Spectroscopic studies of Sm^{3+} -doped phosphate glasses

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Abstract. Optical properties of Sm^{3+} ion in phosphate glassy matrices were studied. The absorption, fluorescence, excitation spectra and decay patterns were obtained at room temperature. The oscillator strengths of the transitions between J manifolds were calculated using Judd–Ofelt theory and compared with the ones obtained experimentally. Various laser intensity parameters such as J–O parameters, radiative transition probabilities, lifetimes, branching ratio, and integrated absorption cross-section were evaluated. Radiative lifetimes of the excited states were determined and used to obtain nonradiative transition rates and quantum yields. Integrated intensity and dynamics of the fluorescence originating from the excited states were also studied as a function of Sm^{3+} concentration.

Keywords. Phosphate; glass; samarium.

1. Introduction

The research interest in solid state laser materials concentrates on evaluating the potential of rare earth ion doped amorphous materials for high average power applications (Emmett *et al* 1984). Several energy level systems capable of producing stimulated emission in the wide range of wavelength region have been found amongst rare earth ions. Muller *et al* (1991) have studied the spectroscopic properties of Sm^{3+} in lithium borate–tungstate glasses. Phosphate glass matrices with suitable compositions have been found to be good hosts for different laser active ions (Ebendorff *et al* 1993; Seeber *et al* 1994). However, spectroscopic studies of Sm^{3+} ion in phosphate glass matrix are relatively limited. In view of this, we report the spectroscopic properties of Sm^{3+} ion in phosphate glass matrix with different compositional network by analyzing the absorption and emission spectra. The present study revealed the origin of variation in some spectroscopic properties of Sm^{3+} for laser action by compositional changes of the glassy matrices.

2. Experimental

The phosphate glasses were prepared from $\text{NaH}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, LiCO_3 , Na_2CO_3 and 99.99% pure Sm_2O_3 (Indian Rare Earths). The general composition of the glass was $\text{NaH}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}((95.5 - x) \text{ mol}\%)$, LiCO_3 (1.5 mol%), Na_2CO_3 (3 mol%) and Sm_2O_3 (x mol%), where x varied from 0.25–1.5 mol%. The incorporation of alkali contents reduced crystallization phenomena

(Amaranath and Buddhudu 1990) and increased stability of the glass. The glass melting temperature was 850–900°C and the melt was quenched in between two well polished brass disks in order to obtain bubble free glass. The prepared glass samples were transparent and 1–1.5 mm in thickness and circular in shape with 1 cm diameter. Density of the glass samples was determined by Archimedes principle using xylene as the immersion liquid. The refractive index was measured using Abbe's refractometer. The absorption spectra were recorded in the UV–VIS–NIR region on Shimadzu (Model 3101 PC) spectrophotometer using undoped phosphate glass as a blank. The time resolved fluorescence studies were done on a Spex Spectrofluorometer. All the measurements were carried out at room temperature.

3. Results and discussion

3.1 Absorption and excitation spectra

The absorption spectra show ten absorption bands corresponding to transitions $^6H_{5/2} \rightarrow ^6H_{13/2}$, $^6F_{1/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^6F_{11/2}$, $^4I_{11/2}$, $^6K_{11/2}$, $^6G_{7/2}$. All the spectra are almost similar in appearance except for the band intensity. Therefore, a representative absorption spectrum corresponding to the glass sample with 1.5 mol% of Sm^{3+} is shown in figure 1. The estimated absorption coefficient of Sm^{3+} bands in different samples follow a linear relationship with the Sm^{3+} concentrations. This indicates that Sm^{3+} content of the glass is the same as that of the starting materials. This is in conformity with the results reported for other zirconium–fluoride glasses (Sanz *et al* 1987). Compositional studies of the phosphate glass have been achieved by using the theory of crystal field-

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induced electric dipole transition between $4f-4f$ state (Judd 1962; Shinn *et al* 1983). The intensity of the absorption bands is determined in terms of oscillator strength f_{exp} using the expression (Ofelt 1962)

$$f_{\text{exp}} = 4.32 \times 10^{-9} \int \epsilon(\nu) d(\nu), \quad (1)$$

where $\epsilon(\nu)$ is the molar extinction coefficient at the wave number ($\nu \text{ cm}^{-1}$) and the symbols have their usual meaning. According to Judd–Ofelt theory, the oscillator strength for electric dipole transition between $4f^n$ states of rare earth ions is given by (Peacock *et al* 1975)

$$f_{\text{ed}} = \frac{\nu}{2J+1} \left[\frac{8\pi^2 mc (n^2 + 2)^2}{27nh} \right] \times \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle \Psi J | U^{\lambda} | \Psi J \rangle^2, \quad (2)$$

Figure 1. Optical absorption spectrum of Sm^{3+} ion in phosphate glass.

where ν is the mean energy of the transition $\Psi J \rightarrow \Psi J'$. The matrix elements $\langle U^{\lambda} \rangle$ have been evaluated for intermediate coupling.

