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Spectroscopic techniques to the characterization of rare earth doped glasses

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ABSTRACT

Rare-earth ions are of interest in several high-tech areas, the two major ones concerning magnetic and optical devices. In the latter field, one can exploit the unique Spectroscopic properties of rare-earth ions to develop novel or advanced lasers and optical amplifiers. Glasses have been known for a long time as a convenient host for rare earths and have been widely used for the fabrication of solid-state lasers. The aim of the present paper is to highlight the spectroscopic techniques to the characterization of rare-earth-doped Glasses. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Rare-earth ions;
Doped glasses;
Spectroscopic properties;
Energy interaction Parameters;
Laser Parameters;
Judd-Ofelt Parameters.

INTRODUCTION

Lanthanides and actinides are mostly denominated as rare earths although these elements are not rare but many of them occur more prevalently than other materials such as silver. Each group consist of 14 elements^[1], beginning with cerium (Ce) and ending with lutetium (Lu) for the lanthanides and for the actinides starting with thorium (Th) and ending with lawrencium (Lr). As most of the isotopes of the actinides are unstable only the lanthanides are of interest for optical applications^[2,3].

The optical properties of the rare earth ions, that are the mostly trivalent ions of the Lanthanides, result from their electronic structure. All of them have the electronic configuration of Xe in common. Additional electrons are added to the 6-s and 5-d shells respectively as it is the case for Cesium and Lanthanium whereas for the Lanthanides these electrons are situated within the 4f shell^[2]. This is due to

an effect called Lanthanide Contraction^[3] which leads to the 4f shell being shielded by the 5s²5p⁶-closed shells of the Xe configuration. On ionization electrons are removed from the outermost shells resulting in trivalent ions with electrons only in the 4f shell except for Lutetium which still has one 6s electron left. For the remaining electrons there are several discrete energy states allowed within the 4f shell. This leads to the numerous optical transitions reported for rare earth ions^[4-6]. As the 4f electrons are shielded by the 5s and 5p shells the position of the energy levels and the transition itself are barely dependent on the surrounding host material into which the ions are incorporated^[7].

ENERGY LEVELS OF RARE EARTH IONS

For every rare earth ion being a multi-electron system the energy levels between which the radiative transitions take place are identified as terms.

They combine the quantum numbers of the single electrons^[8].

For the complete atom or ion respectively the quantum states of every single electron are combined to a term which takes the form $n^{2S+1}L_J$. Here, n is the principle quantum number of the highest excited electron, and $2S+1$ is referred to as multiplicity. It should be noted that for rare earths often n is omitted because for all energy states relevant for radiative transitions $n = 4$ as these processes take place within the 4f-shell. The symbol L represents the sum of the overall angular momenta $L = \sum l_i$ whereas S is the total spin summed up for all electrons $S = \sum s_i$. Then, $J = S + L$ combines both S and L to yield the total angular momentum of the atom^[8,9].

ENERGY LEVEL TRANSITIONS

An electron in an atom can make a transition between discrete energy levels via three different optical processes: absorption, spontaneous emission, and stimulated emission.

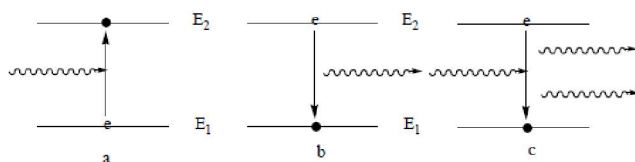


Figure 1 : Illustrates Absorption (a), Spontaneous emission (b), and Stimulated emission (c), E_1 and E_2 represent the energies of the two states

