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NUMERICAL SIMULATIONS OF THE STRUCTURE AND SPECTROSCOPIC PROPERTIES OF RARE-EARTH DOPED GLASSES

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A review of the research that has been devoted to the simulation of the structure and spectroscopic properties of rare-earth doped glasses is presented. Since the seminal papers of Brawer and Weber who have applied Monte-Carlo or molecular dynamics techniques, some other very important results have been reported concerning the local structure of the dopants. As a result, crystal field models have been applied and several peculiarities of the optical spectra of rare earth ions in glasses have been understood.

Keywords: Glasses; rare-earth doped; crystal field models

I. INTRODUCTION

In 1972, Rahman, Fowler and Narten [1] applied Molecular Dynamics simulation to study the structure of glasses. Since the paper of Woodcock, Angell and Cheeseman [2] in 1976 many works have been devoted to the modelling of glasses by numerical simulations. Due to the small size of simulated samples (several hundreds of particles) and the fast quenching (roughly 10^{-9} s) of the simulated liquid, only the local arrangement and the short range order can be investigated by this technique. An example of what can be studied is the local structure surrounding dopant ions in insulating disordered materials.

However, the application of Molecular Dynamics technique to the study of doped glasses have been scarce. The first simulations of rare-earth doped glasses were presented in the 1980's by Brawer and Weber [3–8].

A great amount of work has been devoted to the optical spectra of paramagnetic ions in glasses. Such spectra show large inhomogeneous broadening due to the site-to-site variation in the local structure around these ions. In contrast to insulating crystals, little is known about the local arrangement in glasses. Optical spectroscopy and other spectroscopic techniques have been used, including EXAFS, to study the local environment of the dopant. However, these techniques only provide average structural properties and not a detailed understanding of the local rare-earth environment. The spectroscopic analysis of doped glasses is generally done using the technique of fluorescence line narrowing (FLN) followed by crystal field calculation based upon some structural assumptions. An alternative method that has been used since the works of Brawer and Weber consists in performing a numerical simulation of the glass, analyzing the generated environments and computing spectra without any “*a priori*” knowledge of the local structure.

The first part of this review is devoted to the spectroscopy of rare-earth doped-glasses, the second part will describe briefly the method of modelling based on the FLN results and the third part will introduce the numerical simulation method applied to the study of the rare-earth environment. The last part will be devoted to the simulation of the optical spectra.

II. SPECTROSCOPIC CHARACTERISTIC OF DOPED GLASSES

It is a well established fact that the spectra of rare-earth ions in glasses are inhomogeneously broadened due to the site-to-site variation of the local environment. Distortions of the coordinating polyhedra and variations in the coordination number are two well known reasons. In order to interpret the experimental results, it is necessary to know the position of the ligands and be able to write the corresponding Hamiltonian for the system, that is for the dopant. The effect of the ligands is treated as a perturbative term in the Hamiltonian. The most commonly used model (for this term) is the point charge crystal field model where each ligand is considered as a point-charge.

The crystal field Hamiltonian that describes the interaction of the rare-earth ion with the host lattice can be written as

$$\mathcal{H}_{CEF} = \sum_{nm} A_{nm}^* \sum_i r_i^n C_{nm}(\hat{r}_i), \quad (1)$$

where the first sum covers those values of n and m allowed by the symmetry of the site of the rare-earth. With n even equation 1 is used to calculate the crystal field splitting; for n odd it is used to calculate the transition probabilities. The second sum is over the N electrons of the $4f^N$ configuration of the ion ($N = 6$ for Eu^{3+}). The model neglects both the spatial extent of the ligand charge density and the wave function overlap of the optically active $4f$ electrons with the ligands. For point charges, eq_j located at R_j , the crystal-field components, A_{nm} of equation 1 are given by:

$$A_{nm} = -\frac{e^2}{4\pi\epsilon_0} \sum_j q_j \frac{C_{nm}(\hat{R}_j)}{R_j^{n+1}} \quad (2)$$

The irreducible tensors $C_{nm}(r)$ are related to the spherical harmonics $Y_{nm}(\theta, \phi)$. This widely used model has some shortcomings and need further development. The best results are usually obtained for the most ionic compounds. The reason for this is that this model does not take into account covalency.