Using the values of f_{exp} we have computed the three Judd–Ofelt intensity parameters (Ω_{λ} s) by least square analysis. The factors which are responsible for the variation of intensity of transitions are these three intensity parameters. This effect gets relaxed to some extent when rare earth ion forms a covalent bond with host matrix (Peacock *et al* 1975). From the calculated values of Ω_{λ} , electric line strengths (S_{ed}) and magnetic dipole line strengths (S_{md}) are calculated using the expressions

$$S_{\text{ed}} = e^2 \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle f^N [\gamma SL] J \| U^{\lambda} \| f^N [\gamma SL] J' \rangle|^2, \quad (3)$$

and

$$S_{\text{md}} = \frac{e^2 h^2}{16 \pi^2 m^2 c^2} |\langle f^N [\gamma SL] J \| L + 2S \| f^N [\gamma SL] J' \rangle|^2, \quad (4)$$

where J is the initial level, J' the terminal level. The calculated values of the oscillator strength and electric dipole line strength are given in table 1.

The value Ω_2 for Sm^{3+} in the present glass lies in general, between values observed for crystalline oxide and fluoride glasses. The value of Ω_2 is strongly enhanced by covalent bonding in glasses which is equivalent to the dynamic polarization of the ligands by the quadrupole moment of the transitions. Ω_{λ} values are much higher in phosphate glasses than in fluorides (Jorgensen and Reisfeld 1983). The reason for such a behaviour is the large number of occupation of non equivalent sites and lower symmetry in which the rare earth ions are located. The effect manifests in the form of large line width of the optical spectra. The $6H_{5/2} \rightarrow 4G_{7/2}$ is found to be hypersensitive by its higher value of oscillator strength. Its intensity may vary significantly with environment due to strong $4f-5d$ mixing. This hypersensitivity comes

Table 1. Measured value of energy of levels, oscillator strength (10^{-6}), electrical dipole strength (10^{-20}), of Sm^{3+} ion in phosphate glass with four different mol% of Sm_2O_3 . (1. 0.75 mol%, 2. 1.0 mol%, 3. 1.25 mol%, 4. 1.5 mol%).

Levels	1			2			3			4		
	ν	f	S_{ed}	ν	f	S_{ed}	ν	f	S_{ed}	ν	f	S_{ed}
$4G_{7/2}$	30058	255.02	8.31	30051	251.81	8.01	30049	247.81	8.91	30056	267.64	9.61
$4K_{11/2}$	24384	20.01	4.53	24390	20.80	5.51	24392	21.40	5.82	24389	21.51	4.63
$4I_{11/2}$	20513	9.13	1.17	20491	8.38	1.92	20509	7.97	2.01	20502	8.97	1.51
$6F_{11/2}$	10628	2.31	1.31	10621	2.51	1.53	10630	2.67	1.72	10631	2.63	1.67
$6F_{9/2}$	9084	2.03	2.32	9089	2.38	2.41	9085	2.31	3.01	9081	2.47	2.81
$6F_{7/2}$	8097	1.90	1.75	8091	1.89	1.98	8094	2.21	1.90	8089	2.01	1.89
$6F_{5/2}$	7100	1.81	1.62	7104	1.82	1.72	7109	1.80	1.85	7111	1.93	1.73
$6F_{3/2}$	6694	0.97	0.32	6683	1.10	0.42	6679	0.98	0.46	6667	1.28	0.53
$6F_{12}$	6409	1.53	0.75	6404	1.62	0.82	6407	1.81	0.81	6412	1.72	0.73
$6H_{13/2}$	5255	1.19	0.29	5252	1.21	0.28	5259	1.29	0.31	5260	1.32	0.30

into play with strong covalency of the bonds, or with strong local variation of the dielectric constant (Judd 1979).

