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## Judd-Ofelt calculation of Nd<sup>+3</sup> doped phosphate glasses

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### ABSTRACT

The Judd-Ofelt parameters are useful for calculation of Stimulated emission cross sections. The values of emission cross sections are comparable with those shown by glasses used in solid state laser applications. This theory gives three intensity parameters  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ , which are related to the local structure in the vicinity of rare-earth ions, and / or the covalency of the rare-earth ion sites. The comparison of calculated with measured lifetimes gives information about non-radiative decay rates. In the absence of non-radiative decay processes, it is not possible to assess the agreement between the Judd-Ofelt theory and the experimental results.

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### KEYWORDS

Judd-Ofelt analysis;  
Phosphate glass;  
Rare earth ion in glass.

### INTRODUCTION

The Judd-Ofelt parameters are important for investigations of local structure and bonding in the vicinity of rare earth (RE) ions. The  $\Omega_2$  parameter is sensitive to both asymmetry and covalency at the RE sites<sup>[1]</sup>. Since the f→f transitions of RE ions are parity-forbidden, deviations from inversion symmetry give rise to  $\Omega_2$ <sup>[2]</sup>. Changes of  $\Omega_2$  due to changes of asymmetry were confirmed in Refs<sup>[3-7]</sup>. In many cases, a dependence of  $\Omega_2$  on the covalency between RE ions and ligand anions is observed<sup>[1,6-12]</sup>. The effect of host glass on  $\Omega_6$  is explained by different models. Takebe and Nageno suggested that increasing ionic packing ratio causes an increase of  $\Omega_6$  for silicate and borate glasses<sup>[7, 13-16]</sup>. Tanabe et al. showed that, for oxide and fluoride glasses,  $\Omega_6$  increases due to decreasing local basicity of the ligands<sup>[17-19]</sup>. Further, the rigidity or long-range affects

of glass host was found to be responsible for changes in  $\Omega_6$ <sup>[6,20]</sup>.

The effect of the phosphate host on  $\Omega_6$  is pointed out in Refs<sup>[12-16,18]</sup>. The  $\Omega_4$  parameter is affected by the factors causing changes in both  $\Omega_2$  and  $\Omega_6$ . Especially, if the changes of  $\Omega_2$  and  $\Omega_6$  are opposite, the resolution of the respective affects on  $\Omega_4$  is difficult. Therefore,  $\Omega_2$  and  $\Omega_6$  are mostly studied for local structure investigations. The Judd-Ofelt parameters are useful for calculation of emission properties such as radiative decay rates, lifetimes and branching ratios of emission transitions. The comparison of calculated with measured lifetimes gives information about non-radiative decay rates<sup>[21,22]</sup>. In the absence of non-radiative decay processes, it is not possible to assess the agreement between the Judd-Ofelt theory and the experimental results<sup>[12]</sup>.

The oscillator strength is a dimensionless quantity

## Full Paper

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,  $P_{\text{exp}}$ , of electric dipole transitions is defined as

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

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  $S_{\text{exp}}$ .

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

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,  $\nu$  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,  $S_{\text{md}}$  could be neglected in comparison to  $S_{\text{ed}}$ , which is given by

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

Where  $\left\langle (S, L)J \parallel U^{(\lambda)} \parallel (S', L')J' \right\rangle^2$  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.<sup>[23]</sup> 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,  $\Omega_{\lambda}$  ( $\lambda = 2, 4, 6$ ) can be calculated by a least squares method.

### EXPERIMENTAL

A sodium-lead-barium-aluminium phosphate glass with doping concentration of rare earth ion was prepared by melt quenching technique. The composition (by weight) was approximately Na(PO<sub>3</sub>)<sub>6</sub> 70% -BaO

15%-PbO 10%-Al<sub>2</sub>O<sub>3</sub> 5%-R Ln (Where R=0.5 % and Ln=Nd<sup>3+</sup>). Addition of BaO as secondary modifier shifts the IR cut of edge<sup>[24]</sup> toward longer wavelengths making the rare-earth doped glasses highly suitable for fiber amplifier to be used in telecommunication.

The spectral measurements were carried out by spectrophotometer method. The Absorption spectra in the spectral range 200-800 nm were recorded on UV-Visible double beam spectrophotometer model Perkin Elmer spectrophotometer model lambda 35. The Absorption spectra have been recorded in terms of wavelength (nm) vs. Absorbance (a.u.). The absorption spectra of Nd<sup>3+</sup> doped SLBAP glass have been investigated. From these spectral data Judd-Ofelt parameters ( $\Omega_{\lambda}$ ) have been calculated to study the nature of bonding in these glasses. Intensities of the f-f transitions in the absorption spectra have been analyzed by the application of the Judd-Ofelt theory.

The experimental oscillator strengths, experimental line strength ( $S_{\text{exp}}$ ) and calculated line strength ( $S_{\text{cal}}$ ) with their differences ( $\Delta S$ ) of all the observed bands of Nd<sup>3+</sup> doped glasses are presented in TABLE 1.

