Chapter IX

SUMMARY AND CONCLUSIONS
IX. SUMMARY AND CONCLUSIONS

In this Chapter a brief summary and conclusions of the results obtained in the study of optical absorption and photoluminescence studies of Pr³⁺, Sm³⁺, Eu³⁺, Dy³⁺ and Er³⁺ doped sodium, potassium, magnesium, calcium, sodium-potassium, sodium-magnesium and sodium-calcium chlorophosphate glasses which are presented in Chapters IV to VIII are given.

9.1 OPTICAL ABSORPTION AND PHOTOLUMINESCENCE STUDIES OF Pr³⁺ DOPED DIFFERENT CHLOROPHOSPHATE GLASSES

Spectroscopic parameters such as Racah (E¹, E² and E³), spin–orbit interaction (ζ₄f) parameters and hydrogenic ratios (E¹/E³ and E²/E³) are obtained for Pr³⁺ doped sodium, potassium, magnesium, calcium, sodium-potassium, sodium-magnesium and sodium-calcium chlorophosphate glass matrices. These parameters are not much varied with the glass matrix. The hydrogenic ratios are nearly constant for all the glass matrices except for calcium and sodium-calcium glass matrices indicated unperturbed radial properties.

The spectral intensities of most of the transitions of Pr³⁺ ion are higher in magnesium chlorophosphate glass among the four (sodium, potassium, magnesium and calcium) glass matrices and in sodium-magnesium glass among the three (sodium-potassium, sodium-magnesium and sodium-calcium) mixed chlorophosphate glass matrices indicated higher asymmetry in
magnesium and sodium-magnesium chlorophosphate glass matrices. $\Omega_2$ and $\Omega_6$ parameters are higher in magnesium chlorophosphate glass among the four glass matrices (sodium, potassium, magnesium and calcium) indicated higher covalency of Pr-O bond and higher rigidity of the glass matrix. Among three mixed chlorophosphate glass matrices (sodium-potassium, sodium-magnesium and sodium-calcium), $\Omega_2$ parameter is higher in sodium-potassium glass matrix and $\Omega_6$ parameter is higher sodium-magnesium glass matrix indicated higher covalency of Pr-O bond and higher rigidity of these two glass matrices respectively. $\Omega_2$ and $\Omega_6$ parameters are lower in calcium and sodium-calcium glass matrices, indicating lower covalency of Pr-O bond and lower rigidity of these two glass matrices. These parameters increased largely when sodium is mixed with potassium and magnesium in this chlorophosphate glass matrix.

From the variation of shift in the peak wavelength of hypersensitive transition and $\Omega_2$ parameter it is concluded that some structural changes have taken place for sodium to potassium and sodium to sodium-calcium glass matrices. Radiative lifetimes ($\tau_R$) of the excited states $^3P_1$, $^3P_0$, $^1D_2$ and $^1F_3$ of Pr$^{3+}$ in all the above glass matrices are estimated and the lifetimes is in the order $^3F_3 > ^1D_2 > ^3P_0 > ^3P_1$ for all the glass matrices. Among the four glass matrices (sodium, potassium, magnesium and calcium), calcium glass matrix and magnesium glass matrix showed higher and lower radiative lifetimes for all the excited states. Among the three mixed chlorophosphate glass matrices (sodium-potassium, sodium-magnesium and sodium-calcium), sodium-calcium glass matrix shows higher radiative lifetimes. When sodium is mixed with potassium
and magnesium, the radiative lifetimes are decreased for all the excited states, but when sodium is mixed with calcium the radiative lifetimes are increased.

From the studies of branching ratios ($\beta_n$) and integrated absorption cross-sections ($\Sigma$), $^{3}F_3 \rightarrow ^{3}H_4$ transition in sodium chlorophosphate glass matrix and $^{3}P_0 \rightarrow ^{3}H_4$ transition in magnesium glass matrix are useful for laser transitions. From the emission spectra, peak emission cross-sections ($\sigma_p$) are calculated for the observed emission transitions. Between the two observed emission transitions, $^{3}P_0 \rightarrow ^{3}F_2$ transition in magnesium and sodium-potassium glass matrices showed higher cross section values. Hence these materials are suggested for lasing materials.

9.2 OPTICAL ABSORPTION AND PHOTOLUMINESCENCE STUDIES OF $\text{Sm}^{3+}$ DOPED DIFFERENT CHLOROPHOSPHATE GLASSES

The spectral intensities of most of the absorption bands of $\text{Sm}^{3+}$ are higher in calcium glass matrix among the four glass matrices (sodium, potassium, magnesium and calcium) and in sodium-potassium glass matrix among the three (sodium-potassium, sodium-magnesium and sodium-calcium) mixed chlorophosphate glass matrices indicated higher asymmetry in calcium and sodium-potassium chlorophosphate glass matrices. $\Omega_2$ and $\Omega_4$ parameters are higher in calcium and lower in magnesium glass matrices indicated higher and lower covalencies of Sm-O bond and higher and lower rigidities of the glass matrices in these two chlorophosphate glass matrices respectively. Among the three mixed chlorophosphate glass matrices (sodium-potassium,
sodium-magnesium and sodium-calcium), sodium-potassium glass matrix indicated higher $\Omega_2$ parameter and sodium-calcium glass matrix indicated lower $\Omega_2$ parameter showing that higher and lower covalencies of Sm-O bond in these two glass matrices. When sodium is mixed with potassium, $\Omega_2$ parameter increased but when sodium is mixed with magnesium and calcium, $\Omega_2$ parameter decreased.

From the variation of shift in the peak wavelength of hypersensitive transition and $\Omega_2$ parameter, some structural changes are observed for sodium to potassium, magnesium to calcium, sodium to sodium-magnesium and sodium to sodium-calcium glass matrices. The radiative lifetimes ($\tau_R$) of the excited states $^4G_{5/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$ and $^6F_{1/2}$ of Sm$^{3+}$ ion are estimated in sodium, potassium, magnesium, calcium, sodium-potassium, sodium-magnesium and sodium-calcium glass matrices. The order of magnitude of lifetimes in all the glass matrices is $^6F_{11/2} > ^6F_{9/2} > ^6F_{7/2} > ^6F_{5/2} > ^6F_{3/2} > ^6F_{1/2}$. The radiative lifetime of the excited state, $^6F_{11/2}$ is higher in all the glass matrices. The radiative lifetimes of all the excited states are decreased when sodium is mixed with potassium, magnesium and calcium. From the magnitudes of branching ratios ($\beta_R$), it is concluded that the transition, $^6F_{7/2} \rightarrow ^6H_{5/2}$ in magnesium and sodium-magnesium glass matrices is suggested for laser excitation. Peak emission cross-sections ($\sigma_p$) are obtained for the three emission transitions, $^4G_{5/2} \rightarrow ^4H_{5/2}$, $^4G_{5/2} \rightarrow ^4H_{7/2}$ and $^4G_{5/2} \rightarrow ^4H_{9/2}$ of
Sm$^{3+}$ in all glass matrices. Among the three transitions, $^4G_{5/2}\rightarrow^6H_{7/2}$ transition shows higher emission cross-sections in calcium glass matrix.

9.3 OPTICAL ABSORPTION AND PHOTOLUMINESCENCE STUDIES OF Eu$^{3+}$ DOPED DIFFERENT CHLOROPHOSPHATE GLASSES

The experimental spectral intensities ($f_{\text{exp}}$) are higher for the transition, $^7F_0\rightarrow^5G_4$ among various transitions and it is higher in magnesium glass matrix among four chlorophosphate glass matrices (sodium, potassium, magnesium and calcium). Among the three mixed chlorophosphate glass matrices (sodium-potassium, sodium-magnesium and sodium-calcium), the spectral intensities are higher in sodium-magnesium chlorophosphate glass matrix indicated crystal field asymmetry at the site of Eu$^{3+}$ ion is higher for these two glass matrices. $\Omega_2$ parameter is higher in potassium glass matrix among four glass matrices (sodium, potassium, magnesium and calcium) and in sodium-magnesium glass matrix among the three mixed chlorophosphate glass matrices (sodium-potassium, sodium-magnesium and sodium-calcium) indicated higher covalency of Eu-O bond and higher asymmetry in these two glass matrices respectively. The emission intensity ratio value ($R$) is higher in magnesium glass matrix indicated higher asymmetric ratio which indicates lower symmetry. The estimated radiative lifetime of the excited state, $^5D_0$ is higher in magnesium glass matrix among the four glass matrices (sodium, potassium, magnesium and calcium). Among the three mixed chlorophosphate glass matrices (sodium-potassium, sodium-magnesium and sodium-calcium),
sodium-magnesium shows higher radiative lifetime. The peak emission crosssections are obtained for the four emission transitions, \( ^5D_0 \rightarrow \gamma F_1, \quad ^7F_2, \quad ^7F_3 \) and \( ^7F_4 \). Branching ratio values are obtained experimentally and theoretically. There is a good agreement between these two branching ratios except for \( ^5D_0 \rightarrow \gamma F_1 \) transition. The peak emission cross-section is higher in sodium chlorophosphate glass among the four glass matrices (sodium, potassium, magnesium and calcium) and in sodium-potassium glass matrix among the three mixed chlorophosphate glasses (sodium-potassium, sodium-magnesium and sodium-calcium). Among four observed emission transitions of Eu\(^{3+}\) ion, \( ^5D_0 \rightarrow \gamma F_1 \) transition consists higher emission cross-section in all the glass matrices.