The excitation spectra of Sm^{3+} ions are shown in figure 2 with emission at 597 nm. The strongest band observed for Sm^{3+} peaks is at 397 nm and is assigned to $^4L_{13/2} \rightarrow ^6H_{5/2}$. The other bands observed are $^4H_{13/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4P_{5/2}$, $^4I_{15/2}$, $^4I_{11/2}$ corresponding to the transition within $4f^n$ configuration. In the case of Sm^{3+} ion it is found that energy levels above $^4G_{5/2}$ states are close together and below it they are far apart. The emission spectra and life time measurements confirm that the levels above $^4G_{5/2}$ are non radiatively relaxed to the $^4G_{5/2}$ level through multiphonon processes. Thus luminescence from those levels above $^4G_{5/2}$ are completely quenched

Figure 2. Excitation spectrum of Sm^{3+} ion in phosphate glass.

Figure 3. Fluorescence spectrum of Sm^{3+} ion in phosphate glass.

and we can identify them only by excitation spectra. The excitation peak intensity is independent of the concentration of the rare earth content which means that effect of crystal field on the energy levels is negligible.

3.2 Fluorescence spectra

Figure 3 shows the fluorescence spectra of Sm^{3+} in phosphate glasses. The observed emissions correspond to transitions with higher probabilities. From the spectra we have identified four emission transitions $^4G_{5/2} \rightarrow ^6H_{5/2, 7/2, 9/2, 11/2}$ which are shown in figure 5. The intensity of emission lines varies slightly with Sm^{3+} ion concen-

Figure 4. Variation of intensity of emission bands vs concentration of Sm^{3+} ion in phosphate glass.

Figure 5. Energy level scheme for emission of Sm^{3+} ion in phosphate glass.

tration in the glass samples. This indicates a matrix independent emission per ion for all the four transitions which leads to the assumption that the concentration dependence should result from changes in the absorption alone. Sm^{3+} fluorescence lines are parity forbidden, but they can be observed by the violation of parity for dipole transitions. This is the special case only with selection rule $\Delta J = 0, \pm 1$ (Poulain *et al* 1977). In this case the transitions ${}^4G_{5/2} \rightarrow {}^6H_{5/2, 7/2}$ are dipole in nature and the other two are higher multipole transitions. The break down of the above selection rule must be due to the hybridization of the rare earth 4*f*-state with the nearest neighbour shell (Judd 1966; Bartolo 1985). The fluorescence properties of glasses are analysed by Judd–Ofelt model applied to dipole and multipole transitions. The radiative transition probabilities (*A*) for different transitions are given by

$$A(\Psi J, \Psi J) = \frac{64\pi^4\nu^3}{3h(2j+1)} \left[\frac{n(n^2+2)^2}{9} S_{\text{ed}} + n^3 S_{\text{md}} \right]. \quad (5)$$

By combining these values for all the levels, the radiative life time (τ_{R}) (Caird *et al* 1981) is evaluated from the relation

$$\tau_{\text{R}} = 1/A_{\text{T}}(\Psi J), \quad (6)$$

where

$$A_{\text{T}}(\Psi J) = \Sigma A(\Psi J, \Psi J'). \quad (7)$$

The calculated values of radiative transition probabilities and lifetimes are listed in table 2. The fluorescence branching ratio β_{R} for the transition is given by

$$\beta_{\text{R}} = A(\Psi J, \Psi J)/A_{\text{T}}(\Psi J). \quad (8)$$

The concentration dependence of the fluorescence intensity of Sm^{3+} in the phosphate glass for the three fluorescence bands is given in figure 4. At lower concentrations, intensity increases linearly but at concentration above 1.0 mol% a fall in the intensity is observed due to the fluorescence quenching due to nearest neighbour ion interaction. The variation in intensity for the 706 nm band is observed to be almost negligible and therefore not given in the figure. The time resolved fluorescence decay profiles have been analyzed to extract life time values. The measured life time of the excited level may be written as

$$1/\tau = W_{\text{R}} + W_{\text{NR}},$$

where W_{R} is the radiative transfer rate of the level and W_{NR} the multiphonon relaxation rate of the host lattice and its value is found to be 1.26×10^3 . For the lifetime measurements, the desired level was directly excited. This is especially important for slow non radiative rates. For laser active transition, the corresponding β_{R} value characterizes the laser power of the transitions. In the present samples we found such a possible transition ${}^6H_{5/2} \rightarrow {}^6I_{11/2}$ with β_{R} assuming the maximum value 0.16 (The transition ${}^6H_{5/2} \rightarrow {}^4G_{7/2}$ is hypersensitive). However, the fluorescence spectrum shows a maximum fluorescence efficiency for the ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$. Such a behaviour has been attributed to the nonradiative relaxation from the ${}^6I_{11/2}$ level.