**TABLE 1 : Experimental oscillator strengths, Experimental line strength ( $S_{\text{exp}}$ ) and Calculated line strength ( $S_{\text{cal}}$ ) with their differences ( $\Delta S$ ) for various Absorption levels in SLBAPND Glass**

| Absorption levels   | $P_{\text{exp}}(10^{-6})$ | $S_{\text{exp}}(10^{-20})$ | $S_{\text{cal}}(10^{-20})$ | $\Delta S(10^{-20})$ |
|---|---------------------------|----------------------------|----------------------------|----------------------|
| <sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> F <sub>5/2</sub> , <sup>2</sup> H <sub>9/2</sub> | 7.74                      | 4.179                      | 4.054                      | 0.124                |
| <sup>4</sup> F <sub>7/2</sub> , <sup>4</sup> S <sub>3/2</sub>                                 | 6.85                      | 3.394                      | 3.561                      | -0.167               |
| <sup>4</sup> F <sub>9/2</sub>   | 0.94                      | 0.431                      | 0.265                      | 0.165                |
| <sup>4</sup> G <sub>5/2</sub> , <sup>2</sup> G <sub>7/2</sub>                                 | 17.50                     | 6.908                      | 6.890                      | 0.017                |
| <sup>4</sup> G <sub>7/2</sub>   | 5.62                      | 1.996                      | 1.386                      | 0.609                |
| <sup>4</sup> G <sub>9/2</sub>   | 2.56                      | 0.886                      | 0.580                      | 0.305                |
| <sup>2</sup> P <sub>1/2</sub> , <sup>2</sup> D <sub>5/2</sub>                                 | 0.67                      | 0.195                      | 0.231                      | -0.036               |
| <sup>4</sup> D <sub>3/2</sub> , <sup>4</sup> D <sub>1/2</sub>                                 | 8.90                      | 2.107                      | 0.186                      | 1.920                |

Goodness of fit = 0.8452

### RESULTS AND DISCUSSION

In the Absorption spectrum of Nd<sup>3+</sup> doped Phosphate Glass specimens SLBAPND eight bands have been observed in spectral range 300-800 nm. The transitions from <sup>4</sup>I<sub>9/2</sub> identified in the studied spectral range are considered as having superimposed, the baricenter of each band or group of bands, oscillator strengths

and the matrix elements of Carnall<sup>[25,26]</sup> are also included. The experimental intensity of the Absorption bands have been calculated in terms of line strength ( $S_{exp}$ ), by using the oscillator strength and matrix element, the values of  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$  parameters of SLBAPND specimen have been computed by partial regression and least square method. The computation of  $\Omega\lambda$  parameter is important since these parameter are used in the calculation of radiative properties. These parameters show the general tendency  $\Omega_2 < \Omega_4 < \Omega_6$ . The same tendency is also observed for Nd<sup>+3</sup> ion in various glasses and crystals<sup>[27]</sup>. The small values of  $\Omega_2$  in glass specimen are associated with the micro-structural homogeneity<sup>[28]</sup> around the Nd<sup>+3</sup> ions.  $\Omega_2$  parameter is most sensitive to the local structural changes and involves the long-range terms in the crystal field potential<sup>[29,30]</sup>. The achieved Judd-Ofelt parameters for SLBAPND are  $\Omega_2 = 3.1029$ ,  $\Omega_4 = 5.9872$  &  $\Omega_6 = 4.9870$ .

**TABLE 2 : Judd- Ofelt intensity parameters for other various Nd<sup>+3</sup> doped hosts**

| Glass  | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | Ref. |
|--|------------|------------|------------|------|
| SLBAPND  | 3.1029     | 5.9872     | 4.9870     | -    |
| CANB (0.5 mol% Nd <sub>2</sub> O <sub>3</sub> )<br>glass – Ca, Al, Na & Ba   | 4.40       | 5.20       | 2.70       | 31   |
| CANS (0.5 mol% Nd <sub>2</sub> O <sub>3</sub> )<br>glass – Ca, Al, Na and Sr | 3.70       | 5.00       | 2.90       | 31   |

TABLE 2 exhibits the Judd Ofelt parameters obtained from previous literature for typical Nd-doped hosts. It is currently accepted that the  $\Omega_2$  parameter reveals the dependence of the covalency between Nd<sup>+3</sup> ions and ligand anions, because  $\Omega_2$  is connected to the asymmetry of the local environment around the Nd<sup>3+</sup> sites. In this way, the weaker the value of  $\Omega_2$ , the more Centro symmetrical the ion site and the more ionic its chemical bond with the ligands<sup>[32-34]</sup>. Earlier studies have shown that  $\Omega_2$  parameter is related to covalent chemical bonding between the central rare earth ion and the environment surrounding it and  $\Omega_6$  parameter is related to the rigidity and stability of the medium in which the ions are situated. Addition of Al<sub>2</sub>O<sub>3</sub> in the present glass system decreases the covalency of Nd-O bond by the increase in the coulomb interaction between the central rare earth ion and its surrounding oxygen of PO<sub>4</sub> tetrahedra. This indicates that Nd<sup>+3</sup> ions in SLBAP glass hosts present low covalence and symmetry when compared with CANB and CANS glasses.

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**Full Paper**

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