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Crystal Field Parameters and Optical Parameters of Nd^{3+} in Sodium Bismuth Silicate Glass

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ABSTRACT: Neodymium doped sodium bismuth silicate glasses were prepared by the melt quench technique. Optical absorption spectra of the Nd^{3+}ion in the present glassy systems were recorded in the UV-Vis-NIR region. Taylor series expansion method was adopted for theoretical evaluation of various crystal field parameters such as the Slater-Condon (F_2,F_4,F_6), spin orbit (ξ_{4f}) and Racah parameters (E_1,E_2,E_3). Oscillator strength and electric dipole line strength of the observed transitions were evaluated with the help of Judd-Ofelt (JO) theory. Radiative transition probability (A), total radiative transition probability (A_t), radiative life time (τ_{rad}), branching ratios (β) and integrated absorption (σ_a) cross section for stimulated emission between the meta stable state $^4F_{3/2}$ and ^4I_J (J= 15/2,13/2,11/2 and 9/2) levels were calculated using JO parameters. Optical basicity of the glass was found to increase with the addition of bismuth.

Keywords: Silicate glasses; Optical absorption spectroscopy; Racah parameters.

عوامل مجال البلور و العوامل الضوئية لسيليكات بزموث الصوديوم الزجاجى المشوبة بايونات النوديوم

فينوي تومس، رام كاريشنا بيلاي جوبالا سوفين، ماثيو الن و هيسن تومس

ملخص: تم تحضير سيلكات صوديوم البزموث الزجاجية المشوبة بايونات النوديوم Nd^{3+} بواسطة تقنية الزوبان الإخمادى. كما تم قياس مطياف الإمتصاص الضوئى لايونات Nd^{3+} فى هذا النظام فى حيز UV-Vis-NIR كما تم استخدمت سلسلة تيلر (Taylor) الإمتدادية لحساب عوامل المجال البلورى المختلفة نظريا مثل: Slater-Condon(F_2,F_4,F_6) و spin orbit (ξ_{4f}) و Racah parameters (E_1,E_2,E_3) كذلك تم حساب شدة التذبذب وشدة خط ثنائى القطب الكهربى للإنتقالات الملاحظة بالإستعانة بنظرية Judd-Ofelt (JO) لحساب كل من إحتمالية الإنتقال الإشعاعى و إحتمالية الإنتقالية الإشعاعية المتكاملة وعمر الحياة الإشعاعى و النسبة الفرعية ومساحة المقطع الإمتصاصية المتكاملة الموحاة من الإنبعاث بين ميتا الحالة المستقرة و المستويات الأخرى للحالة. لوحظ زيادة القاعدة الضوئية للزجاج

كلمات مفتاحية: سيليكات الزجاج ، مطياف الإمتصاص الضوئى و معاملات راخ.

1. Introduction

Ever since the discovery of the solid state laser in 1961, a great deal of effort has been made to study the optical properties of rare earths and rare earth doped systems due to their unique uses in optical amplifiers, fiber lasers, telecommunications and display devices [1-3]. Attractive optical absorption and emission in the UV-vis-NIR region of the rare earths make them ideal candidates for optical applications in this region. A large variety of laser glasses doped with the Nd^{3+} ion have been investigated with the purpose of generating efficient emission around 1050 nm [4] . Heavy-metal silicate glasses possess lower phonon energies compared to other oxide glasses and display strong visible and near infra-red fluorescence of rare earth ions within the system [5]. Though there have been a large number of reports on various rare earth doped glassy systems, the synthesis and optical analysis of neodymium doped bismuth silicate glasses has rarely been studied. At comparatively low Bi_2O_3 content ($\leq$10 mol%), Bi_2O_3 incorporates into the interstices of glass as a network changer which does not cause a large-scale structural rearrangement of the local glassy network. At higher concentrations of Bi_2O_3 (>10 mol%), Bi_2O_3 enters into glasses as a network former and a large-scale structural rearrangement of the local glass network takes place, which leads to significant variation of its optical properties [6-7]. In this context, an optical analysis of neodymium doped bismuth (10 mol%) sodium silicate glass is deserving of special attention and importance. The purpose of the present study is to derive various spectroscopic parameters such as Slater Condon, Racah, spin-orbit and Judd Ofelt parameters and to evaluate the radiative parameters, such as radiative transition probability, radiative life time and absorption cross section for stimulated emission for the possible transitions.

