non parametric model for B_q^k is the well known point charge electrostatic model (PCEM) [28]. In the PCEM g_j is the NN valence, located at the NN site. Such assumptions has led to non-satisfactory predictions from the quantitative point of view, which gave rise to a substantial variety of parametric models, mainly to describe the crystal field parameters (CFP) [29]. Our idea is to present a theoretical discussion on the CFP.

4.1. The simple overlap model

The simple overlap model is a non-parametric theoretical model based on the PCEM. In the SOM g_j is a charge factor and is treated as a variable, indeed, not necessarily limited to the NN valence, and a small covalent contribution is introduced. The effective interacting charge is then defined as $-g_j e \rho_j$ and is located in a small region around the middle point between the central ion and each NN, the

position of the overlap (ρ_j) of the interacting ions wavefunctions [18]. For each NN, ρ_j is defined by

$$\rho_j = \rho_0 \left(\frac{R_{min}}{R_j} \right)^{3.5} \quad (3)$$

$\rho_0 = 0.05$ is the maximum overlap of the 4f and ns or n'p orbitals ($n, n' = 2, 3$) [30], R_{min} is the smaller Ln-NN distance, R_j is the j-th NN distance, and 3.5 is a phenomenological value [31].

With these considerations it is possible to relate the SOM CFP with the PCEM CFP as follow [18]

$$B_q^k(SOM) = \rho_j \left(\frac{2}{1-\rho_j} \right)^{k+1} B_q^k(PCEM). \quad (4)$$

One has to point out that only the minus sign is being used in denominator, because it is assumed that the distance between the charge of interaction and the lanthanide nucleus is always smaller than Ln-NN half distance [21]. This theoretical crystal field model has had satisfactory predictions for crystal field parameters and energy level positions and splitting of lanthanide ions containing systems [15, 29, 32, 33, 34]. However, the only multiplet with a very well tested expression is the ⁷F₁ energy level, because there is a closed simple equation describing its splitting as a function of the crystal field strength parameter (N_V , [19]) and, in this case, only the CFP of rank 2 plays a role [19, 21]. Thus, one has only diagonalised the crystal field energy matrix within the ⁷F₁ manifold.

4.2. The Method of Equivalent Nearest Neighbours

The Method of Equivalent Nearest Neighbours (MENN) [20, 21, 35] can be viewed as a modified SOM, but indeed is an effort to systematize it. The method consists of three basic considerations: (i) equivalent NN are identified through the local symmetry of the luminescent site and c, the *equivalency number* (degrees of freedom), is defined; (ii) the experimental energy sublevel positions of the ⁷F₁ manifold are predicted by a set of phenomenological g_j [27]; and (iii) the sum $\sum g_j$ must be equal the central ion charge. By taking a glance on the CFP equations [36], one can readily note that the charge factors are the variable. The goal of the MENN is establishing a systematic way of determining the charge factor.

In this way the method reduces the difference between the experimental and predicted values of CFP and ΔE respecting the symmetry and electrostatic equilibrium conditions for the optically active site.

5. Results and discussions

87 (86) sites of the Eu³⁺ ion with six (seven) NN obtained by MD procedure were analysed in order to discuss the local structure and spectroscopic features of the luminescent site. By diagonalizing the tensor of the quadrupolar field experienced by each luminescent site,

Table 1

Spherical coordinates of the europium ions (a) with six NN and (b) seven NN. The europium ion is at the origin.

O	Site 1			Site 2		
	R(Å)	$\theta(^{\circ})$	$\varphi(^{\circ})$	R(Å)	$\theta(^{\circ})$	$\varphi(^{\circ})$
O1	2.253	0	0	2.383	9.7	10.42
O2	2.322	86.16	44.6	2.381	128.77	0
O3	2.318	90.50	136.28	2.354	77.02	68.85
O4	2.334	89.45	225.83	2.374	59.82	181.71
O5	2.322	90.72	313.18	2.402	129.19	232.19
O6	2.283	178.98	21.58	2.380	75.59	291.03
O7	–	–	–	2.382	127.42	129.56