9.4 OPTICAL ABSORPTION AND PHOTOLUMINESCENCE STUDIES OF Dy\(^{3+}\) DOPED DIFFERENT CHLOROPHOSPHATE GLASSES

The spectral intensities of most of the absorption bands are higher in calcium glass matrix and lower in magnesium glass matrix among the four chlorophosphate matrices (sodium, potassium, magnesium and calcium). Among the three mixed chlorophosphate glass matrices (sodium-potassium, sodium-magnesium and sodium-calcium), the spectral intensities are higher in sodium-calcium glass matrix and lower in sodium-magnesium glass matrix indicated crystal field asymmetry at the site of Dy\(^{3+}\) ion is higher and lower in these two glass matrices respectively. \( \Omega_2 \) parameter is higher in calcium glass matrix and lower in potassium glass matrix among four glass matrices (sodium,
potassium, magnesium and calcium) indicated higher and lower covalences of Dy-O bond in these two glass matrices respectively. \( \Omega_2 \) parameter is higher in calcium glass matrix and lower in magnesium glass matrix indicated higher and lower rigidities of the glass matrices. Judd-Ofelt intensity parameters are decreased when sodium is mixed with potassium, magnesium and calcium.

From the variation of shift in the peak wavelength hypersensitive transition and \( \Omega_2 \) parameter, the structural changes are not influencing the covalency for sodium to potassium, potassium to magnesium and sodium to sodium-magnesium. But for sodium to calcium, potassium to sodium-potassium and calcium to sodium-calcium, structural changes are influencing the covalency of Dy-O bond. The radiative lifetimes of the excited states \(^{4}I_{15/2}, \)^{4}F_{9/2}, \(^{6}F_{3/2}, \)^{6}F_{5/2} and \(^{6}F_{11/2} \) of \( \text{Dy}^{3+} \) are estimated in all the glass matrices studied. Among all the states, \(^{4}I_{15/2} \) and \(^{6}F_{11/2} \) states show higher and lower radiative lifetimes in all the glass matrices. The lifetimes of the all excited states are increased when sodium is mixed with potassium, magnesium and calcium. The branching ratios of the transitions \(^{4}I_{15/2} \rightarrow ^{6}H_{15/2}, \)^{6}F_{9/2} \rightarrow ^{6}H_{13/2}, \)^{6}F_{3/2} \rightarrow ^{6}H_{13/2}, \)^{6}F_{5/2} \rightarrow ^{6}H_{13/2} \) and \(^{6}F_{5/2} \rightarrow ^{6}H_{15/2} \) of \( \text{Dy}^{3+} \) are obtained. Among the five transitions, the transition, \(^{6}F_{5/2} \rightarrow ^{6}H_{15/2} \) showed higher branching ratios in sodium and sodium calcium glass matrices. Integrated absorption cross section values are also higher for this transition in all the glass matrices. Among all the glass matrices, sodium and sodium-calcium glass matrices showed higher branching ratios for this transition.
Two emission peaks are observed due to emission transitions $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^6F_{9/2} \rightarrow ^6H_{13/2}$ of Dy$^{3+}$ in all the seven glass matrices. The peak emission cross sections are obtained and these values are higher in calcium glass matrix and lower in potassium glass matrix among the four glass matrices (sodium, potassium, magnesium and calcium). Among the three mixed chlorophosphate glass matrices (sodium-potassium, sodium-magnesium and sodium-potassium), sodium-calcium glass matrix showed higher emission cross sections for the two transitions. Between these two transitions, $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition showed higher emission cross section in calcium and sodium-calcium glass matrices.

9.5 OPTICAL ABSORPTION AND PHOTOLUMINESCENCE STUDIES OF Er$^{3+}$ DOPED DIFFERENT CHLOROPHOSPHATE GLASSES

Spectroscopic parameters such as Racah ($E^1$, $E^2$ and $E^3$), spin–orbit interaction ($\xi_{so}$), configuration interaction ($\alpha$) parameters and hydrogenic ratios ($E^1/E^3$ and $E^2/E^3$) of Er$^{3+}$ doped sodium, potassium, magnesium, calcium, sodium-potassium, sodium-magnesium and sodium-calcium chlorophosphate glass matrices are observed. The hydrogenic ratios are nearly constant for all the glass matrices (except for sodium-potassium glass matrix) indicated unperturbed radial properties. The spectral intensities of most of the absorption bands of Er$^{3+}$ are higher in calcium glass matrix and lower in potassium glass matrix among the four glass matrices (sodium, potassium, magnesium and
Among three mixed chlorophosphate matrices (sodium-potassium, sodium-magnesium and sodium-calcium), sodium-magnesium glass shows higher spectral intensities and sodium-calcium glass shows lower spectral intensities. These results indicated higher and lower asymmetries of calcium and potassium glass matrices among the four glass matrices. $\Omega_2$ and $\Omega_6$ parameters are higher in calcium chlorophosphate glass among the four glass matrices (sodium, potassium, magnesium and calcium) indicated higher covalency of Er-O bond and higher rigidity of the glass matrix. Among the three mixed chlorophosphate glass matrices (sodium-potassium, sodium-magnesium and sodium-calcium), $\Omega_2$ and $\Omega_6$ parameters are higher in sodium-magnesium glass matrix indicated higher covalency of Er-O bond and higher rigidity of the glass matrix. Judd-Ofelt intensity parameters are increased when sodium is mixed with potassium, magnesium and calcium in the glass matrix.

From the variation in shift in peak wavelength of hypersensitive transition and $\Omega_2$ parameter, structural changes are not influencing covalency of Er-O bond for sodium to potassium and sodium to magnesium. But for sodium to calcium, sodium to sodium-potassium, sodium to sodium-magnesium and sodium to sodium-calcium glass matrices some structural changes are observed. The radiative lifetimes ($\tau_R$) of the excited states $^4G_{11/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ of Er$^{3+}$ in all the above seven glass matrices are estimated. Potassium glass matrix showed higher radiative lifetimes and calcium glass matrix showed lower radiative lifetimes for all the excited states among the four glass matrices. The radiative lifetimes of all the
excited states are decreased when sodium is mixed with potassium, magnesium and calcium. The branching ratios ($\beta_R$) of different transitions are calculated and certain transitions which are having higher branching ratios are identified. Among various transitions, the transitions $^2G_{11/2} \rightarrow ^4I_{15/2}$, $^4F_{5/2} \rightarrow ^4I_{15/2}$, $^4F_{7/2} \rightarrow ^4I_{15/2}$, $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, $^4F_{9/2} \rightarrow ^4I_{15/2}$, $^4I_{9/2} \rightarrow ^4I_{15/2}$, $^4I_{11/2} \rightarrow ^4I_{15/2}$ and $^1I_{13/2} \rightarrow ^4I_{15/2}$ showed higher branching ratios. Among the four glass matrices (sodium, potassium, magnesium and calcium), calcium glass matrix showed higher branching ratios for all the transitions. From the magnitude of branching ratios, the transitions $^4I_{11/2} \rightarrow ^4I_{15/2}$ and $^1I_{13/2} \rightarrow ^4I_{15/2}$ in calcium glass matrix may be useful for laser excitation.

The emission spectra of Er$^{3+}$ doped seven glass matrices showed three emission peaks due to transitions, $^4F_{5/2} \rightarrow ^4I_{15/2}$, $^4F_{7/2} \rightarrow ^4I_{15/2}$ and $^2H_{11/2} \rightarrow ^4I_{15/2}$. Peak emission cross-sections ($\sigma_p$) of the three transitions are evaluated in all the glass matrices. Among the four glass matrices (sodium, potassium, magnesium and calcium), sodium glass shows higher emission cross-section. The emission cross-sections are increased when sodium is mixed with potassium, magnesium and calcium. Hence sodium chlorophosphatate glass matrix may be useful for laser material.
Articles published and presented at various conferences/seminars
Optical and luminescence studies of Pr$^{3+}$ and Er$^{3+}$ doped different phosphate glasses


Department of Physics, Sri Venkateswara University, Tirupati 517 502, AP, India

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ABSTRACT

Optical absorption and emission spectra of Pr$^{3+}$ and Er$^{3+}$ doped different chlorophosphate glasses have been studied. Optical properties of these two rare earth ions were characterized through optical absorption and emission spectra using Judd-Ofelt theory. Judd-Ofelt intensity parameters $Q_i$ (i = 2, 4, and 6) are calculated for both the ions from their absorption spectra, which in turn was used to derive the radiative properties such as radiative transition probabilities $(A_i)$, radiative lifetimes $(\tau)$, branching ratios $(\beta)$ and integrated absorption cross-sections $(\sigma)$. An attempt has been made to discuss structural changes considering the hyper-Rayleigh transitions and tendency of rare earth ions (RE-O) bonds for the present glass systems. From emission spectra, peak emission cross-sections $(\sigma_p)$ are obtained for the observed emission bands of Pr$^{3+}$ and Er$^{3+}$ ions in all these chlorophosphate glasses. Variation of peak emission cross-sections with the glass matrix has been studied.

