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

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(Received November 1996; Accepted February 1997)

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 $10^{-3}$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.

127
II. SPECTROSCOPIC CHARACTERISTIC OF DOPED CLASSES

The result will be devoted to the simulation of the optical spectra. The simulation method is applied to the study of the interval electron. The results of the EELS data and the optical data will introduce the numerical simulation of the EELS spectrum, explaining the correlation between the spectroscopic and computational simulation of the DOS. The work of theory and the calculation of the local environment are performed by Professor L.X. X. and Professor G. S....
of the Rare-Earth Doped Glasses
The rare earth dopant glass is a type of glass that contains rare earth elements as dopants. These dopants can alter the optical properties of the glass, making it useful in various applications such as laser materials and optical fibers. The presence of rare earth elements in the glass structure can lead to unique optical behaviors, such as the emission of light at specific wavelengths under certain conditions. This makes rare earth dopant glasses an important material in the field of optical and laser technology.
A. SIMULATION OF SPECTROSCOPIC PROPERTIES

which would improve the statistical significance of the current sample size.

By exploring the potential of the new databases for the aims of the present study, we
planned to identify previously unknown proteins that may be involved in the
interaction with the miRNA target. In this way, we aimed to improve the
understanding of the molecular basis of the disease and to identify new
potential therapeutic targets.

The current database also contains a large number of proteins that are
commonly found in different tissues and cell types. This information is
important for understanding the role of these proteins in disease
progression, as well as for identifying new potential biomarkers for
early diagnosis.

In conclusion, the new database offers a wealth of information that
will be useful for researchers in the field of miRNA biology and for
practitioners in the development of new therapeutic strategies.
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 $(3 \times 3)$ matrix such that its quadratic form is:

$$M_{ij} = \sum \frac{q_i q_j}{r_{ij}^5} X_{L_i} X_{L_j}$$

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 $^7F_0$ and the $^7F_1$ manifolds were treated; (ii) no J-mixing was assumed; (iii) only ligands within 2.75 Å 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 $^5D_0 \rightarrow ^7F_0$ emission profile together with the magnitude of the inhomogeneous broadening of the $^5D_0 \rightarrow ^7F_1$ 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 BeO$_2$ 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 $^5D_0 \rightarrow ^7F_2$ transition can 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 $^5D_0 \rightarrow ^7F_0$, $^5D_1 \rightarrow ^7F_0$ absorption spectrum and (ii) the $^5D_0 \rightarrow ^7F_J$ ($J = 0 \ldots 6$) 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 $^5D_0 \rightarrow ^7F_J$ transitions for the sodium silicate glasses reported in references [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 linewidth of the simulated transitions.

Although the authors were not able to simulate the FLN spectra for the Na$_2$O–SiO$_2$–Eu$^{3+}$ glass, they were still able to derive various features normally associated with FLN spectroscopy [13, 26].

Chaussevent 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 Na$^{18}$O$^\beta$ alumina [41, 42]. In such crystals the lattice is compound of spinel blocks separated by conductive planes where the ion position (Na$^{18}$O 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 Na$^{18}$O$^\beta$ alumina. The coefficient $Q_2$ was shown to be more sensitive to the long range environment of the rare-earth ion.
VIT. CONCLUSION

\[ \text{Figure 4: Comparison between ZnO on Ni and ZnO on Cu.} \]

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure4.png}
\caption{Comparison between ZnO on Ni and ZnO on Cu.}
\end{figure}

\section*{References}


Since the initial work of Brown and White, molecular nanotechnology has