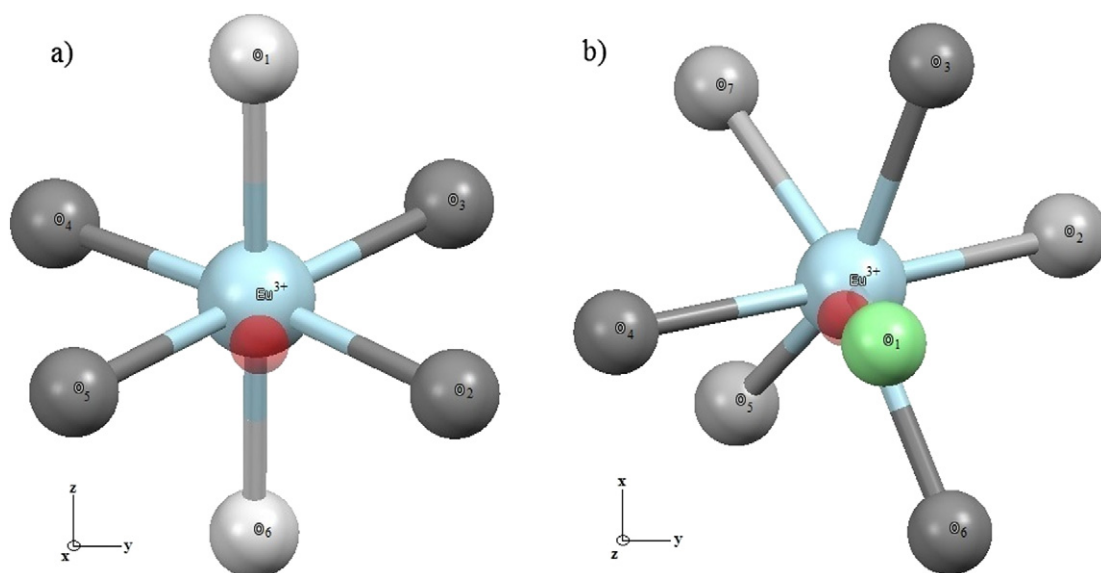


Fig. 3. Symmetry axis adopted to obtaining the angular coordinates a) 6NN b) 7NN. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

the eigenvector corresponding to the highest eigenvalues was chosen as the principal axis of symmetry (z axis). In such a way, one has obtained the average spherical coordinates of the Eu^{3+} ions for both cases (Table 1).

As one is dealing with an amorphous structure, all Eu–O distances are slightly different and, as a consequence, all symmetry considerations are approximate. In fact, C_1 is the only possible site symmetry to be assigned, rigorously. However, by combining the simulated local structures with the spectroscopic results, we will demonstrate that such considerations are very close to the reality, even in the case of site 2.

According to the MENN, the choice of the equivalent NN is made by the Eu^{3+} local symmetry. The site 1 (Fig. 3a) contains one plane of symmetry (σ_1), containing four oxygen ions (O2, O3, O4, O5), very approximately perpendicular to the z axis. Then, the two oxygen ions out of this plane (O1 and O6) are on the z axis and equivalent to each other. The four oxygen ions on the plane are equivalent to each other, because a sequence of three C_4 operations leads very approximately any oxygen ion on σ_1 to the position of any other in the same plane. Then, $c = 2$ and one needs two different charge factors. For the site 2, the oxygen O1 (green color) in Fig. 3b is very close to the z-axis. Thus, there are approximately two perpendicular planes of symmetry (σ_1

and σ_2) through the z-axis and containing O2 and O4 (σ_1) and O6 and O7 (σ_2), showing that the 3 oxygen ions of both triad (O3, O4, O6 and O2, O5, O7) are equivalent to each other or a C_3 symmetry operation leads very approximately any oxygen ion of each triad to any other in the same triad. So, the oxygen ions of each triad are equivalent to each other. Clearly, oxygen O1 is individual, $c = 3$ and one needs three charge factors. In both sites, the red circle is associated to axis: in the former, x-axis, and in the latter, z-axis.