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1. Introduction

In recent years extensive research work has been done for improved functionality of new materials for various applications. In particular, spectroscopic and laser characteristics of rare earth doped glass materials are optimized for broad band fiber amplifier, efficient lasing and frequency conversion processes [1–3]. Rare earth ions are used to probe the local structural variations in the host glass matrices because of their unique spectroscopic properties resulting from the radiative transitions in the 4f intra-configuration. Among various rare earth ions, Pr$^{3+}$ and Er$^{3+}$ have been recognized as most efficient rare earth ions for obtaining laser emission, frequency doubling conversion, waveguide lasers and in optical amplifiers [4,5]. Recently, Ratnakaram et al. [6] reported optical absorption and emission properties of Pr$^{3+}$ and Er$^{3+}$ in lithium–cesium mixed alkali borate glasses. Moothry et al. [7] reported optical properties of Er$^{3+}$ doped alkali fluorophosphates glasses. Bodal et al. [8] studied optical properties of Pr$^{3+}$, Sm$^{3+}$ and Er$^{3+}$ ions inapatite, fluorite and phosphate glasses. Optical absorption, fluorescence decay and decay properties of Pr$^{3+}$ doped PbO-H$_2$BO$_3$-TiO$_2$-AIF glasses were reported by Jamalalad [9]. Optical spectra and Judd-Ofelt analysis of Pr$^{3+}$ and Er$^{3+}$ in different phosphate glasses have been reported by Seshadri et al. [10].

The host glass matrix is very important factor for the development of rare earth doped optical devices. Among different host glass matrices, phosphate glasses are important hosts for Pr$^{3+}$ and Er$^{3+}$ ions because of their spectroscopic characteristics such as laser emission cross-section, weak interaction among active ions and may cause concentration quenching which have been extensively used for lasers and fiber amplifiers [11,12]. Recently, the authors reported spectroscopic properties and Judd-Ofelt analysis of Sm$^{3+}$ and Dy$^{3+}$ doped phosphate glasses [13]. In the present work, characterization of Pr$^{3+}$ and Er$^{3+}$ doped different chlorophosphate glasses has been reported. Various spectroscopic parameters (Racah $(B')$, $B^*$ and $D_0$), spin-orbit $(C_4)$ and configuration interaction $(c)$ are deduced for both the ions in different chlorophosphate glasses. Using Judd-Ofelt theory and from the measured absorption spectra, the local environment of Pr$^{3+}$ and Er$^{3+}$ ions and bond covalency of RE-O bond have been studied. Judd-Ofelt intensity parameters $(Q_0, Q_2$ and $Q_4$) have been used to calculate radiative transition rates $(A)$, radiative lifetimes $(\tau)$, branching ratios $(\beta)$ and integrated absorption cross-sections $(\sigma)$ for certain excited states of Pr$^{3+}$ and Er$^{3+}$ in different chlorophosphate glasses. Peak stimulated emission cross-sections $(\sigma_p)$ of the observed emission transitions of both the ions in all the glass matrices are reported.

2. Experimental

Pr$_2$O$_3$ and Er$_2$O$_3$ (0.2 mol%) doped different chlorophosphate glass matrices of the glass compositions 68BaF$_2$O$_3$-20Na$_2$HPO$_4$-10BC (R=La, K, Mg and Ca) and 88BaF$_2$O$_3$.20Na$_2$HPO$_4$.8NaCl.5SrCl$_2$ (R=K, Mg and Ca) were prepared using melt quenching
method. All these chemicals are reagent grade with 99.8% purity. The anhydrous chlorides were dried by heating at appropriate temperatures under vacuum. A small amount of ammonium chloride was added to these dehydrated chlorides in order to drive off impurities. About 5-10 g batch compositions were thoroughly ground using agate mortar and heated in a silica crucible for 2 h in an electric furnace at a temperature of 400 °C. This allowed the phosphorous pentoxide to decompose and react with other batch constituents before melting. Then the crucible with the mixture was kept at 950°C. During melting, the liquids were shaken at 15 min interval in order to obtain bubble free glass and ensure homogeneity. When the melting was completed, the liquid was poured and quenched between two well polished brass plates. The obtained glass samples were annealed at 400°C for 3 h to eliminate the mechanical stress. Glass samples of about 1-2 mm thickness were obtained. Densities of the glass samples were determined using Archimedes principle (using xylene as immersion liquid) and the refractive indices of the samples were measured using Abbe-refractometer with sodium lamp. Optical absorption spectra were measured in the UV-Vis-NIR regions using JASCO V-570 spectrophotometer with the spectral resolution of 0.1 nm. Fluorescence spectra were measured using Fluoro-Max 3 fluorescence spectrophotometer under excitation wavelengths, 405 and 315 nm for Pr3+ and Er3+ ions, respectively, with the spectral resolution of 1 nm.

3. Results and discussion

3.1. Spectral intensities and intensity parameters

Figs. 1 and 2 show the optical absorption spectra of Pr3+ and Er3+ ions doped Na, K, Mg, Ca, Na-K, Na-Mg and Na-Ca chlorophosphate glasses measured at room temperature in the wavelength region 350–2200 nm. The precise transition energies are found and their absorption bands are assigned for both the ions as follows:

For Pr3+ ion, $^3H_{4} \rightarrow ^1G_{4}, ^3S_{1} \rightarrow ^1D_{2}, ^1S_{0} \rightarrow ^1P_{1}, ^3P_{0} \rightarrow ^1D_{2}, ^3P_{2} \rightarrow ^1F_{2}, ^1D_{2} \rightarrow ^1H_{11/2}, \ldots$

For Er3+ ion, $^4I_{13/2} \rightarrow ^4I_{15/2}, ^4I_{15/2} \rightarrow ^4I_{13/2}, ^4I_{11/2} \rightarrow ^4I_{13/2}, \ldots$

Fig. 1. Optical absorption spectra of Pr3+ doped different chlorophosphate glasses.

Fig. 2. Optical absorption spectra of Er3+ doped different chlorophosphate glasses.
From the optical absorption spectra of $\text{Er}^{3+}$ in different chlorophosphate glasses it is observed that the absorption band corresponding to the transitions, $\Delta m = 0 \rightarrow 0$ is not observed in potassium, magnesium and calcium glass matrices, because of the shifting of absorption edge towards near ultraviolet region in the above glass matrices. Using the method of Wong [14] and Taylor's series expansion and using the observed band energies, $E_j$ ($j = 1, 2$ and $3$), zero order energies $E_0$ and partial derivatives [15], the correction factors $\Delta A_0$ and $\Delta A_e$ of $\text{Er}^{3+}$ ion have been evaluated by the least square fit method. In the case of $\text{Er}^{3+}$ ion, the correction factor $\Delta A$ is also obtained. Using these values, the calculated energies are obtained for all the absorption bands in different glass matrices. The rms deviations between experimental and calculated energies are small, indicating full matrix diagonalization procedure leads to a good fit between experimental and calculated energies. In the present work, the rms deviations are obtained using the formula

$$\delta_{\text{rms}} = \left[ \sum (\Delta E_j^2/\langle \delta - \epsilon \rangle)^{1/2} \right] (1)$$

where $\Delta E_j$ is the sum of the squares of deviations between the experimental and calculated spectral intensities; $\epsilon$ and $\delta$ are the transition number and the need fixed parameters, respectively, Rach [5], $\langle \delta - \epsilon \rangle$ spin-orbit interaction ($\delta_0$) parameters and hydrogenic ratios $\langle \delta \rangle^2$ and $\langle \delta \rangle^2$ of $\text{Er}^{3+}$ and $\text{Er}^{2+}$ ions doped different chlorophosphate glasses are obtained and are presented in Table 1 for all the glass matrices. In the case of $\text{Er}^{3+}$ ion, configuration interaction (a) parameter is also obtained and is presented in the table. It is observed that the hydrogenic ratios are nearly the same for all the glass matrices except for $\text{Pb}^{2+}$ doped calcium and sodium–calcium glass matrices indicating unperturbed radial properties.

From the absorption spectra, the experimental and calculated spectral intensities were obtained for the observed bands of $\text{Pb}^{2+}$ and $\text{Er}^{3+}$ ions using the formula given in Ref. [14] and are presented in Tables 2 and 3, respectively. The small rms deviations indicate the good quality of fit between the experimental and calculated spectral intensities. In the case of $\text{Pb}^{2+}$ ion, because of the overlapping of the absorption bands, $\text{Pb}^2$ and $\text{Pb}^{2+}$, there is with $\text{Pb}^2$ and $\text{Pb}^{2+}$, respectively, the absorption bands were treated as two single bands and the matrix elements correspond to the two transitions were combined and treated as single experimental point. From Tables 2 and 3, it is observed that among the four phosphate glass matrices (Na, K, Mg and Ca), the magnitude of spectral intensities for most of the transitions of $\text{Pb}^{2+}$ ion are higher in magnesium chlorophosphate glass and for $\text{Er}^{3+}$ ion, the spectral intensities are higher in calcium chlorophosphate glass indicating higher asymmetry in these two glass matrices. In the case of doped phosphate glass matrices, sodium–magnesium glass shows higher spectral intensities for both the ions indicating higher asymmetry of the glass matrix. Based on Judd–Ofelt theory, a static wave function mixing perturbation between ground and excited configurations have been taken into account, the Judd–Ofelt parameters are given by [17]

$$\Omega_{\text{ji}} = (2J+1) \sum A_{\alpha} \frac{J(J+1)}{\Omega} \left( \frac{\Omega}{\text{cm}^{-1}} \right)$$

where $A_{\alpha}$ are components of the crystal field operator that depends on the nature, symmetry and strength of the ion ligand

Table 1

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interaction in the host; \( S(\tau, J) \) is a function of radial integrals reciprocally on the energy separation of the \( 4f \) level and admixing levels, e.g., 5d, 5g.