The stimulated emission cross-section (σ) for ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ has been calculated and has the same order of magnitude for other rare earth ions in phosphate glasses (Bartolo 1985). We have used the expression

$$\sigma = \frac{\lambda_{\text{p}}^4}{8\pi c n^2 \Delta \lambda_{\text{eff}}} A(\Psi J, \Psi J') \quad (9)$$

where λ_{p} corresponds to the peak position of emission

Table 2. Measured value of transition probability A (s^{-1}), total transition probability (A_{T}), radiative life time τ_{rad} (μs) and Judd–Ofelt intensity parameters Ω_{λ} s (10^{-20} cm^2) Sm^{3+} ion in phosphate glass with four different mol% of Sm_2O_3 (1. 0.75 mol%, 2. 1.0 mol%, 3. 1.25 mol%, 4. 1.5 mol%).

Levels	1			2			3			4		
	<i>A</i>	β		<i>A</i>	β		<i>A</i>	β		<i>A</i>	β	
${}^4G_{7/2}$	753.5	0.27	$A_{\text{T}} =$	721.2	0.28	$A_{\text{T}} =$	733.7	0.25	$A_{\text{T}} =$	728.3	0.26	$A_{\text{T}} =$
${}^4K_{11/2}$	241.1	0.08	2776.2	239.6	0.09	2571.7	251.7	0.08	2829.0	248.9	0.09	2785.9
${}^6I_{11/2}$	415.3	0.15	$\tau =$	421.8	0.16	$\tau =$	418.1	0.14	$\tau =$	428.5	0.15	$\tau =$
${}^6F_{11/2}$	218.1	0.76	360.2	224.1	0.08	388.8	219.5	0.08	353.4	227.5	0.08	358.9
${}^6F_{9/2}$	241.8	0.08	$\Omega_2 =$	244.8	0.09	$\Omega_2 =$	237.8	0.08	$\Omega_2 =$	229.6	0.08	$\Omega_2 =$
${}^6F_{7/2}$	354.1	0.13	5.37	357.1	0.14	5.45	351.6	0.12	5.30	348.2	0.12	5.21
${}^6F_{5/2}$	231.3	0.079	$\Omega_4 =$	233.8	0.09	$\Omega_4 =$	218.1	0.08	$\Omega_4 =$	219.3	0.07	$\Omega_4 =$
${}^6F_{3/2}$	41.8	0.015	4.13	56.8	0.02	4.17	66.1	0.023	4.16	51.4	0.01	4.21
${}^6F_{1/2}$	136.8	0.04	$\Omega_6 =$	140.6	0.05	$\Omega_6 =$	161.7	0.06	$\Omega_6 =$	147.8	0.05	$\Omega_6 =$
${}^6H_{13/2}$	142.4	0.05	2.13	141.9	0.06	2.09	170.7	0.06	2.16	156.4	0.05	2.21

Table 3. Measured life time (μs), half band width (nm), emission cross-section (10^{-20} cm^2) of identified emission bands for Sm^{3+} doped phosphate glass.

λ_p (nm)	Transition	τ_m	$\Delta\lambda_{\text{eff}}$	σ
561	$^4G_{5/2} \rightarrow ^6H_{5/2}$	141	10.3	6.1
597	$^4G_{5/2} \rightarrow ^6H_{7/2}$	264	9.8	8.3
644	$^4G_{5/2} \rightarrow ^6H_{9/2}$	154	12.6	6.4
706	$^4G_{5/2} \rightarrow ^6H_{11/2}$	192	13.3	5.0

line and $\Delta\lambda_{\text{eff}}$ is the effective line width which is used because of asymmetry of emission bands. The results are summarized in table 3. The $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition is found to have high cross-section and hence high optical gain.

4. Conclusion

Phosphate glasses with different compositions doped with Sm^{3+} have been prepared. The absorption spectra of Sm^{3+} in phosphate glass matrix have been analysed for spectral and Judd-Ofelt parameters. From the optical absorption spectra of Sm^{3+} in phosphate glass various radiative properties such as transition probabilities, radiative life time, branching ratios were determined. The higher value of Ω_2 compared to crystalline lattice supports the presence of ions occupying sites with non centro symmetric potential. The fluorescence studies confirmed the quenching mechanism at high ion concentration and low phonon relaxation rate. It is concluded that the transition $^4G_{5/2} \rightarrow ^6H_{7/2}$ has the potential in realizing optical amplification.

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