The emission spectra (Fig. 4) with excitation in the charge transfer band (CTB, $\lambda_1 = 257$ nm [37, 38]) lead to quite different profiles when compared to that with excitation in the $^5\text{L}_6$ level ($\lambda_2 = 394$ nm) of the Eu^{3+} ion. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (0-2) transition is hypersensitive and allowed by forced electric dipole mechanism. Its intensity is smaller than the intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (0-1) transition, this latter allowed by the magnetic dipole mechanism, when excited at λ_1 , which indicates that λ_1 is exciting the site with higher symmetry. This is a clear indication that the luminescent site is trying occupies a centrosymmetric site. The excitation at λ_2 shows the contrary: the 0-2 transition is more intense than the 0-1 transition, meaning that the less symmetric site is being excited. Thus, one has a strong indication that site 1 is more excited at λ_1 and site 2 is more excited at λ_2 . Further, one can readily note that the intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ (0-0)

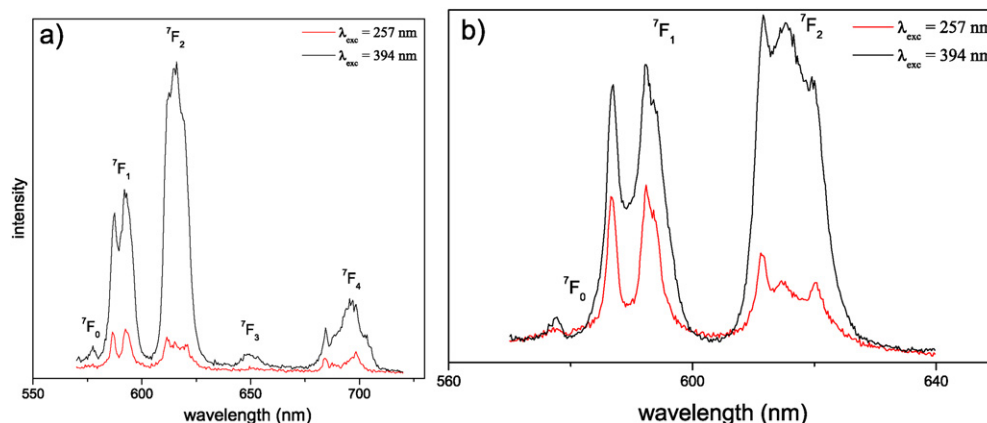


Fig. 4. Emission spectra of Eu-borate glass with annealed a) 30 min and b) 17 h.

Table 2
Charge factors of both sites.

Site 1				Site 2			
g_j	g_1	g_2	$\sum g_j$	g_1	g_2	g_3	$\sum g_j$
MENN	0.576	0.348	3	0.062	0.438	0.811	3.81

transition is weak in both spectra and the profiles of the 0-1 transitions are very similar under both excitations with sample annealed for 17 h. This could be an indication that only site 1 will remain after cumulative annealing. In this way site 1 is being associated to the 6NN site and site 2 is being associated to the 7NN site. Further, the opaque aspect of the final product (annealed for 17 h) was a strong indication that one has obtained a glassceramics, the europium ions being the nucleation units.

The structures of microporous Eu-silicates have been reported with similar local environment with 6NN and 7NN, but prepared through a completely different way [39, 40]. Even the emission spectra are similar, in the sense that the 0-2 transition is less intense than the 0-1 transition. This may possibly be a feature of Ln-silicates.

Table 2 shows the set of phenomenological charge factors used to calculate the set of B_q^k for both sites (Table 3) which has led to a good prediction of the 7F_1 energy sublevels and, consequently, ΔE (Table 4). For this, the maximum overlap, ρ_0 , is stronger than that obtained by Axe and Burn [30]. In this case, we used $\rho_0 = 0.092$ for the site 1 and $\rho_0 = 0.13$ for the site 2. Such stronger ρ_0 has been already used elsewhere [29].