Judd-Olfet intensity parameters \( \Omega_2, \Omega_3 \) and \( \Omega_4 \) were obtained from the least square analysis of the observed spectral intensities for these two ions in all the chlorophosphate glasses using the formulae given in Ref. [18]. As there is some uncertainty in the measurement of the spectral intensity of the transition, \( \Omega_3 = \Omega_4 \) of \( \text{Pr}^{3+} \) ion, only six absorption transitions were used in the least squares fitting procedure. Similarly in the case of \( \text{Er}^{3+} \) ion, eight absorption bands (except \( \Omega_2 \) and \( \Omega_4 \) absorption bands) were used in least square fit. The best set of Judd-Olfet intensity parameters of \( \text{Pr}^{3+} \) and \( \text{Er}^{3+} \) doped different chlorophosphate glass matrices studied in the present work are presented in Table 4 along with the parameters in borate [19], tellurite [19] and phosphate [19] glass matrices. The sum of the Judd-Olfet intensity parameters \( \Sigma \Omega \) is also presented in the table.

Normally the magnitude of \( \Omega_2 \) (or \( \Sigma \Omega \)) parameter depends on the symmetry of the rare earth ion site and strongly affected by covalency between rare earth ion and ligand ions, whereas \( \Omega_3 \) and \( \Omega_4 \) parameters depend on the host medium in which the ions are situated. It is observed that in the case of \( \text{Pr}^{3+} \) ion, among the four glass matrices (Na, K, Mg and Ca), \( \Omega_3 \) parameter is higher in magnesium and lower in calcium glasses indicating higher and lower covalencies of \( \text{Pr}^3-\text{O} \) bond in the glass matrices. Among the three mixed chlorophosphate glasses (Na-K, Na-Mg and Na-Ca), sodium-potassium glass shows higher \( \Omega_2 \) parameter indicating higher covalency. It is also observed that the Judd-Olfet intensity parameters increased largely when sodium is mixed with potassium and magnesium in this glass matrix. The order of magnitude of Judd-Olfet parameters is \( \Omega_3 > \Omega_2 > \Omega_4 \) for Na, K, Ca and Na-Ca glass matrices. For the remaining glass matrices there is no systematic order.

In the case of \( \text{Er}^{3+} \) ion, among the four glass matrices (Na, K, Mg and Ca), the \( \Omega_2 \) parameter is higher in calcium and lower in potassium glass matrices indicating higher and lower covalencies for these two glass matrices. Among the three mixed chlorophosphate glass matrices (Na-K, Na-Mg and Na-Ca), sodium-magnesium glass matrix shows higher \( \Omega_2 \) parameter indicating higher covalency. It is also observed that the Judd-Olfet intensity parameters increased when sodium is mixed with potassium, magnesium and calcium in the glass matrix. The magnitude of Judd-Olfet intensity parameters is in the order \( \Omega_2 > \Omega_3 > \Omega_4 \) for all the glass matrices except for calcium glass matrix.

### Table 4

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### Table 3

Experimental and calculated spectral intensities in \( \times 10^3 \) of observed absorption bands of \( \text{Pr}^{3+} \) ions doped in different chlorophosphate glasses.

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<td>0.84</td>
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Interaction parameters are given in Table 4 along with the parameters in borate [19], tellurite [19] and phosphate [19] glass matrices.
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1946.3 and 1947.2 nm, respectively. It is observed that there is no shift in the peak wavelength of hypersensitive transition for sodium to potassium glass matrix but the $Q_3$ parameter largely increased indicating some structural changes (according to Eq. (2)). From potassium to magnesium and magnesium to calcium, the order of change in the shift of peak wavelength of the hypersensitive transition and the $Q_0$ parameter is same indicating that the structural changes are not influencing the covalency of Br-O bond in these two glass matrices. From sodium to sodium-potassium and sodium-magnesium, there is a shift in the peak wavelength of the hypersensitive transition towards longer wavelengths. $Q_3$ parameter also increased for these two glass matrices indicating that the influence of structural change is very less on covalency. From sodium to sodium-calcium glass matrix, there is a shift in the peak wavelength towards longer wavelength but the $Q_3$ parameter decreased slightly indicating some small structural changes. In the case of Er$^{3+}$ ion, there is not much change in the peak wavelengths of two hypersensitive transitions with the variation of glass matrix. Hence, the change in $Q_0$ parameter with the glass composition indicates that the influence of structural changes on the covalency of Br-O bond is very small.

3.3. Radiative properties

Using Judd–Ofelt intensity parameters, the radiative transition probabilities ($A$), radiative lifetimes ($τ$), branching ratios ($β$) and integrated absorption cross-sections ($σ$) of certain excited states of Pr$^{3+}$ and Er$^{3+}$ doped different chlorophosphate glasses are obtained using the formulae given in Ref. [14]. In the case of Pr$^{3+}$ ion, the radiative lifetimes of the excited states, $τ_{54}$, $τ_{63}$, $τ_{12}$, and $τ_{2}$ are calculated and these values are given in Table 5. The radiative lifetimes are found to be decreased in the order $τ_{2} > τ_{12} > τ_{63} > τ_{54}$ for all the glass matrices. Among the four glass matrices (Na, K, Mg, and Ca), calcium glass matrix shows higher radiative lifetimes and magnesium glass matrix shows lower radiative lifetimes for all the excited states. It is observed that when sodium is mixed with potassium and magnesium, the radiative lifetimes are decreased for all the excited states, but

![Graph](image-url)}

**Table 5**: Variation of $Q_0$, $Q_1$, and $Q_2$ parameters with the variation of glass matrix.

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</table>

**Fig. 3**: Variation of $Q_0$, $Q_1$, and $Q_2$ parameters with the variation of glass matrix.
when sodium is mixed with calcium the radiative lifetimes are increased. Among the three mixed chlorophosphate glass matrices (Na-K, Na-Mg and Na-Ca), sodium-calcium glass matrix shows higher radiative lifetimes. The magnitude of branching ratios is higher for the transitions, \( \Delta_{1} \rightarrow \Delta_{4} \), \( \Delta_{2} \rightarrow \Delta_{4} \) and \( \Delta_{4} \rightarrow \Delta_{4} \) among various transitions and these values are in the range 0.26-0.36, 0.41-0.55, 0.19-0.43 and 0.76-0.83, respectively, for different glass matrices. Among the four transitions, \( \Delta_{1} \rightarrow \Delta_{4} \) transition has higher branching ratio value in sodium glass matrix (0.936). Among the three mixed chlorophosphate glass matrices (Na-K, Na-Mg and Na-Ca), sodium-calcium glass matrix (0.793) shows higher branching ratio for this transition.

In the case of Er\(^{3+}\) ion, the radiative lifetimes of the excited states, \( C_{110} \), \( C_{400} \), \( C_{400} \), \( C_{110} \), \( C_{620} \), \( C_{620} \), \( C_{620} \), \( C_{110} \), \( C_{110} \), and \( C_{110} \) are calculated for all the chlorophosphate glasses. It is observed that among the four glass matrices (Na, K, Mg and Ca), potassium matrix indicates higher radiative lifetimes and calcium glass matrix indicates lower radiative lifetimes. It is also observed that when sodium is mixed with potassium, magnesium and calcium, the radiative lifetimes are decreased. Among the three mixed chlorophosphate glass matrices (Na-K, Na-Mg and Na-Ca), sodium-calcium glass matrix shows higher radiative lifetimes. Branching ratios (\( \beta \)) for certain transitions of Er\(^{3+}\) ion which have higher in magnitudes are \( C_{110} \rightarrow \Delta_{100} \), \( C_{320} \rightarrow \Delta_{110} \), \( C_{400} \rightarrow \Delta_{110} \), \( C_{620} \rightarrow \Delta_{110} \), \( C_{120} \rightarrow \Delta_{110} \), \( C_{620} \rightarrow \Delta_{110} \), \( C_{120} \rightarrow \Delta_{110} \), \( C_{120} \rightarrow \Delta_{110} \), and these values are in the range 0.81-0.96, 0.41-0.52, 0.71-0.96, 0.68-0.67, 0.89-0.91, 0.61-0.81, 0.87-0.88 and 1.00, respectively, for different glass matrices. Among the four glass matrices (Na, K, Mg and Ca), the branching ratios are higher in calcium glass matrix for all the transitions and among the three mixed chlorophosphate glass matrices (Na-K, Na-Mg and Na-Ca), sodium-magnesium glass matrix shows higher branching ratio values. Hence, Er\(^{3+}\) doped calcium glass matrix may be useful for laser excitation among various glass matrices. Integrated absorption cross-sections also higher in calcium glass matrix among the four glass matrices (Na, K, Mg and Ca).