2. Experimental

A neodymium (1.5 mol %) doped sodium bismuth silicate glassy system with composition (in mol%) 15 Na_2O-$10Bi_2O_3$-75 SiO_2 was prepared by the well-known melt quenching method. Appropriate amounts of Bi_2O_3 (99.99% purity, Sigma Aldrich), Na_2CO_3 and SiO_2 (99.99% purity, Sigma Aldrich) were mixed and ground continuously using an agate mortar. The powder mixture was placed in a porcelain crucible and melted in a box furnace at a temperature of 1200 ^{0}C for 3 hours. The melt mixture was poured into a stainless steel mold heated to 100 ^{0}C. Then the sample was annealed at a temperature of 200 ^{0}C for 1hour. The density of the sample was measured by Archimedes' principle using xylene as the immersion liquid. The U-V Visible-NIR absorption spectrum of the sample was measured on a UV-Visible-NIR spectrophotometer Varian Cary 5000 in the wavelength span of 450 nm to 950 nm.

3. Results and discussion

Figure 1 shows the optical absorption spectra of 1.5 mol % Nd_2O_3 doped sodium bismuth silicate glass. The transitions of the Nd^{3+} ion occurs due to the transition from the ground state $^4I_{9/2}$ to various excited states [8-9]. The location intensity and breadth of the absorption bands are determined by the interaction of Nd^{3+} ions with the local crystalline field. Each absorption band usually consists of a multiplicity of stark levels; unlike the regular local crystal field experienced by Nd^{3+} in crystalline hosts, the crystal field's sites in glass are randomly distributed. This distribution results in the inhomogeneous broadening of the absorption spectra of the Nd^{3+} ion.

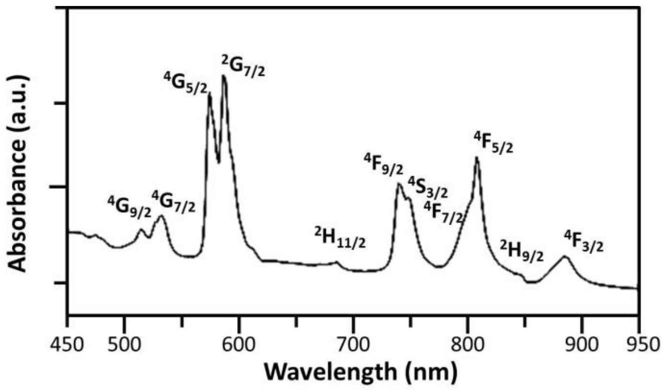

Figure 1. Absorption spectra of Nd^{3+} in sodium bismuth silicate glass.

3.1 Bonding properties and nephleuxetic ratio

Indirect but convincing information regarding the RE-ligand bond strength can be obtained from the nephelauxatic ratio(β). The nephelauxatic ratio is given by

$$\beta = {}^{\nu_m}/_{\nu_a} \tag{1}$$

where ν_m and ν_a are the wavenumbers (cm^{-1}) of the particular transitions in the host matrix and aqua, respectively. The larger value of the nephelauxatic ratio indicates a reduction in the strength of the covalent bond between the RE ion and ligand. The nephelauxatic parameter is directly related to the bonding parameter (δ) as

$$\delta = {}^{(1-\bar{\beta})}/_{\bar{\beta}} \tag{2}$$

and $\bar{\beta}$ is the average value of the β for observed transitions. The positive or negative sign of δ indicates covalent or ionic bonding of the rare earth-ligand bond. The small positive value of δ (0.0166) in the sodium bismuth silicate glass indicates the decrease in strength of covalency of the RE-O bond in the prepared sodium bismuth silicate glass compared to other silicate glass systems [10].