Absorption, part a of the above Figure 1, occurs when an incoming photon causes an electron to enter a higher energy state. The photon no longer exists, having 'given' all its energy to the particle. The probability for a single particle to absorb a single incident photon is dependent on the particle's absorption cross section, a quantity in units of area that varies with wavelength. The photon must have energy equivalent to the difference in energy levels, E_1 and E_2 , for it to be absorbed. If the electron begins in its lowest energy state, this is referred to as 'ground state absorption'. If the electron is already in an excited state, and its energy level is raised further by an incoming photon, this is referred to as 'excited state absorption'. The following relation relates the energy of a photon to its frequency, ν , or

wavelength, λ :

$$E = h\nu = \frac{hc}{\lambda}$$

Spontaneous emission occurs when an electron in an elevated energy state decays to a lower, unoccupied, level. The energy difference between the two levels is accounted for by the release of a photon with that energy. Multiple photons emitted by spontaneous emission between two energy levels will have the same frequency and wavelength because they have the same energy, but will have random phase and polarization. It is also possible for an electron to decay from an excited state via phonons, in which case no light is emitted. In general, the smaller the energy gap between two levels, the more likely an electron would decay via phonons. Each excited state has an effective lifetime, after which $1/e$ of the electrons originally in that state will remain. Transitions with a higher probability of decaying via phonons generally have much shorter lifetimes. An electron can also decay to a lower level through an interaction with a photon. If an excited electron is struck by a photon with energy equal to the difference in energy between the electron's current state and an unoccupied lower state, there is a probability the electron will decay to that state. If it does so, the excess energy is released in the form of a photon identical to the incident photon traveling in the same direction, with the same phase and polarization. This process is known as stimulated emission and is illustrated in part c of Figure 1. This probability, like that of absorption, is also governed by a cross section.

ENERGY LEVEL SCHEME CALCULATIONS

The Hamiltonian (H) that explains the complex energy level scheme of Ln^{+3} ions in any environment consists of two parts, one being the free-ion Hamiltonian (H_{FI}) that describes the interactions within the 4fⁿ electrons and the other being the Crystal Field Hamiltonian (H_{CF}) that describes the interactions between Ln^{+3} ion and its surrounding environment:

$$H = H_{FI} + H_{CF}$$

H_{FI} contains the isotropic parts of the total Hamiltonian^[10] and is defined as

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$$H_{\text{FI}} = H_e + H_m + H_c$$

Where H_e , H_m and H_c are Hamiltonian corresponding to electrostatic, magnetic and configuration interactions respectively.

When the Ln^{+3} ion is introduced into a solid matrix, it experiences an inhomogeneous electrostatic field produced by the surrounding charge distributions. The H_{CF} can be expressed as

$$H_{\text{CF}} = \sum_k \sum_q B_q^k C_q^k$$

Where the B_q^k parameters are the coefficients of the CF expansion that are the functions of the radial distances. The C_q^k are tensor operators of rank 'k' closely related to the spherical harmonics^[11]. The CF strength in any host can be expressed by an overall scalar CF strength parameter (S) defined as.^[12-15]

$$S = \left\{ \frac{1}{3} \sum_k \frac{1}{2k+1} \left(|B_0^k|^2 + 2 \sum_{q>0} |\text{Re } B_q^k|^2 + |\text{Im } B_q^k|^2 \right) \right\}^{1/2}$$

Electrostatic Interaction

The Hamiltonian for electrostatic repulsion between the outer electrons is given by

$$H_e = \sum_{i>j}^N \frac{e^2}{r_{ij}}$$

Coulomb repulsion between the $4f^n$ electrons is written as F^k ($k=2,4,6$), which are the Slater radial electrostatic integrals, giving the electrostatic energy E_e as

$$E_e = \sum_{k=2,4,6} f_k F^k$$

Where f_k is the coefficient of the linear combination of $4f$ radial functions and represent the angular part of the electrostatic interaction and k is even. F^4/F^2 and F^6/F^2 ratios approximate those of the hydrogenic wavefunctions, which are 0.668 and 0.495 respectively. However, in a crystalline lattice, actual parameter values may be reduced significantly from free-ion values^[16]. F^k is known as direct integral and is necessarily a positive and decreasing function of k and is given by

$$F^k = \int_0^\infty \int_0^\infty \frac{r^k <}{r^{k+1} >} R_i^2(r_i) R_j^2(r_j) r_i^2 r_j^2 dr_i dr_j$$