3.4. Emission spectra

Good laser transitions are characterized by large stimulated emission cross-sections. Judd-Ofelt theory can successfully account for the induced emission cross-sections. In the present work, stimulated emission cross-sections are calculated for the observed emission transitions of Er\(^{3+}\) and Er\(^{3+}\) in different chlorophosphate glasses using the formulae given in Ref. [10].

Fig. 4 shows the emission spectra of Pr\(^{3+}\) and Er\(^{3+}\) in different chlorophosphate glasses. From the emission spectra of Pr\(^{3+}\), it is observed that in all the glass matrices, two emission peaks are observed and these are designated as \( \Delta_{1} \rightarrow \Delta_{4} \) (\( \approx 610 \text{ nm} \)) and \( \Delta_{2} \rightarrow \Delta_{4} \) (\( \approx 640 \text{ nm} \)) transitions. It is also observed that there is not much change in the peak positions of the two emission transitions but their structural profiles varied with modifiers. The emission peak at lower wavelength side (607 nm) shows well resolved splitting in potassium and sodium-potassium glass matrix indicating structural changes. Peak wavelengths (\( \lambda_{p} \)), radiative transition probabilities (\( \sigma_{\text{rad}} \)), effective line-widths (\( \Delta \lambda_{\text{eff}} \)) and peak emission cross-sections (\( \sigma_{\text{em}} \)) of two transitions of Er\(^{3+}\) in different chlorophosphate glass matrices are presented in Table 6. It is observed that between the two emission peaks, \( \Delta_{2} \rightarrow \Delta_{4} \) transition shows higher emission cross-section. Among the four glass matrices (Na, K, Mg and Ca), magnesium glass matrix contains higher emission cross-section for both the transitions.

In the case of Er\(^{3+}\) ion, three emission peaks are observed in all the glass matrices and these are designated as \( \Delta_{1} \rightarrow \Delta_{4} \), \( \Delta_{2} \rightarrow \Delta_{4} \), and \( \Delta_{4} \rightarrow \Delta_{4} \).
Here also there is not much change in the peak positions of the emission transitions in different glass matrices. The spectral profiles of the emission peaks are nearly same for all the glass matrices indicating that the influence of structural changes is less on emission peaks. Table 7 gives peak wavelengths ($\lambda_p$), radiative transition probabilities ($A_{rad}$), effective line-widths ($\Delta \lambda_{rad}$) and peak emission cross-sections ($\sigma_p$) of three transitions of Er$^{3+}$ in different chlorophtate glass matrices. It is observed that among the three emission transitions, $^2$H$_{11/2} \rightarrow ^4$I$_{15/2}$ transition shows higher emission cross-section for all the glass matrices. Among the four glass matrices (Na, K, Mg and Ca), sodium glass matrix shows higher emission cross-section. It is also observed that when sodium is mixed with potassium, magnesium and calcium, the emission cross-sections are increased. Among the three mixed glass matrices (Na-K, Na-Mg and Na-Ca),

Table 6
Certain fluorescence properties of P$_{2+}$ ions doped in different chlorophtate glasses.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Glass</th>
<th>$\lambda_p$-Er$^{3+}$</th>
<th>$\lambda_{em}$-Er$^{3+}$</th>
<th>$\lambda_{em}$-Er$^{3+}$</th>
<th>$\lambda_{em}$-Er$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{em}$ (nm)</td>
<td>$\Delta \lambda_{em}$ (nm)</td>
<td>$\sigma_p$ (10^{-18} cm$^2$)</td>
<td>$\lambda_{em}$ (nm)</td>
</tr>
<tr>
<td>1</td>
<td>Na</td>
<td>567.0</td>
<td>608.0</td>
<td>0.112</td>
<td>627.6</td>
</tr>
<tr>
<td>2</td>
<td>K</td>
<td>606.4</td>
<td>638.8</td>
<td>0.027</td>
<td>636.4</td>
</tr>
<tr>
<td>3</td>
<td>Mg</td>
<td>606.6</td>
<td>632.0</td>
<td>0.245</td>
<td>686.6</td>
</tr>
<tr>
<td>4</td>
<td>Ca</td>
<td>606.2</td>
<td>639.7</td>
<td>0.177</td>
<td>638.6</td>
</tr>
<tr>
<td>5</td>
<td>Na-K</td>
<td>606.8</td>
<td>632.7</td>
<td>0.213</td>
<td>624.6</td>
</tr>
<tr>
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<td>Na-Mg</td>
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<td>0.226</td>
<td>636.6</td>
</tr>
<tr>
<td>7</td>
<td>Na-Ca</td>
<td>606.0</td>
<td>1469</td>
<td>0.041</td>
<td>624.6</td>
</tr>
</tbody>
</table>

Table 7
Certain fluorescence properties of Er$^{3+}$ ions doped in different chlorophtate glasses.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Glass</th>
<th>$\lambda_{em}$-Er$^{3+}$</th>
<th>$\lambda_{em}$-Er$^{3+}$</th>
<th>$\lambda_{em}$-Er$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{em}$ (nm)</td>
<td>$\Delta \lambda_{em}$ (nm)</td>
<td>$\sigma_p$ (10^{-18} cm$^2$)</td>
</tr>
<tr>
<td>1</td>
<td>Na</td>
<td>497.8</td>
<td>1967</td>
<td>0.007</td>
</tr>
<tr>
<td>2</td>
<td>K</td>
<td>496.2</td>
<td>8460</td>
<td>0.062</td>
</tr>
<tr>
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<td>Mg</td>
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<td>1757</td>
<td>0.058</td>
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<tr>
<td>4</td>
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<td>4051</td>
<td>0.163</td>
</tr>
<tr>
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<td>497.9</td>
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<td>Na-Mg</td>
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<tr>
<td>7</td>
<td>Na-Ca</td>
<td>497.8</td>
<td>2397</td>
<td>0.076</td>
</tr>
</tbody>
</table>

Fig. 5. Variation of emission cross-sections ($\sigma_p$) of the emission transitions of P$_{2+}$ and E$^{3+}$ with the variation of glass matrix.
sodium–magnesium glass matrix shows higher emission cross-sections for the three emission transitions. Fig. 5 shows the variation of emission cross-sections (εₚ) with the variation of glass matrix for both Pr³⁺ and Eu²⁺ ions.

4. Conclusions

The spectral intensities of most of the transitions of Pr³⁺ ion are higher in magnesium chlorophosphate glass among the four (Na, K, Mg and Ca) glass matrices and in sodium–magnesium glass among the three mixed (Na–K, Na–Mg and Na–Ca) phosphate glass matrices indicating higher asymmetry in these glass matrices. In the case of Eu³⁺ ion, the spectral intensities of most of the transitions are higher in calcium and sodium–magnesium chlorophosphate glass matrices indicating higher asymmetry. Judd–Ofelt intensity parameter, O₃ is higher in Pr³⁺ doped magnesium and sodium–potassium glass matrices indicating higher covalency of Pr–O bond. In the case of Eu³⁺ ion, the magnitude of O₂ parameter is higher in calcium and sodium–magnesium glass matrices indicating higher covalency of Eu–O bond in these glass matrices. From the variation of peak wavelengths of the hypersensitive transition and O₂ parameter some structural changes were observed for sodium to sodium–calcium glass matrix doped with Pr³⁺. In the case of Eu²⁺ ion, the structural changes are not influencing the covalency of Eu–O bond. Radiative lifetimes of different excited states of Pr³⁺ and Eu²⁺ doped different chlorophosphate glass matrices are reported. Radiative lifetimes are decreased when sodium is mixed with potassium and magnesium for both the ions. The branching ratio value is higher for Pr³⁺→Na transition of Pr³⁺ ion in sodium glass matrix among various glass matrices. In the case of Eu²⁺ ion, calcium glass matrix shows higher branching ratios. The peak emission cross-sections of the observed emission transitions are also higher in calcium glass matrix for both the ions.

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References

Spectroscopic properties and Judd-Ofelt analysis of Sm\textsuperscript{3+} and Dy\textsuperscript{3+} doped chlorophosphate glasses

K.Venkatarao, M.Seshadri, C.Venkateswarlu and Y.C.Ratnakaram*  
Department of physics, Sri Venkateswara University Post-Graduate Centre.  
Kavali-524201  
Email: ratnakaram yc@yahoo.co.in

Abstract: Spectroscopic properties of Sm\textsuperscript{3+} and Dy\textsuperscript{3+}(1mol\%) doped chlorophosphate glasses of the type 69P\textsubscript{2}O\textsubscript{5} 20Na\textsubscript{2}HPO\textsubscript{4} 10RCl (R=Na, K, Mg and Ca) and 69P\textsubscript{2}O\textsubscript{5} 20Na\textsubscript{2}HPO\textsubscript{4} 5NaCl 5RCl (R=K, Mg and Ca) are studied. The spectroscopic parameters such as oscillator strengths (f), Judd-Ofelt intensity parameters (\Omega\textsubscript{a}), radiative transition probabilities (A\textsubscript{r}), radiative lifetimes (\tau\textsubscript{a}), branching ratios (\beta\textsubscript{a}) and absorption cross-sections (\Sigma) have been determined and are reported. The hypersensitive nature has been discussed in the present work. The magnitudes of branching ratios (\beta\textsubscript{a}) are higher for \textsuperscript{5}F\textsubscript{9/2} \rightarrow \textsuperscript{5}H\textsubscript{11/2} transition of Sm\textsuperscript{3+} ion (except Na-Ca) and \textsuperscript{5}F\textsubscript{5/2} \rightarrow \textsuperscript{5}H\textsubscript{13/2} transition of Dy\textsuperscript{3+} ion among various transitions. From the fluorescence spectra, emission cross-sections (\sigma\textsubscript{e}) are obtained for the three transitions, \textsuperscript{5}G\textsubscript{7/2} \rightarrow \textsuperscript{5}H\textsubscript{9/2}, \textsuperscript{5}G\textsubscript{5/2} \rightarrow \textsuperscript{5}H\textsubscript{11/2} and \textsuperscript{5}G\textsubscript{5/2} \rightarrow \textsuperscript{5}H\textsubscript{13/2} of Sm\textsuperscript{3+} ion and two transitions, \textsuperscript{5}G\textsubscript{7/2} \rightarrow \textsuperscript{5}H\textsubscript{9/2} and \textsuperscript{5}F\textsubscript{5/2} \rightarrow \textsuperscript{5}H\textsubscript{13/2} of Dy\textsuperscript{3+} ion. From these studies certain transitions have been selected for laser excitation.