Amongst the rare earth ions Eu^{3+} has been the favorite ion to use in modelling, because of the relative simplicity of its energy levels, it possesses non degenerate ground (7F_0) and emitting states (5D_0) and these states are sensitive to the crystal field environment. Figure 1 shows a typical emission spectrum of Eu^{3+} in a glass.

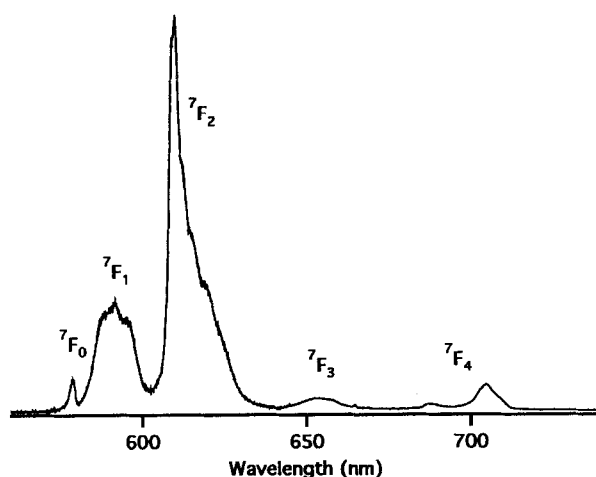


FIGURE 1 Emission spectrum of a Eu^{3+} -doped silicate glass, for the transition $^5D_0 \leftarrow ^7F_J$ ($J = 0 - 4$). From Cormier *et al.* [12].

III. MODELLING RARE-EARTH DOPED GLASSES: GEOMETRICAL MODEL

Laser-excited site-selective spectroscopy, commonly called fluorescence line narrowing (FLN), has been demonstrated to be an extremely useful technique for the study of structural inhomogeneities in glass. In this technique, energy subsets of the whole ensemble of doped ions are resonantly excited by a narrow band source such as a tunable dye laser. The observed changes of the emission spectra as a function of the excitation wavelength are related to the local environment of the dopant ions in the glass using elementary crystal field theory. Using FLN measurements Brecher and Riseberg [9, 10] developed a geometric model for the Eu^{3+} ion in a modified silicate glass and in a fluoroberyllate glass. This model limits its consideration to the immediate environment of the Eu^{3+} ion, and it involves eight equidistant coordinating oxygens arranged in a distorted Archimedean antiprism with C_{2v} symmetry into which a ninth coordinator intrudes along the C_2 axis (Fig. 2). Brecher and Riseberg [9] introduced a distortion parameter in their model in order to take into account the continuous variation of the crystal field as shown by the FLN experiments. They calculated the crystal field parameters with respect to the

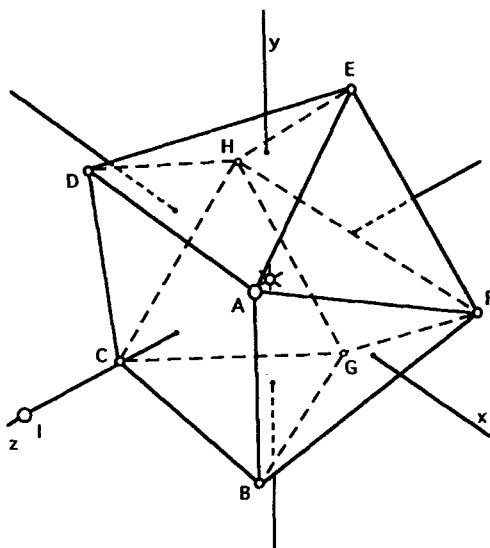


FIGURE 2 Geometric model for the environment of the Eu^{3+} ion in silicate glass. The Eu^{3+} sits at the center of this structure with a principal coordination of eight equidistant oxygens. A ninth oxygen (*I*) introduced along the *z*-axis distorts this structure by enlarging the *ABCD* area and by stretching the *EFGH* plane towards negative *z*-values. From Brecher and Riseberg [9].