Where R is the radial wave function for the $4f$ orbital, i and j represents respectively to the i^{th} and j^{th} electrons under consideration. Later Condon and

Shortley^[17] have defined reduced integral F_k , which is given by

$$F_k = \frac{F^k}{D_k}$$

Where D_k is the denominator, whose values have been tabulated by Nielson and Coster^[18]. Thus reduced Slater integrals can be written as

$$F_k = \frac{1}{D_k} \int_0^\infty \int_0^\infty \frac{r^k <}{r^{k+1} >} R_i^2(r_i) R_j^2(r_j) r_i^2 r_j^2 dr_i dr_j$$

These F_2 , F_4 and F_6 are known as Slater Condon parameters. New kind of operators has been introduced by Racah^[19-21], which have simple transformation properties under the groups of transformation employed to classify the wave functions. The electrostatic energy E_e can be written as

$$E_e = \sum_{k=1}^3 e_k E^k$$

Where E^k is the Racah parameter and can be expressed as linear combination of F_k . The parameters E^k and F_k are determined from the observed energy levels.

$$E^1 = 1/9(70F_2 + 231F_4 + 2002F_6)$$

$$E^2 = 1/9(F_2 - 3F_4 + 7F_6)$$

$$E^3 = 1/3(5F_2 + 6F_4 - 91F_6)$$

Magnetic Interaction

The spin-orbit coupling is caused by interaction of the spin magnetic moment of the electron and the magnetic field originating from the movement of the electron around the nucleus. In the Hamiltonian it is described by $\zeta_{4f} A_{\text{so}}$, where A_{so} represents the angular part of the spin-orbit interaction and ζ_{4f} is the spin orbit coupling constant and is known as Lande' parameter.

The Hamiltonian due to spin-orbit coupling is given^[22] by

$$H_{\text{s-o}} = \sum_{i=1}^n \xi_i(r_i) (\vec{s}_i \cdot \vec{l}_i)$$

Where r_i, s_i and l_i are radial co-ordinates, spin angular momentum and orbital angular momentum of i^{th} electron and $\xi_i(r_i)$ is given by

$$\xi_i(r_i) = \frac{h^2}{2m^2 c^2 r_i} \frac{dU(r_i)}{dr_i}$$

Where $U(r_i)$ is a spherically symmetric potential function.

The integral of ξ_i over the 4f radial wave function (R) is given by^[22]

$$\zeta_{4f} = \int_0^{\infty} R_{4f}^2 \xi(r_i) dr_i$$

The energy E_{s_0} corresponds to the Hamiltonian H_{s_0} and may be written as

$$E_{s_0} = A_{s_0} \zeta_{4f}$$

Where A_{s_0} represents the angular part of spin-orbit interaction.

Configuration Interaction

Configuration interaction has not been considered here because the theoretical calculations of energy of the levels are found to be different from the observed energies of the levels^[23]. The main reason of this deviation is the neglect of different configurations of the same parity that differ in the co-ordinates of not more than two electrons^[24].

ENERGY INTERACTION PARAMETERS

The energy, E_j , having a particular value of the energy interaction parameter F_k and ζ_{4f} can be expanded as a Taylor series expansion for a small variation of the energies^[25-26]. In the first order approximation the energy E_j of the j^{th} level is given by

$$E_j(F_k, \zeta_{4f}) = E_{0j}(F_k^0, \zeta_{4f}^0) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f}$$

Where E_{0j} is the zero order energy of j^{th} level. The values of zero order energy (E_{0j}) and partial derivatives $\partial E_j / \partial F_k$ and $\partial E_j / \partial \zeta_{4f}$ for the observed levels of Nd^{+3} and Er^{+3} calculated by Wong^[25-26] have been used. The value of ΔF_k and $\Delta \zeta_{4f}$ have been computed by partial regression method. The values of F_k and ζ_{4f} are then evaluated using equations.

$$F_k = F_k^0 + \Delta F_k$$

$$\zeta_{4f} = \zeta_{4f}^0 + \Delta \zeta_{4f}$$

Where F_k^0 and ζ_{4f}^0 are zero order values of corresponding parameters.