1. Introduction  
Glasses doped with rare earth ions are well known for fluorescent substances because of their luminescence efficiency. Glasses containing various rare earth ions are seen as promising materials for quantum devices [1]. Rare earth ions exhibit distinct optical properties due to their electronic transitions within the 4f shell, when incorporated in solid or liquid environments. Rare earths in glassy host matrices exist usually in its triply ionized state [2]. However, Sm\textsuperscript{3+} and Dy\textsuperscript{3+} containing glasses have received relatively less attention than other Ln\textsuperscript{3+} ions despite many features of interest. The Sm\textsuperscript{3+} ion is one of the most interesting ions for analyzing fluorescence properties, because of its use in high density optical storage, color displays and visible solid state lasers. The decay of excited states in Sm\textsuperscript{3+} involves different mechanisms depending on the matrix [3]. Therefore these ions can be useful in lasers, solar energy converters, etc. The hypersensitive transition, \textsuperscript{5}H\textsubscript{11/2} \rightarrow \textsuperscript{5}H\textsubscript{13/2} of Dy\textsuperscript{3+} at 1.3\mu m has potential for fibre amplifiers [4]. In this paper, the authors discussed the spectroscopic properties such as Judd-Ofelt intensity parameters (\Omega\textsubscript{a}), radiative transition probabilities (A\textsubscript{r}), radiative lifetimes (\tau\textsubscript{a}), branching ratios (\beta\textsubscript{a}) and integrated absorption cross-sections (\Sigma) and also emission.

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properties from the fluorescence spectra of all the Sm\textsuperscript{3+} and Dy\textsuperscript{3+} doped different chlorophosphate glass matrices.

2. Experimental

Glasses with the batch compositions 69P_{2}O_{5}.20Na_{2}HPO_{4}.10RCI (R= Na, K, Mg and Ca), 60P_{2}O_{5}.20Na_{2}HPO_{4}.5NaCl.5RCI (R= K, Mg and Ca) with 1mol\% of Sm\textsubscript{2}O_{3} and Dy\textsubscript{2}O_{3} were prepared using melt quenching technique. All these chemicals are reagent grade with 99.99\% purity. Appropriate amounts of weighted chemicals were mixed and thoroughly ground to homogenize the mixture. The mixture was heated in a silica crucible at 950°C in electronic furnace for about 3hrs. Then the melt was quickly quenched between two well polished brass plates. The glass samples were annealed at 330°C for 3hrs to eliminate the internal stress and slowly cooled to room temperature. Glass samples of about 1-2mm thickness were obtained. Optical absorption spectra were measured with a UV-VIS-NIR regions using JASCOV-570 spectrophotometer. Fluorescence spectra of Sm\textsuperscript{3+} and Dy\textsuperscript{3+} ions were recorded using Fluoro-Max-3 fluorescence spectrophotometer under excitation wavelengths of 400nm and 392nm respectively. Densities of the samples were measured using Archimedes principle with xylene as an immersion liquid and also the refractive indices of the samples were measured by using Abbe-refractometer.

3. Results and Discussion

3.1. Absorption spectra and spectral intensities

Optical absorption spectra of Sm\textsuperscript{3+} and Dy\textsuperscript{3+} doped sodium chlorophosphate glass matrix are shown in figures, 1(a) and 1(b) respectively. The observed bands involve excitation from the ground state, \textsuperscript{4}H\textsubscript{14}\textsuperscript{2} of Sm\textsuperscript{3+} ion and \textsuperscript{4}H\textsubscript{11}\textsuperscript{2} of Dy\textsuperscript{3+} ion. It is observed that the spectral profile of the absorption peak, \textsuperscript{4}F\textsubscript{5/2} \rightarrow \textsuperscript{4}I\textsubscript{15/2} of Sm\textsuperscript{3+} splits into three peaks clearly for all the glass matrices and \textsuperscript{4}I\textsubscript{15/2} \rightarrow \textsuperscript{4}F\textsubscript{7/2} of Dy\textsuperscript{3+} splits into two peaks clearly for all the glass matrices (except for sodium magnesia glass matrix). The shapes of the spectral profiles vary with the variation of glass matrix. It indicates some structural changes in the glass matrix. The experimental spectral intensities are obtained for the observed absorption bands of Sm\textsuperscript{3+} and Dy\textsuperscript{3+} ions and calculated spectral intensities are obtained from the Judd-Ofelt theory. It is observed that there is a good agreement between the experimental and calculated spectral intensities indicating the validity of Judd-Ofelt theory. The Judd-Ofelt intensity parameters (Ω\textsubscript{2}, Ω\textsubscript{4} and Ω\textsubscript{6}) are obtained from the least squares fit method for both the Sm\textsuperscript{3+} and Dy\textsuperscript{3+} ions and are presented in table 1. The Judd-Ofelt intensity parameters are important for investigating the local structure and bonding in the vicinity of rare earth ions. Normally Ω\textsubscript{2} parameter is related to covalent chemical bonding and Ω\textsubscript{4} and Ω\textsubscript{6} are related to the rigidity of the host matrix.

In the present work, it is observed that for Sm\textsuperscript{3+} ion, Ω\textsubscript{2} parameter is higher for calcium glass matrix among four (Na, K, Mg and Ca) glass matrices. Among the seven glass matrices studied, Ω\textsubscript{2} parameter is also higher in calcium glass matrix, which indicates higher rigidity of the medium. In the case of Dy\textsuperscript{3+} ion also, Ω\textsubscript{2} and Ω\textsubscript{4} parameters are higher for calcium glass matrix when compared to above four glass matrices indicating higher covalency and higher rigidity of the medium. \textsuperscript{4}H\textsubscript{14}\textsuperscript{2} \rightarrow \textsuperscript{4}I\textsubscript{15/2} is the hypersensitive transition for Sm\textsuperscript{3+} ion and \textsuperscript{4}H\textsubscript{11}\textsuperscript{2} \rightarrow \textsuperscript{4}F\textsubscript{7/2}, \textsuperscript{4}H\textsubscript{11}\textsuperscript{2} is hypersensitive transition for Dy\textsuperscript{3+} ion. Normally the intensity parameter Ω\textsubscript{4} (or Σ Ω\textsubscript{6}) which indicates covalency decrease/increase with the decrease/increase of intensity of hypersensitive transition. In the present work also, the Ω\textsubscript{2} parameter decreased with decrease (except for potassium glass) of intensity of the hypersensitive transition for Sm\textsuperscript{3+} ion. Among various glass matrices studied in the present work, the spectral intensity of the hypersensitive transition is more for calcium and sodium potassium glass matrices indicating higher asymmetry of the crystal field around the rare earth ions for this glass matrix. In the
case of Dy$^{3+}$ ion, the sum of the intensity parameters ($\Omega_k$) increases with the increase of spectral intensity of the hypersensitive transition. It is observed that among various glass matrices studied, calcium glass matrix has higher spectral intensity indicating higher asymmetry of the crystal field around the rare earth ion.

Using Judd-Ofelt intensity parameters, electric dipole line strengths ($S_{00}$), radiative transition probabilities ($A$), radiative lifetimes ($\tau$), and integrated absorption cross sections ($\Sigma$) of certain transitions are estimated for Sm$^{3+}$ and Dy$^{3+}$ ions doped in alkali, alkaline earth and other chlorophosphate glasses. In the case of Sm$^{3+}$ ion, the total radiative transition probabilities for the excited states $^4G_{5/2}$, $^4H_{15/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, and $^4I_{11/2}$ are estimated. It is observed that the order of magnitude of total radiative transition probabilities ($A_T$) is $^4F_{11/2}>^4F_{9/2}>^4F_{7/2}>^4F_{5/2}>^4I_{11/2}$ for all the glass matrices. Also observed that the radiative lifetimes ($\tau$) are higher for sodium calcium glass matrix and lower for calcium glass matrix among the seven chlorophosphate glasses. In the case of Dy$^{3+}$ ion, the total radiative transition probabilities for the excited states $^4I_{15/2}$, $^2F_{5/2}$, $^2F_{7/2}$, $^2F_{9/2}$ and $^2F_{11/2}$ are estimated. It is observed that the order of magnitude of total radiative transition probabilities for all the glass matrices is $^2F_{11/2}>^2F_{9/2}>^2F_{7/2}>^2F_{5/2}>^2F_{11/2}$. Also observed that the radiative lifetimes are higher for sodium magnesium glass matrix and lower for sodium glass matrix.