3.2 Crystal field parameters (Slater-Condon, Racah and spin-orbit parameters)

The Slater-Condon parameters (F_λ) generally represent the radial integral part of the electrostatic interaction matrix elements of a trivalent rare earth ion and can be represented as [11]

$$F_k = \frac{e^2}{D_k} \iint \frac{r^k <}{r^{k+1} >} R^2(r_i) R^2(r_j) dr_i dr_j \tag{3}$$

where k = 2, 4, and 6: $r_<$ and $r_>$ represent the distances from the nucleus to the nearer and farther electrons respectively. $R(r_i)$ and $R(r_j)$ represent the normalized wave functions of the i^{th} and j^{th} electron, D_k are constants. Similarly the spin orbit interaction parameter ξ_{4f} represents the radial integral part of the spin orbit interaction matrix element and is given by

$$\xi_{4f} = \hbar^2 \int_0^\infty r^2 R^2{}_{4f}(r) \xi(r) dr \tag{4}$$

where $\xi_{4f} = \frac{\hbar}{2m^2c^2r} \frac{\partial V(r)}{\partial r}$ and V(r) is a potential function for the interaction. For a free ion these interaction parameters are constants. But, when the ion is under the influence of another interacting field (ligand field or crystal field), these parameters change due to the overlapping of the 4f wave functions of the rare earth ion with that of the surrounding ligand ion. As a result of this overlapping effect, the distance between the nucleus and the electron of the rare earth ion changes slightly, which in turn affects the energy levels and spectroscopic parameters.

The observed energy levels of the neodymium ion can be calculated using the Taylor series method. In this method the energy of any level in the rare earth spectra is taken as a function of various types of interactions, such as electrostatic interaction spin-orbit interaction etc. [12]. According to this method, the energy of a rare earth ion can be represented as

$$E_i = f(F_{k,} \xi_{4f}) \tag{5}$$

where F_k is the Slater radial integral and (ξ_{4f}) the spin-orbit interaction parameter. Relation (5) can be expanded in a Taylor series as [13]

$$E_j = E_{oj} + \sum_{i=2,4,6} \frac{\partial E_j}{\partial F_i} \Delta F_i + \frac{\partial E_j}{\partial \xi_{4f}} \Delta \xi_{4f} + \ldots \tag{6}$$

The values of the partial derivatives were taken from the literature [8]. Knowing the values of the partial derivatives and zero order energy values, $\Delta F_2, \Delta F_4, \Delta F_6$ and (ξ_{4f}) can be determined. Once these Δ values are determined the Slater Condon parameters can be determined as

$$F_2 = F_2^0 + \Delta F_2$$

$$F_4 = F_4^0 + \Delta F_4$$

$$F_6 = F_6^0 + \Delta F_6$$

$$\xi_{4f} = \xi_{4f}{}^0 + \Delta \xi_{4f} \tag{7}$$

where F_2^0, F_4^0, F_6^0 and ξ_{4f}^o represent the zero order parameters.

The Racah parameters (E^i) are related to Slater-Condon parameters as

$$E^1 = \frac{1}{9}\left[70F_2 + 231F_4 + 2002F_6\right]$$

$$E^2 = \frac{1}{9}\left[F_2 - 3F_4 + 7F_6\right]$$

$$E^3 = \frac{1}{3}\left[5F_2 + 6F_4 - 91F_6\right] \tag{8}$$

The calculated values of all the spectroscopic parameters are given in Table 1.

All the spectroscopic parameters, viz. the Slater-Condon (F_2,F_4,F_6), spin-orbit (ξ_{4f}) and Racah parameters (E^1,E^2,E^3), and the hydrogenic ratios (E^1/E^3, E^2/E^3, F^4/F^2, F^6/F^2) are found to be constants irrespective of the matrix composition. Therefore these parameters can be considered to be fundamental constants for trivalent neodymium in a given matrix.

Table 1. Calculated values of Slater-Condon(F_λ), Racah (E^λ) and spin-orbit (ξ_{4f}) parameters in sodium bismuth silicate glass and similar glasses.