distorsion parameter, using a point charge model. The crystal field parameters were then compared to those derived from the FLN experiment and a good agreement was found. Although the model developed by Brecher and Riseberg has given reasonable results in a variety of cases it fails one of the basic requirements, that is, that the model be generalized. The authors considered only the first coordinating shell and ignored the rest of the immediate environment. In effect their model is too simple to effectively represent the average local environment of a rare-earth dopant ion in an oxide glass.

IV. APPLICATION OF THE MD TECHNIQUE TO THE STUDY OF THE RARE-EARTH ENVIRONMENT

Although molecular dynamics simulation have been used extensively to study the structure of glasses, application to the study of rare-earth doped glasses has been scarce. In this section we will discuss the methodology in general terms and review only the simulations studies undertaken over the past 15 years which have dealt with the rare-earth environment in glasses.

In a molecular dynamics simulation one solves Newton's equation of motion for an ensemble of particles interacting with one another by virtue of an appropriate potential energy field, at some specified temperature. The most critical step in a molecular dynamics simulation is the choice of a function representing the interparticle force or potential energy. This mathematical function describing the interaction between particles "the model" is chosen such as to reproduce as closely as possible the corresponding experimental situation. A molecular dynamics simulation generates the evolution of the system in time and simulations are conducted from picosecond to nanosecond durations. Computer programs for conducting molecular dynamics are available from a variety of sources and the methodology used is reviewed in the literature [5, 11].

The first simulations of rare-earth doped glasses were presented in the 1980's by Brawer and Weber [3-8]. They published a series of articles on the structure simulation of rare-earth doped fluoroberyllate glasses by the Monte-Carlo technique and by molecular dynamics. The modelled glasses were BeF_2 and alkali-modified BeF_2 doped with RE^{3+} ion. The modifiers were Na^+ , Rb^+ and Ca^{2+} . Since for fluorides the atomic interactions are essentially ionic in character Brawer and Weber used an electrostatic pairwise potential. Ions were assumed to interact with a Coulomb potential and a Born-Mayer

repulsion of the form

$$v(r) = \frac{q_i q_j}{r} + A_{ij} e^{-\sigma r} \quad (3)$$

A typical simulation involved several hundreds of ions in a cubic cell of dimensions to yield the correct final glass density. Completely random ion positions were used in the initial configuration in order to avoid structural bias. Periodic boundary conditions were used to eliminate any possibility of surface effects.

Brawer and Weber, in their pioneering simulation studies of Eu^{3+} in BeF_2 , characterized for the first time the environment of the rare-earth ion. From the results of the simulations for BeF_2 and various fluoroberyllate glasses, they were able to predict the environment of the rare-earth using RE-F, RE-Be and RE-M (M = modifier cation) radial distribution functions (RDF). In addition, the average nearest-neighbour number about the RE may be obtained under the first peak of the RDF $g(r)$ that is

$$N(R) = \int_0^R g(r) 4\pi r^2 dr \quad (4)$$

Recently, Capobianco and his group [11–17] have performed similar calculations for Eu^{3+} and Yb^{3+} in silica, sodium disilicate, lead metaphosphate and lead silicate glasses. The force law used in their molecular dynamics calculations is derived from a pairwise (two body) ionic potential which includes the Pauling repulsive term. It is of the same form as that described by Mitra *et al.* [18]. The associated force law is given by

$$F(r_{ij}) = \frac{q_i q_j}{r_{ij}^2} \left[1 + \text{sign}(q_i q_j) \left(\frac{\sigma_i + \sigma_j}{r_{ij}} \right)^n \right] \quad (5)$$

where q_i and q_j are the ionic charges, and σ_i and σ_j are the ionic radii of atoms i and j , n is a measure of the hardness of the repulsion and r_{ij} is the distance between atoms i and j . From the molecular dynamics simulation of silica and sodium disilicate they suggest that the europium ions form quasi-molecular complexes and they do not behave as a network modifier. Another conclusion of their molecular dynamics simulations is that the local structure of the europium ions is influenced to a greater degree by its bonding and energetic requirements than by the topology of the silicate network. Figure 3 shows an example of simulated local environment for the Eu^{3+} ion in SiO_2 . The