![Figures. 1(a) & (b) Optical absorption spectra of Sm$^{3+}$ and Dy$^{3+}$ doped sodium chlorophosphate glass.](image)

**Table 1. Judd-Ofelt intensity ($\Omega_k \times 10^2$) parameters of Sm$^{3+}$ and Dy$^{3+}$ doped alkali, alkaline earth and other chlorophosphate glasses.**

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\Omega_0$</th>
<th>$\Omega_2$</th>
<th>$\Omega_4$</th>
<th>$\Omega_6$</th>
<th>$\Omega_0$</th>
<th>$\Omega_2$</th>
<th>$\Omega_4$</th>
<th>$\Omega_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm$^{3+}$</td>
<td>0.90</td>
<td>0.36</td>
<td>0.31</td>
<td>0.28</td>
<td>1.03</td>
<td>0.59</td>
<td>0.53</td>
<td>0.52</td>
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<tr>
<td>Dy$^{3+}$</td>
<td>11.86</td>
<td>5.93</td>
<td>9.17</td>
<td>15.29</td>
<td>6.21</td>
<td>7.41</td>
<td>11.57</td>
<td>0.78</td>
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<tr>
<td>$\Omega_0$</td>
<td>13.17</td>
<td>6.70</td>
<td>6.26</td>
<td>6.49</td>
<td>3.27</td>
<td>2.78</td>
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<td>0.78</td>
</tr>
<tr>
<td>$\Omega_2$</td>
<td>2.40</td>
<td>1.64</td>
<td>1.42</td>
<td>3.23</td>
<td>1.67</td>
<td>1.24</td>
<td>1.67</td>
<td>0.78</td>
</tr>
</tbody>
</table>
From the magnitudes of branching ratios ($b_\text{B}$) of various transitions of Sm$^{3+}$ ion it is observed that the transitions, $^4\text{G}_{5/2}$-$^4\text{H}_{15/2}$, $^4\text{F}_{7/2}$-$^4\text{H}_{11/2}$, $^4\text{F}_{5/2}$-$^4\text{H}_{11/2}$, $^4\text{F}_{3/2}$-$^4\text{H}_{11/2}$ and $^4\text{F}_{1/2}$-$^4\text{H}_{11/2}$ have higher branching ratio values. Among these five transitions, the transitions, $^4\text{F}_{7/2}$-$^4\text{H}_{11/2}$ and $^4\text{G}_{5/2}$-$^4\text{H}_{11/2}$ have higher and lower values. In the case of Dy$^{3+}$ ion, among various transitions, transitions $^4\text{H}_{9/2}$-$^4\text{H}_{11/2}$, $^4\text{F}_{7/2}$-$^4\text{H}_{13/2}$, $^4\text{F}_{5/2}$-$^4\text{H}_{13/2}$ and $^4\text{F}_{3/2}$-$^4\text{H}_{13/2}$ have higher branching ratio values. It is observed that among these four transitions, $^4\text{F}_{7/2}$-$^4\text{H}_{13/2}$ has higher value and $^4\text{F}_{1/2}$-$^4\text{H}_{13/2}$ has lower value for all the glass matrices.

3.2. Fluorescence spectra

The fluorescence spectra of Sm$^{3+}$ and Dy$^{3+}$ doped sodium chlorophosphate glass recorded at room temperature in the wavelength regions 500-700 and 425-650 nm under the excitation wavelengths 400 and 392 nm respectively are shown in figures 2(a) and 2(b). Similar spectra were observed for all the glass matrices. The peak stimulated emission cross-sections ($\sigma$) were obtained using standard formulae. For Sm$^{3+}$ ion, three peaks are observed nearly at 561, 597 and 644 nm and they are due to transitions, $^4\text{G}_{5/2}$-$^4\text{H}_{15/2}$, $^4\text{G}_{5/2}$-$^4\text{H}_{11/2}$ and $^4\text{G}_{5/2}$-$^4\text{H}_{10}$ for all the glass matrices.

![Figure 2 (a) & (b) Fluorescence spectra of Sm$^{3+}$ and Dy$^{3+}$ doped sodium chlorophosphate glass.](image)

It is observed that the transition, $^4\text{G}_{5/2}$-$^4\text{H}_{15/2}$ has higher emission cross-section for calcium glass matrix, hence it may be useful for laser excitation. In the case of Dy$^{3+}$ ion, two peaks are observed nearly at 482 and 573 nm and they are due to transitions, $^4\text{F}_{7/2}$-$^4\text{H}_{15/2}$ and $^4\text{F}_{1/2}$-$^4\text{H}_{15/2}$. It is also observed that the transition $^4\text{F}_{7/2}$-$^4\text{H}_{13/2}$ has higher emission cross-section for calcium glass matrix and it may be useful for laser excitation.

4. Conclusions

For Sm$^{3+}$ ion, Judd-Ofelt intensity parameter, $\Omega_2$, is higher for calcium glass matrix among four (Na, K, Mg and Ca) glass matrices. Among the seven glass matrices, $\Omega_2$ parameter is also higher in calcium glass matrix. In the case of Dy$^{3+}$ ion also, $\Omega_2$ and $\Omega_4$ parameters are higher for calcium glass matrix. It indicates higher covalency of Sm-O and Dy-O bonds and higher rigidity of the glass matrix. From the magnitudes of total radiative transition probabilities ($A_T$) it is observed that calcium glass matrix shows higher value for both Sm$^{3+}$ and Dy$^{3+}$ doped glass matrices. The radiative lifetimes ($\tau_\text{r}$) of all the excited states of Sm$^{3+}$ ion are higher for sodium calcium glass matrix and lower for calcium glass.
matrix among different glass matrices. For Dy$^+$ ion, the radiative lifetimes are higher for sodium magnesium glass matrix and lower for sodium glass matrix. Branching ratios ($\beta_\lambda$) and integrated absorption cross-sections ($\Sigma$) of certain transitions of these two ions are also reported. The peak stimulated emission cross-sections ($\sigma_\text{em}$) of certain transitions of Sm$^{3+}$ and Dy$^{3+}$ are reported and these value are higher for calcium glass matrix for both the ions.

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**References**

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Abstracts of Presentations
Spectroscopic properties and Judd–Ofelt analysis of Sm$^{3+}$ and Dy$^{3+}$ doped chlorophosphate glasses

K. Venkata Rao, M. Seshadri, C. Venkateswarulu and Y.C. Ratnakaram
Department of Physics, Sri Venkateswara University Post-Graduate Centre, Kavali-524 201
E-mail: ratnakaram_yc@yahoo.co.in

Spectroscopic properties of Sm$^{3+}$ and Dy$^{3+}$ (1 mol%) doped chlorophosphate glasses of the type $69P_{2}O_{5}$, $20Na_{2}HPO_{4}$, $10RCI$ (R=Na, K, Mg and Ca) and $69P_{2}O_{5}$, $20Na_{2}HPO_{4}$, $5NaCl$. 5RCI (R=K, Mg and Ca) are studied. The spectroscopic parameters such as oscillator strengths ($f$), Judd–Ofelt intensity parameters ($U_{i}$), hypersensitive band positions ($\Delta$), radiative transition probabilities ($A_{r}$), radiative lifetimes ($\beta_{r}$), branching ratios ($B_{r}$) and absorption cross-sections ($\sigma$) have been determined and are reported. The spectral profile of the absorption peak $\nu_{F}^{32}$$\rightarrow$$\nu_{F}^{13}$ splits into three peaks clearly for all the glass matrices for Sm$^{3+}$ ion and $\nu_{F}^{13}$$\rightarrow$$\nu_{F}^{22}$ splits into two peaks clearly for all the glass matrices (except Na-Mg glass matrix) for Dy$^{3+}$ ion. The shapes of the spectral profiles vary with the variation of glass matrix. It indicates some structural changes in the glass matrix. The Judd–Ofelt intensity parameter $U_{i}$ is more for sodium potassium glass matrix for Sm$^{3+}$ ion and calcium glass matrix for Dy$^{3+}$ ion among various chlorophosphate glasses. It indicates higher covalency of RE-O bond in these glass matrices. $U_{i}$ parameter is less in sodium calcium glass matrix for Sm$^{3+}$ ion and for Dy$^{3+}$ ion, it is less in potassium glass matrix, indicating lower covalency. $^4H_{15/2}$$\rightarrow$$^4F_{7/2}$ and $^4H_{15/2}$$\rightarrow$$^4F_{9/2}$ are the hypersensitive transitions for Sm$^{3+}$ and Dy$^{3+}$ ions respectively. The hypersensitive nature has been discussed in the present work. The magnitude of branching ratios ($\beta_{r}$) are higher for $^4F_{7/2}$$\rightarrow$ $^4H_{15/2}$ transition of Sm$^{3+}$ ion (except Na-Ca) and $^4F_{7/2}$$\rightarrow$ $^4H_{15/2}$ transition of Dy$^{3+}$ ion among various transitions. From the fluorescence spectra, emission cross-sections ($\sigma_{e}$) are obtained for the three transitions, $^4G_{5/2}$$\rightarrow$ $^4H_{15/2}$, $^4G_{5/2}$$\rightarrow$ $^4H_{11/2}$ and $^4G_{5/2}$$\rightarrow$ $^4H_{9/2}$ of Sm$^{3+}$ ion and two transitions, $^4F_{7/2}$$\rightarrow$ $^4H_{15/2}$ and $^4F_{7/2}$$\rightarrow$ $^4H_{13/2}$ of Dy$^{3+}$ ion. From these studies certain transitions have been selected for laser excitation.
ABSTRACTS

DEPARTMENT OF PHYSICS
SRI VENKATESWARA UNIVERSITY
TIRUPATI - 517 502
Optical and luminescence properties of Pr$^{3+}$ and Er$^{3+}$ doped phosphate glasses


Department of Physics, Sri Venkateswara University, Tirupathi-517 502, A.P. India.