This method has been used by Tandon group^[27-30] our group^[31-34] and others^[35-40]. The Racah parameter, E^k , can be calculated. The E_j values (E_{cal}) have been calculated by substituting the calculated values of F_k and ζ_{4f} parameters for justifying the experimental calculation.

The root mean square (r.m.s.) deviation (σ) between calculated (E_{cal}) and experimental (E_{exp}) energies of the levels has been calculated and is defined by

$$\sigma = \left[\sum_i \frac{\Delta E_i^2}{N} \right]^{1/2}$$

Where ΔE_i is the difference between observed and calculated values of energies of the i^{th} level and N is the number of experimental levels fitted. Small values of σ indicate the justification for calculating parameters.

The Slater-Condon parameter F_2 and Lande' parameter ζ_{4f} for lanthanide ions have been calculated empirically for aquo ions using the following equations^[25,26].

$$F_2 = 12.4(Z - 34)$$

$$\zeta_{4f} = 142Z - 7648$$

In the case of doped glasses these relations do not yield good results and following new equation have been suggested.

$$F_2 = 13.815(Z - 36.027)$$

$$\zeta_{4f} = 187.57Z - 10371.18$$

Where Z is the atomic number of the Lanthanide ions.

Due to electronic transition of an ion the bands have been found to shift to longer wavelength (Red Shift) on complexation or putting it in the crystal field of the ligand^[41,42]. In the case of transition metal ions it is due to expansion of metal d-orbitals on complexation, resulting in the decrease of inter electronic repulsion parameter and in the case of lanthanide ions the metal 4f orbitals, being shielded ones, expand to a lesser degree. This phenomenon is known as Nephelauxetic effect^[43] and is quantitatively measured in terms of nephelauxetic ratio (β') defined by^[44]

$$\beta' = \frac{F_k^g}{F_k^f}$$

Where g and f refer to the glass and free ions respectively in the present case. If β' is less than one, it indicates covalent bonding, while greater than one indicates ionic bonding.

Henrie and Choppin^[45] have defined another bonding parameter $b^{1/2}$ in terms of β' , is given by

$$b^{1/2} = \left[\frac{1 - \beta'}{2} \right]^{1/2}$$

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A real value of $b^{1/2}$ indicates covalent bonding. This parameter is very useful for comparative study of bonding.

JUDD-OFFELT PARAMETERS

The Judd–Ofelt (J–O) theory^[46-47] has been one of the most successful theories in estimating the magnitude of the forced electric dipole transitions of rare-earth ions in a large variety of host media. This theory gives three intensity parameters Ω_2 , Ω_4 and Ω_6 which are related to the local structure in the vicinity of rare-earth ions, or the covalency of the rare-earth ion sites. This theory was originally applied to the solution spectra of lanthanide ions by Carnall and coworkers^[48-49]. Later it was extended to Lanthanide ions in state of powders^[50-53]. Weber^[54-56], Reisfeld^[57-60] and Tandon group^[27-30] have tried to extend it in the case of glasses. The oscillator strength (P_{exp}) is a dimensionless quantity, which is related to the quantum probability of a transition and hence gives the intensity of absorption band corresponding to that particular transition. The experimental oscillator strength, P_{exp} , of electric dipole transitions is defined as

$$P_{\text{exp}} = 4.6 \times 10^{-9} \times \frac{1}{cl} \log \frac{I_0}{I} \times \Delta\nu^{1/2}$$

Where c is the concentration of the absorbing ion per unit volume, l is the path length and $\log(I_0/I)$ is the absorbance and $\Delta\nu_{1/2}$ is half bandwidth. However for a solid material it is generally expressed in terms of line strength S_{exp} .

$$P_{\text{exp}} = \frac{8\pi^2 m c v}{3h(2J+1)} \left[\frac{(n^2+2)^2}{9n} \right] S_{\text{exp}}$$

Where $(2J+1)$ is the degeneracy of the ground state of the rare-earth ions, n is the refractive index of the medium, m is the mass of the electron, v is the mean energy of the transition, the factor $(n^2+2)^2/9$ represents the local field correction for an ion embedded in a dielectric medium.