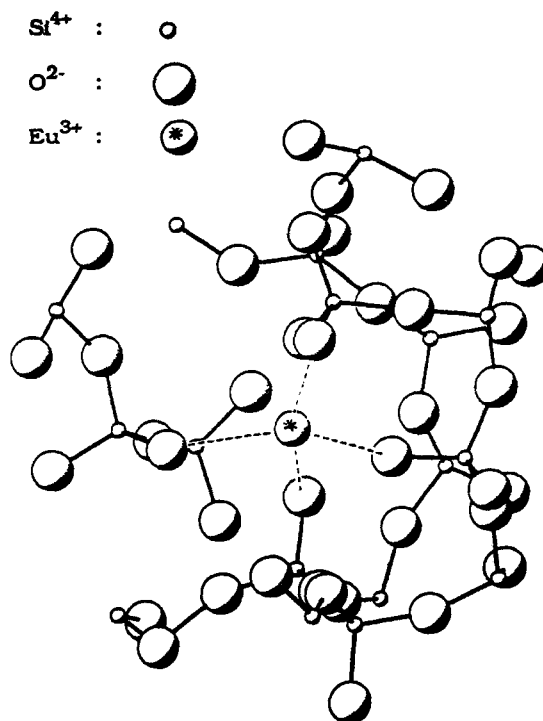


FIGURE 3 Schematic representation of the local environment around the ion Eu^{3+} in silica glass. In this example the coordination is 4. From G. Cormier *et al.* [16].

simulations yield average coordination numbers of four and six for the Eu^{3+} ion in SiO_2 and $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glasses respectively. Photoluminescence and EXAFS measurements have been performed on Er-doped glasses: silica and sodium silicate [19]. EXAFS data show that in the studied glasses the Er^{3+} ions have six oxygen first neighbours confirming the simulation results.

Molecular dynamics simulations have also been used to investigate the local environment of Eu^{3+} ions doped into lead metaphosphate [15]. The structural model of $\text{Eu}^{3+}:\text{Pb}(\text{PO}_3)_2$ glass, shows that the doping Eu^{3+} ions are bonded in their first coordination shell to approximately six non-bridging oxygen atoms. The non-bridging oxygen atoms are themselves an intrinsic part of the phosphate backbone. Furthermore, the Eu^{3+} ions are situated in secondary network, which is made up of the modifier lead cations linked by non-bridging oxygen atoms. Another important prediction of the molecular dynamics simulations, is the substantial medium range order observed in the local environment of Eu^{3+} ions. This was attributed to the ordering of the phosphate backbone.

Lead containing glasses are used extensively in numerous industrial and technological applications. Recently, high technology applications such as nuclear scintillations and upconversion laser devices have demanded a greater understanding and control over structurally related optical properties. Using molecular dynamics Cormier *et al.* [17] have reported a simulated structural model of $\text{PbO} \cdot \text{SiO}_2$ doped with Yb^{3+} . The nature of the structural arrangement of the rare-earth ion, Yb^{3+} was discussed. The simulations indicate that the average coordination of the Yb^{3+} ions to be 6. Six co-ordinated lanthanide ions in amorphous oxide matrices have been previously postulated to explain observed spectroscopic features. Robinson, Fournier and Bartram wrote a series of articles [20–22] studying Yb^{3+} doped phosphate, silicate and germanate glasses, Er^{3+} in alkali silicate glasses [23,24] and Nd^{3+} doped in barium rubidium silicate glass [25]. They postulated from the low temperature absorption and emission spectra of the lanthanide ions that the principal rare-earth environment in these glasses is a distorted sixfold polyhedron. The immediate coordination scheme of the Yb^{3+} ions was investigated by determining the speciation of oxygen types as ligands. The results clearly supported the fact that the Yb^{3+} ions are located in the secondary lead network.