From Table 2 the reader can readily note that the sum of the charge factors is equal to the own valence of Eu^{3+} ion for the site 1. However, in order to reproduce the 7F_1 energy sublevels and consequently ΔE , the sum of the charge factors is larger than the Eu^{3+} ion valence for the site 2. The Batista-Longo Improved Model (BLIM, [41]), describes the Eu^{3+} ion charge as a function of the distance for Eu-complex systems. The imperfect screening of the 4f electrons is one of the arguments of the BLIM. However, the shielding of the 4f orbitals by the eight 5s and 5p electrons of the lanthanide ions is valid no matter the host. Thus, we used the BLIM to calculate the europium ion charge (g_{Eu}) at the middle Eu-NN distance to give 4.116. This is now the strong argument inside the group to the understanding of this electrostatic behaviour.

The first point to be highlighted is the fact that the set of charge factors in both cases has been obtained as an solution of a system of

Table 3
CFP of a) 6NN and b) 7NN (B_q^k in cm^{-1}). δ means the error in percentage when the B_1^2 parameter is neglected in N_V calculations.

B_q^k	Site 1	Site 2
B_0^2	−632	−621
B_1^2	−30 − 62i	−126 − 30i
B_2^2	44	−50
B_0^4	2420	−1683
B_1^4	21 − 95i	44 + 61i
B_2^4	−32 − 8i	795 − 357i
B_3^4	−43 − 47i	−2359 + 1347i
B_4^4	498 + 1016i	32 − 68i
B_0^6	−470	986
B_1^6	−37 + 74i	304
B_2^6	42 + 17i	−464 + 346i
B_3^6	−61 + 67i	−390 + 260i
B_4^6	−514 − 1049i	−109 + 183i
B_5^6	−84 + 14i	−275 + 393i
B_6^6	34 + 35i	602 − 921i
δ	1.7	4.0

two equations composed by the Auzel-Malta expression for ΔE [32] and the electrostatic equilibrium. The same sets of charge factors just obtained entered in the energy sublevel equations, obtained by diagonalizing the crystal field energy matrix within the 7F_1 manifold, to reproduce very satisfactorily the experimental sublevel positions. The charge versus distance behaviour is discussed using the average distance. The g_j versus R_j growing linear behaviour has been predicted in the both cases [42].

Table 3 shows the set of CFP for both sites. As expected, all CFP are non-zero, since we are dealing with an amorphous structure. For both sites, the influence of the B_1^2 is negligible, since its contribution to N_V is less than or equal to 4%, and a rotation about the principal axis has been made in order to vanish the imaginary part of B_1^2 .

The sign of B_0^2 defines the position of the ground sublevel from the barycenter. Table 4 shows that this has been correctly predicted in both cases, because B_0^2 is negative, and the ground sublevel of the 7F_1 manifold of the Eu-borate sample is non degenerate. ΔE can be noticed by $E_{+1} - E_0$ and has been calculated by the Auzel-Malta expression without (with) considering B_1^2 . Comparing the most unfavorable prediction (197 cm^{-1}) with the experimental ΔE (205 cm^{-1}), the error is less than 4 %, even though sites 1 and 2 have different local environment. We have to point out that different charge factors combined with different NN positions or with different local symmetries can lead to the same splitting (see ref. [43] for experimental evidence). Further, $|B_0^2| \gg |B_1^2|$, which explains the small separation of the doubly degenerate sublevel [27].

The emission patterns of Eu ions in different glassy systems are similar to each other [16, 44]. In the present case we have then compared very satisfactorily our 7F_1 Stark levels calculations with those observed in the emission spectra of a Eu-borate glass annealed for 30 min and 17 h.

Some points deserve comments:

- $\Delta E < 350 \text{ cm}^{-1}$ indicates cubic symmetry [27];
- one has a strong indication that site 1 has a distorted C_{4h} symmetry, because the B_0^2 , B_0^4 , B_4^4 , B_0^6 and B_4^6 are clearly the dominant parameters, with non negligible imaginary part of the B_4^4 and B_4^6 parameters. The set of non-negligible CFP and the dominant magnitude of the B_3^4 , B_3^6 and B_6^6 lead to no more than a suggestion of a distorted (or approximate) C_{3i} local symmetry for the 7NN site, because the magnitude B_4^4 , B_4^6 parameters are not negligible. The 0-1 transition has very nearly two lines, and the 0-0 and 0-2 transitions are going to null intensity with increasing annealing time. With such landscape, taking a glance on the cascade of the Tanner diagram [45], C_{4h} and C_{3i} are the most adequate point groups for these sites.
- The comparison with the emission spectra of a Eu-borate glass annealed for 30 min and 17 h shows a satisfactory agreement. This comparison is meaningful regarding the fact that emission spectra of Eu^{3+} in different glassy hosts are quite similar [16, 17, 46] displaying a clear splitting of the 7F_1 level in 3 components: the double-peak feature of the ${}^5D_0 \rightarrow {}^7F_1$ transition obtained in our Eu-borate glass is therefore an indication that the Eu^{3+} ions occupy sites which are