Energy parameters	Sodium Bismuth Silicate [present glass]	Sodium Borate [9]	Sodium Phosphate [8]
F_2(cm^{-1})	284.36	330.05	314
F_4(cm^{-1})	46.54	50.8	47
F_6(cm^{-1})	2.642	5.14	4.8
ξ_{4f}(cm^{-1})	865.61	870.47	926
E^1(cm^{-1})	3993.3	5001.5	4792
E^2(cm^{-1})	18.13	23.89	22.6
E^3(cm^{-1})	486.87	494.81	471

3.3 Judd Ofelt parameters

The electronic transitions of the trivalent lanthanides can be regarded as a sum of the electric dipole (f_{ed}) and magnetic dipole (f_{md}) contributions, i.e.

$$F = f_{ed}+f_{md} \tag{9}$$

For rare earth ions, line strengths of magnetic dipole (md) transitions are much less than the line strengths of electric dipole (ed) transitions ($S^{md}_{JJ'}<<S^{ed}_{JJ'}$) and are usually neglected in the calculation of oscillator strengths**.** The experimentally measured oscillator strengths of various absorption transitions of the Nd^{3+} ion in the present glassy systems are found to be in good agreement with those of other oxide systems (see Table 2). Oscillator strength (f) can be expressed in terms of the molar extinction coefficient (ε), and the energy of the transition in wave number (ν) by the relation (10) [14].

$$f_{exp}= 4.32 \times 10^{-9}\int\varepsilon(\nu)d\nu \tag{10}$$

According to JO [15-16] theory, oscillator strengths of 4f→4f transitions of a rare earth ion can be described as a simple linear combination of three phenomenological parameters $\Omega_\lambda(\lambda=2,4,6)$ as

$$f_{ed} = \frac{\nu}{(2J+1)}\left[\frac{8\pi^2 mc}{3h}\frac{(n^2+2)^2}{9n}\right]\sum_{\lambda=2,4,6}\Omega_\lambda\left\langle\psi J\left\|U^\lambda\right\|\psi' J'\right\rangle^2 \tag{11}$$

Table 2. Energy oscillator strength and electric dipole line strength of all observed transitions in sodium bismuth silicate glass.

Transition from $^4I_{9/2}$ to	Energy (cm^{-1})	$F_{measured}$ (10^{-6})	S_{ed} (10^{-20})
$^4G_{9/2}$	19504	1.07	0.504
$^4G_{7/2}$	18527	0.669	0.3324
$^4G_{5/2}$	17390	1.239	0.665
$^2G_{7/2}$	16946	1.543	0.837
$^2H_{11/2}$	16621	0.268	0.148
$^4F_{9/2}$	14602	0.138	0.086
$^4S_{3/2}$	13467	1.562	1.066
$^4F_{7/2}$	13260	0.269	0.186
$^4F_{5/2}$	12500	0.459	0.3376
$^2H_{9/2}$	12317	1.053	0.786
$^4F_{3/2}$	11211	0.645	0.529

where (2J+1) is the degeneracy of the ground state, m the mass of the electron, and ν the mean energy of the $|\psi J\rangle \rightarrow |\psi' J'\rangle$ transition, U^λ is a unit tensor operator of rank λ and U^λ 's are parameters known as J-O intensity parameters. The calculated values of JO parameters (-0.41 x 10^{-20} cm^2, 3.14 x 10^{-20} cm^2, 2.61 x 10^{-20} cm^2) and the quality factor (Ω_4/Ω_6 = 1.2) for the sodium bismuth silicate glass are found to be in good agreement with those of other similar glasses [17].

3.4 Radiative transition parameters

Once the JO parameters Ω_λ have been determined, they can subsequently be utilized to calculate the properties of transitions that have not been experimentally measured, including the radiative lifetime. The values of the radiative transition probability (A), total radiative transition probability (A_T), radiative lifetime (τ) fluorescence branching ratio (β_R) and the integrated absorption crossection for stimulated emission are evaluated using the expressions

$$A^{ed}{}_{JJ} = \frac{64\pi^2 e^2 \upsilon^3}{3h(2J+1)}\left[\frac{n(n^2+2)^2}{9}\right]S_{ed} \tag{12}$$

$$A^{ed}{}_{JJ} = \tau^{-1}{}_{Rad} \tag{13}$$

$$\tau_{rad} = \frac{1}{\sum_{J'} A_{JJ'}} \tag{14}$$

The relative amplitudes of the fluorescence transitions or fluorescence branching ratio is given by