In addition to the series of papers from Weber and Bräwer and Capobianco *et al.* only three other accounts of the simulation of doped glasses can be found in the literature [26–28]. Hirao and Soga [26] studied a series of four europium-doped sodium borate glasses using a two-body potential of the Born-Mayer-Huggins type. The authors report large site-to-site variations in the europium local environment with an average coordination number found to be between 7.5 and 8.6. They showed that the average coordination number of the europium ion to be composition dependent. Recently, Soga *et al.* [27] and Takahashi *et al.* [28] have performed similar simulations for Eu^{3+} in fluorozirconate and chlorofluorozirconate glasses respectively. It is interesting to note that the authors report an average coordination number of 8 for the Eu^{3+} ion, in contrast to the lower average coordination number reported for the Eu^{3+} in oxide glasses [11,12]. Takahashi *et al.* [28] also examined the local structural changes around the Eu^{3+} ion with the anion (F^- and Cl^-) substitution. Based on their results they suggest that Cl^- substitutes for F^- around Eu^{3+} and the Cl^- coordination number around Eu^{3+} increases in proportion to the concentration and the existence of Cl^- produces high energy phonons modes around the Eu^{3+} ion. It is difficult to make rare-earth doped SiO_2 by the conventional fusion technique. Therefore, in order to study the optical properties of rare-earth ions doped in SiO_2 researchers have synthesized $\text{SiO}_2 : \text{RE}^{3+}$ using sol-gel techniques. The optical spectra of Eu^{3+} in gel derived silica glasses have been studied and models have been proposed for

the Eu^{3+} environment [29–31]. Monteil *et al.* [14] have reported a simulated structural model of Eu^{3+} ions in a porous silica gel. The authors found the average coordination of the Eu^{3+} to be 4 and postulated that each europium ion modifies the network locally to provide an environment which not only satisfies its bonding requirements but also its local field requirements. Since the doping ions are mainly surrounded by solvent molecules in the early stages of sol-gel processing, the luminescence of rare-earth ions in such an environment is known to be very similar to the one observed in aqueous solutions. Thus, recently, Chaussedent and Monteil [32] have performed molecular dynamics simulation of the Eu^{3+} ion in aqueous solution. The authors have found that the Eu^{3+} ion is co-ordinated to eight water molecules. The water molecules are arranged in a distorted archimedean square antiprism around the Eu^{3+} ion resulting in a pseudo D_{4d} symmetry.

Feuston and Garofalini [33] have demonstrated that it is possible to simulate gel polymerization. In their work, Feuston and Garofalini have clearly shown that it is possible to follow the polymerization mechanism in sol-gels.

Substantial progress in accurately predicting the rare-earth environment in glasses has been made using molecular dynamics. However, further improvements may be brought to the simulation method by using a three body potential in order to simulate bond directionality in the framework created by the network-former and by implementation of a greater dopant sample size, which would improve the statistical reliability of the rare-earth environment.

V. SIMULATION OF SPECTROSCOPIC PROPERTIES

The optical properties of rare-earth ions doped in glasses are closely related to the glass structure and composition. Over the past 30 years, a tremendous effort has been placed on relating the chemical bonding, symmetry and coordination within the glass network to the observed optical properties. The advent of laser techniques such as fluorescence line narrowing, spectral hole burning and coherent optical transient have been used extensively in attempts to elucidate the structural dependence of the luminescence properties of rare-earth doped glasses. Some insight into the rare-earth local environment has been gained from such studies. Nevertheless, these experiments still correspond to the investigation of a macroscopic behaviour of a doped glass. Attempts have been made to interpret this data using simple models however the overwhelming presence of accidental degeneracy has been the bane of researchers seeking uniqueness in an atomic structural model for doped glasses.