Since the bands produced by the magnetic dipole mechanism have very low spectral intensity compared to that of the electric dipole bands, S_{md} could be neglected in comparison to S_{ed} , which is given by

$$S_{\text{ed}}[(S, L)J : (S', L')J'] = \sum_{\lambda=2,4,6} \Omega_{\lambda} \left\langle (S, L)J \| U^{(\lambda)} \| (S', L')J' \right\rangle^2$$

where $\left\langle (S, L)J \| U^{(\lambda)} \| (S', L')J' \right\rangle^2$ are the reduced matrix elements of a unit tensor operator evaluated in the intermediate coupling approximation. The values of these matrix elements reported by Carnall et al.^[61] have been used since these elements are host invariant. Substituting the oscillator strengths calculated from the absorption spectra and using the values of reduced matrix elements and other parameters, Ω_{λ} ($\lambda = 2, 4, 6$) can be calculated by a least squares method.

A reduced chi-square test between S_{exp} and S_{cal} values has been performed to test the validity of Judd-Ofelt approach. The low value of this statistical parameter is a measure of the goodness of fit. The reduced chi-square is given by

$$\text{Reduced chi-square} = \Sigma (S_{\text{cal}} - S_{\text{exp}})^2 / K - 3$$

Where K is the number of absorption bands taken into account. The position, intensity and shape of certain electric dipole transitions of rare-earth ions are found to be very sensitive to the environment of the rare-earth ion. Such transitions are termed as hypersensitive transitions by Jorgensen and Judd^[62].

These transitions are found to obey the selection rule $\Delta J \leq 2$, $\Delta L \leq 2$ and $\Delta S = 0$ ^[62]. These are associated with a very large value of the reduced matrix element $\|U^2\|^2$; hence hypersensitivity is much related with the Ω_2 parameter. For Nd^{+3} ion, ${}^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$ is the hypersensitive transition since it obeys the above selection rule.

LASER PARAMETERS

The calculated Laser parameters are used to find out the useful Fluorescence transitions as Laser transitions and are very useful in predicting laser action in various lanthanide doped glass specimens. These parameters have been widely used by Reisfeld^[63-67], Weber^[68-71] and Tandon groups^[27-29].

The obtained Judd-Ofelt (JO) parameters have been used to predict the important radiative properties such as transition probabilities, branching ratios, lifetimes and stimulated emission cross-sections.

tions for the excited states of Ln^{+3} ions.

Spontaneous Emission Probability (A)

The spontaneous emission probability (A) for a transition $\Psi J \rightarrow \Psi' J'$ is given by

$$A = \frac{64\pi^4 e^2}{3h(2J+1)\lambda_p^3} \frac{n(n^2+2)^2}{9} \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle \Psi J \| U^{(\lambda)} \| \Psi' J' \rangle|^2$$

Radiative Lifetime (τ)

The predicted radiative lifetime of an excited state in terms of A, is given by

$$\tau(\Psi J) = \frac{1}{A(\Psi J)}$$

Fluorescence Branching Ratio (β)

The fluorescence branching ratio corresponds to the emission from an excited level to its lower level is

$$\beta(\Psi J, \Psi' J') = \frac{A(\Psi J, \Psi' J')}{A_T(\Psi J)}$$

Stimulated emission cross-section (σ_p)

The other important radiative property, the stimulated emission cross-section $\sigma_p(\Psi J, \Psi' J')$ between the ΨJ and $\Psi' J'$ states with a probability $A(\Psi J, \Psi' J')$ is given by^[36].

$$\sigma_p(\Psi J, \Psi' J') = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{\text{eff}}} A(\Psi J, \Psi' J')$$

Where λ_p is the transition peak wavelength and $\Delta\lambda_{\text{eff}}$ is the effective line width defined as full width in half maximum (FWHM). With the help of the above equations, various spectroscopic parameters have been obtained.

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