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum_{J'} AJJ'} \tag{15}$$

The branching ratio is the ratio of the radiative transition probability to the total radiative relaxation rate. It measures the percentage of emission for a given transition from a state with respect to all other transitions from this state. For the Nd^{3+} ion, the only excited manifold that is not relaxed predominantly by the multiphonon process is the $^4F_{3/2}$ manifold. This level fluoresces in four bands centered at approximately 880, 1060, 1350 and 1800 nm corresponding to the $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, $^4I_{15/2}$ excited states respectively. Since the matrix elements $\left({}^4F_{3/2}\left\|U^2\right\|{}^4I_J\right)$ are zero for the Nd^{3+} ion, the Ω_2 parameter will not have any effect on the stimulated emission parameters of Nd^{3+} ions. The calculated values of the radiative transition probability (A), total radiative transition probability (A_T), radiative life time (τ_{rad}) and fluorescence branching ration are given in Table 3.

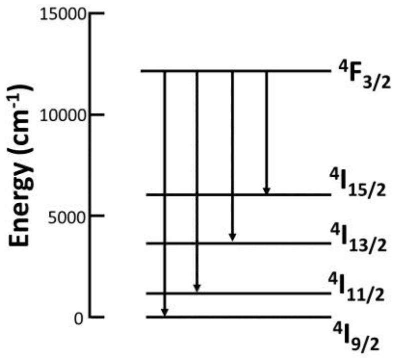

Figure 2. Possible radiative channels of Nd^{3+} from $^4F_{3/2}$ level.

The integrated absorption crossection or effective crossection (σ_a) for a stimulated emission of the active ion are directly evaluated using the expression

$$\sigma_a = \frac{1}{\nu^2}\frac{A}{8\pi c n^2} \tag{16}$$

From Table 3 it is clear that the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition has a promising stimulated absorption crossection and branching ratio and hence this transition in sodium bismuth silicate glass can be utilized for optical applications.

Table 3. Radiative transition rate, radiative life time, branching ratio and absorption crossection for stimulated emission for all the relevant transitions.

Level from $^4F_{3/2}$	Energy cm^{-1}	S_{ed} $x10^{22}cm^2$	A (s-1)	A_t (s-1)	β	Radiative life time $\tau_{rad}(\mu s)$	Absorption cross section for stimulated emission (σ_a) 10^{18} cm^2
$^4I_{15/2}$	5450	7.308	9	1760	0.005	568	0.12
$^4I_{13/2}$	7520	55.33	144		0.08		1.38
$^4I_{11/2}$	9520	150.8	794		0.451		4.69
$^4I_{9/2}$	11530	86.83	813		0.461		3.34

3.4 Optical basicity and ionic polarisability of the glass

Optical basicity represents the basicity of glasses in terms of electron density carried by oxygen. The theoretical optical basicity of a glass system is calculated using the relation [18-19].

$$\Lambda_{th}= X(Na_2O)\ \Lambda(Na_2O)+ X(SiO_2)\ \Lambda(SiO_2)+ X(Bi_2O_3)\ \Lambda(Bi_2O_3) \tag{17}$$

where $X(Na_2O)$,$X(SiO_2)$ and $X(Bi_2O_3)$ are the equivalent fractions of different oxides and Λ (Na_2O),Λ (SiO_2) and Λ (Bi_2O_3) are the optical basicity values assigned to the constituent oxides [5, 20].
The oxide ion polarisability can be calculated from the theoretical optical basicity as

$$\Lambda_{th}= 1.67\left(1-\frac{1}{\alpha_0^{2-}}\right) \tag{18}$$

It was observed that ionic polarisability increases when optical basicity increases. The bismuth free glass has an optical basicity of 0.787 which increased to 1.185 on addition of 10 mol % of Bi_2O_3. The glass hence possesses high optical basicity and ionic polarisability compared to other similar glasses [21].

4. Conclusion

UV-Vis-NIR absorption spectroscopy of Neodymium doped sodium bismuth silicate glasses, prepared by the melt quench technique, was carried out. From the detailed analysis of the spectra, various crystal field parameters such as Slater-Condon, spin-orbit and Racah parameters were calculated. Oscillator strength, electric dipole line strength and different radiative properties of the observed transitions were evaluated with the help of Judd-Ofelt theory. Optical basicity of sodium silicate glass was found to increase with the addition of bismuth.

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