The first attempts to generate the emission spectrum of the Eu^{3+} ion in glasses were made by Brawer and Weber [3, 4, 7]. Using a principal axis transformation of each of the Eu^{3+} configurations, derived from the molecular dynamics simulation, the authors correlated the energy levels with the structure and charge distribution at each rare-earth site. Starting with a Eu^{3+} ion at the centre of a cartesian coordinate system representing the glass configuration, the authors defined the components of the quadrupole moment tensor at the rare-earth site as a (3×3) matrix such that its quadratic form is:

$$M_{ij} = \sum_L \frac{q_L}{R_L^5} X_{L,i} X_{L,j}$$

where a summation over the entire ensemble of L ligands is carried out. The symmetric matrix M_{ij} is diagonalized and yields eigenvalues $\lambda_1, \lambda_2, \lambda_3$ and eigenvectors A_1, A_2, A_3 . Sorting the eigenvalues such that $\lambda_1 > \lambda_2 > \lambda_3$ and rearranging the eigenvectors correspondingly permitted the authors to carry out an alignment of each quadrupolar moment ellipsoid. This orientation allowed the authors to calculate the crystal field parameters. Brawer and Weber examined the range and distribution of energy-level splittings of the ground-state manifold of the Eu^{3+} ion. Certain simplifications were introduced in their calculations: (i) only the ${}^7\text{F}_0$ and the ${}^7\text{F}_1$ manifolds were treated, (ii) no J-mixing was assumed, (iii) only ligands within 2.75 \AA were considered in the point charge calculation, (iv) only the second order crystal field parameters were included in the calculation, and (v) only relative energy level splittings of the electronic manifolds were inferred. Qualitative observations were made which agreed with the results of experiment. Firstly, the range and distribution of crystal field energy levels agreed with observations of both broadband and FLN spectra. Secondly, the high-energy asymmetry of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ emission profile together with the magnitude of the inhomogeneous broadening of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ band were both successfully predicted. Finally, the overall linewidth and average energy-level splittings were predicted to be smaller in the modified glasses than in BeF_2 glass.

In retrospect, Weber [4] felt that although a qualitative agreement was obtained by the simple electrostatic model, accurate calculations and simulations of both the local structure and electronic energy levels would be required to quantitatively predict and interpret optical spectra of glasses.

Following the work of Weber and Brawer [3–8], Hirao and Soga [26] published a study on sodium borate glasses. In their work, the authors showed that using the ideas developed by Weber and Brawer [3–8] the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition could be predicted. Recently, Soga *et al.* [27] and Takahashi *et al.*

[28] have simulated fluorozirconates and chlorofluorozirconates respectively, using the methods developed by Brawer and Weber [3–8].

Since 1993 a series of articles have been published from the research laboratories of Capobianco [11–13, 15, 16] and Monteil [14], extending the technique employed by Weber and Brawer [3–8]. The authors used a full treatment, including *J*-mixing, of the point charge crystal field method developed for doped crystalline material [34–36] in order to simulate (i) the 5L_6 , $^5D_{3,2,1,0} \leftarrow ^7F_{0,1}$ absorption spectrum and (ii) the $^5D_0 \rightarrow ^7F_J (J=0\ldots6)$ emission spectrum of the Eu^{3+} ion. The method employed is related to the “lattice summation” technique [37, 38] where crystal field parameters are derived from the interaction between the impurity ion and the electrostatic potential of the surrounding lattice. Knowing the position and charge of each atom they calculated the electrostatic potential at the rare-earth site by summing each individual atomic contribution. The calculated crystal field parameters were used (i) in the calculation of the splitting of each *J* manifold and (ii) in the calculation of the transition probabilities between individual components of each *J* manifold. They showed that this gives a simulated emission or absorption spectrum with correct energies and relative intensities. Figure 4 shows a comparison between the experimental and simulated emission spectrum of the $^5D_0 \rightarrow ^7F_J (J=0 \text{ to } 4)$ transitions for the sodium silicate glasses reported by Cormier *et al.* [12]. Using the technique developed by Capobianco’s group [12] of spectral simulation, it is possible to generate dilution narrowed laser spectroscopy spectra [13] by reducing considerably the associated linewidths *w* of the simulated transitions.