Table 4
Experimental and predicted sublevels of the 7F_1 level and ΔE . E_{exp} in parenthesis relate the energy sublevels in respect to the 7F_0 level. ΔE is calculated using Auzel-Malta expression, without (with) B_1^2 .

$E(\text{cm}^{-1})$	E_{exp}	Site 1	Site 2
E_0	−122 (277)	−122	−122
E_{-1}	38 (437)	37	38
E_{+1}	83 (482)	85	83
ΔE	205	202 (200)	197 (205)

nucleating a crystalline phase, which grows with the annealing time. This is a clear indication that we have obtained a transparent glass-ceramics experimentally and by simulation;

- iv) the similarity of the 0-1 lines in both excitations and annealed for 17 h, together with the reduction of the 0-2 transition intensity, is indicative that the site 2 is a transient site. Further cumulative annealing may turn the 7NN site out to be a 6NN site; and
- v) the charge factor of the O1 ion of the site 2 is 0.067. Clearly, it has minor contribution to the calculations. Thus, effectively, $c = 2$ even for the site 2.

By analytical equations, only the 7F_1 level has a quite simple description and its splitting has been very well tested, and can be used in a quite distorted symmetry. Besides, we know how to associate B_0^2 and B_2^2 for the 7F_1 in any symmetry. The number of lines in the 0-2 transition can be three or four and it is not a simple task to associate experimental 0-2 lines with parameters, even in high symmetry cases [47]. Thus, for the 7F_2 level we have not performed any calculations. Further, as we are assuming that the Eu^{3+} ions are nucleating centrosymmetric sites, no 0-J(=0, 2, 3, 4, 5, 6) transitions could be observed.

6. Conclusions

Molecular dynamics simulations were used to obtain the $\text{Eu}_2\text{O}_3\text{-PbO-SiO}_2$ glass system submitted to a long annealing time. 87/86 sites of the Eu^{3+} ion with six (site 1)/seven (site 2) NN have been identified, from which one has obtained the average spherical coordinates of both sites. The method of equivalent nearest neighbours was then applied in order to discuss the local symmetry and spectroscopic features (7F_1 energy sub-levels and its splitting) of the luminescent site. The sign of the B_0^2 parameter and the 7F_1 energy sub-levels were satisfactorily predicted. The set of two charge factors in the case of site 1 has been obtained as an exact solution. However, for the site 2 a phenomenological procedure have to be adopted, because three charge factors are required, even though the small magnitude of one of them makes $c = 2$ effectively. The sum of the charge factors larger than the Eu^{3+} ion valence for the site 2 is explained, because we obtain $g_{\text{Eu}} = 4.116$ using the BLIM calculations. The set of non-negligible crystal field parameters lead to the suggestion of a distorted C_{4h} and C_{3i} local symmetries for the site 1 and site 2, respectively. In both cases, the magnitude of the B_0^2 and the sub-levels positions of the 7F_1 multiplet are very similar. The emission spectra of a Eu-borate glass with different annealing times are the available experimental data that is being used to verify very satisfactorily the predictions. The reduction of the 0-0 and 0-2 transition intensity with the annealing time under excitation at the CTB is indicative that the Eu^{3+} ions are seeking to occupy an unique centrosymmetric site after cumulative annealing.

Acknowledgments

The Inct-INAMI, CNPq, CAPES, and FAPITEC Brazilian agencies are deeply acknowledge for financial support. They also gratefully acknowledge the support of Région Pays de la Loire for the post-doctoral fellowship of T. S. Santos.

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