Although the authors were not able to simulate the FLN spectra for the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot \text{Eu}^{3+}$ glass, they were still able to derive various features normally associated with FLN spectroscopy [12].

Chaussedent *et al.* [39] have performed a molecular dynamics simulation of trivalent europium in aqueous solution and have calculated the ligand field parameters using a model that takes into account both point charges and the point dipoles of the water molecules [40]. These simulations are important and will be very useful in modelling the rare-earth ions in sol-gels.

The usefulness of numerical simulations has also been demonstrated in $\text{Na}^+ \beta''$ alumina [41, 42]. In such crystals the lattice is compound of spinel blocks separated by conductive planes where the ion position (Na^+ or dopant) is disordered. The authors have shown the influence of the cut off radius used for the crystal field calculations on the determination of the Judd-Ofelt coefficients for Nd^{3+} doped in $\text{Na}^+ \beta''$ alumina. The coefficient Ω_2 was shown to be more sensitive to the long range environment of the rare-earth ion.

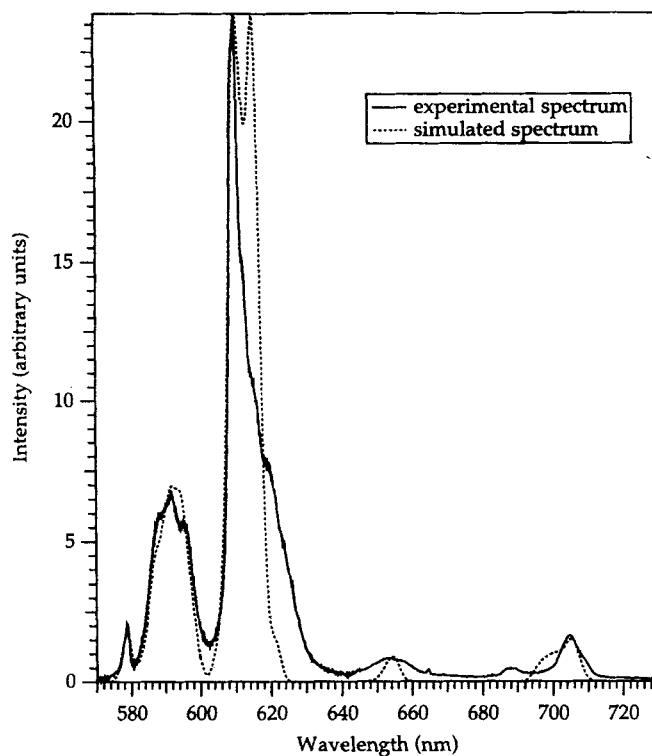


FIGURE 4 Comparison between room-temperature emission spectra of the experimental and simulated Eu^{3+} -doped sodium disilicate glasses. From Cormier *et al.* [12].

VI. CONCLUSION

Since the initial work of Brawer and Weber molecular dynamics technique has allowed researchers to simulate models of rare-earth environment in oxide, fluoride, borate, phosphate and chlorofluoro glasses. Using crystal field theory and transition probabilities of the rare-earth ions, the simulation of absorption and emission spectra has been possible. Numerical simulations have shown that the rare-earth environments are composed of continuous distribution of local fields which satisfy energetic bonding requirements of the rare-earth ion and that the presence of a limited number of distorted sites for rare-earth ions doped in glasses may be fallacious. Future research in this field should concentrate on: (i) the clustering of rare-earths in glasses, (ii) the simulation of energy transfer, (iii) the use of a multibody potential and (iv) ligand field theory should be used in the calculations of the simulated spectra.

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