Abstract:

Pr$^{3+}$ and Er$^{3+}$ doped different chlorophosphate glasses of the glass compositions, 69.8P$_2$O$_5$+20Na$_2$HPO$_4$+10RCI (R=Na, K, Mg and Ca) and 69.8P$_2$O$_5$+20Na$_2$HPO$_4$+5NaCl+5RCI (R=K, Mg and Ca) were prepared by melt quenching method. Optical properties of these two rare earth ions were characterized through optical absorption and emission spectra using Judd-Ofelt theory. Judd-Ofelt intensity parameters $\Omega_4$ ($\lambda$=2, 4 and 6) were calculated for both the ions from their absorption spectra, which in turn used to derive the radiative properties such as radiative transition probabilities ($A_T$), radiative lifetimes ($\tau_r$), branching ratios ($B$) and integrated absorption cross-sections ($\Sigma$). An attempt has been made to discuss structural changes considering the hypersensitive transitions and covalency of RE-O bonds for the present glass systems. Peak emission cross-sections ($\sigma_p$) are obtained for the observed emission bands of Pr$^{3+}$ and Er$^{3+}$ ions in different chlorophosphate glasses. Variation of peak emission cross sections with the variation of glass matrix has been discussed.
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BOOK OF ABSTRACTS

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Emission Properties of Eu$^{3+}$ Doped Different Chlorophosphate Glasses

K. Venkata Rao, M. Seshadri and Y C. Ratnakaram

Sri Venkateswara University, Tirupati, A.P., INDIA

*Email: ratnakaram.yc@yahoo.co.in

Absorption and emission spectra of 0.5 mol% of Eu$^{3+}$ in different chlorophosphate glasses have been studied. Judd-Ofelt analysis was performed to evaluate the emission properties such as radiative transition probabilities ($A_{r0}$), branching ratios ($B$), radiative lifetimes ($\tau_r$) and emission cross-sections ($\sigma_{\text{em}}$) for observed emission transitions of emission spectra of these glass matrices.
Spectroscopic investigations and luminescence spectra of Nd\textsuperscript{3+} and Dy\textsuperscript{3+} doped different phosphate glasses

M. Seshadri \textsuperscript{a}, K. Venkata Rao \textsuperscript{a*}, J. Lakshmana Rao \textsuperscript{a}, K.S.R. Koteswara Rao \textsuperscript{ab}, Y.C. Ratnakaram \textsuperscript{ac, b}

\textsuperscript{a} Department of Physics, Sri Venkateswara University, Tirupati-517 502, India
\textsuperscript{b} Department of Physics, Indian Institute of Science, Bangalore-560 012, India

1. Introduction

Optical properties of trivalent lanthanides have been extensively investigated in various host matrices. This is mainly because of their potential use in lasers in the spectral region, UV to IR and in upconversion devices and so on [1,2]. A systematic change in the composition of glassy host leads to substitutional changes in local structure, covalency and hence the relaxed optical properties of doped rare-earth ions [3]. Glasses activated with rare-earth ions emitting in the NIR region are of current interest because of their potential use as laser host materials and optical amplifiers for use in telecommunication devices [4,5]. Among different rare-earth ions, Nd\textsuperscript{3+} has been recognized as one of the most efficient ions for obtaining laser action, frequency up-conversion and optical fiber amplification [6-7].

Similarly, Dy\textsuperscript{3+} doped glasses are of practical interest because its emission at 1.3 μm may be utilized for optical amplification in telecommunication and long wavelength lasers (4-10 μm) [8-9]. \textsuperscript{9}F\textsubscript{11/2} \rightarrow \textsuperscript{9}H\textsubscript{11/2} (3.2 μm) transition of Dy\textsuperscript{3+} has been identified as laser transition [10]. Dy\textsuperscript{3+} gives very strong emission in yellow region, which is expected to give lasing. Dy\textsuperscript{3+} ions give the emission transitions \textsuperscript{6}I\textsubscript{11/2} \rightarrow \textsuperscript{6}H\textsubscript{15/2} and \textsuperscript{6}I\textsubscript{15/2} \rightarrow \textsuperscript{6}H\textsubscript{11/2} in the visible and NIR regions. Within these emission transitions, \textsuperscript{6}I\textsubscript{11/2} \rightarrow \textsuperscript{6}H\textsubscript{11/2} (573 nm) in yellow and \textsuperscript{6}I\textsubscript{15/2} \rightarrow \textsuperscript{6}H\textsubscript{15/2} (481 nm) in blue regions are the predominant transitions [11,12]. Among various glass matrices, phosphate glass possess a series of interesting properties such as low glass transition temperature (T\textsubscript{g}), low melting temperature, high thermal expansion coefficient and biocompatibility [13]. Recently Chel et al. [14] reported fluorescence and non-radiative properties of Nd\textsuperscript{3+} in novel heavy metal contained fluorophosphate glasses. Seshadri et al [15] reported spectroscopic and laser properties of Sm\textsuperscript{3+} doped different phosphate glasses.

In the present work, we report the spectroscopic and laser properties of Nd\textsuperscript{3+} and Dy\textsuperscript{3+} doped different phosphate (Li, Na, K, Ca, Li-Na, Li-K and Na-K) glasses matrices. Using Judd-Oelft (16,17) theory, J-O intensity parameters (Q\textsubscript{2}, Q\textsubscript{4} and Q\textsubscript{6}) are calculated for both the ions in these glass matrices. Total radiative transition probabilities (A\textsubscript{v}) and radiative lifetimes (\texttau\textsubscript{r}) of certain excited states are estimated. Branching ratios (B\textsubscript{v}) and integrated absorption cross-sections (\Sigma) are obtained for certain transitions of both the ions in these different phosphate glass matrices. From the emission spectra, peak stimulated emission cross-sections (c\textsubscript{e}) are calculated. Our main interest in the present work is to see the variation of above spectroscopic parameters by varying different modifiers in the phosphate glass matrix and to identify the good transitions for laser excitation.
2. Experimental

Rare-earth doped different phosphate glasses were prepared using melt quenching technique with the following chemical compositions:

1. Li—(69P₂O₅+15Na₂O)+15Li₂O+1R₂O₃
2. Na—(69P₂O₅+15Na₂O)+15Na₂O+1R₂O₃
3. K—(69P₂O₅+15Na₂O)+15K₂O+1R₂O₃
4. Ca—(69P₂O₅+15Na₂O)+15CaO+1R₂O₃
5. Li—Na—(69P₂O₅+15Na₂O)+7.5Li₂O+7.5Na₂O+1R₂O₃
6. Li—K—(69P₂O₅+15Na₂O)+7.5Li₂O+7.5K₂O+1R₂O₃
7. Na—K—(69P₂O₅+15Na₂O)+7.5Na₂O+7.5K₂O+1R₂O₃

where R = Nd and Dy. The chemicals used in the above glass preparation are NH₄H₂PO₄, Na₂HPO₄, Li₂CO₃, Na₂CO₃, K₂CO₃, CaCO₃, Nd₂O₃ and Dy₂O₃. All the chemicals used in the present work are 99.9% purity. The chemicals used in the glass preparation were thoroughly mixed in an agate mortar and melted in an electric furnace in the temperature range 950-1050°C for 1 h depending on the chemical composition. The melt was then poured on to a preheated brass disc and pressed by an identical disc to get glasses of desired shapes and annealed at 400°C for two hours to remove thermal strains. The samples were polished to obtain smooth, transparent and uniform surface for optical measurement.

The densities of the glass samples were determined by the Archimedes method using xylene as the immersion liquid and they are accurate to ± 0.001 g/cm³. The refractive indices of the glasses were measured using an Abbe refractometer at sodium wavelength (589.3 nm) using 1-bromonaphthalene as an adhesive coating. These values are 1.646, 1.642, 1.640, 1.642, 1.644, 1.640 and 1.645 for Nd³⁺ and Dy³⁺ ions, respectively. Fluorescence spectra were recorded at room temperature using TRiX 550 monochromator with liquid nitrogen cooled under excitation wavelength 514.5 nm of Ar⁺ for Nd³⁺ and Fluoro-Max 3 fluorescence spectrophotometer, 348 nm being the excitation wavelength for Dy³⁺.

3. Results and discussions

3.1. Absorption spectra and Judd-Ofelt analysis

Optical absorption spectra of Nd³⁺ (in the wavelength region 325-900 nm) and Dy³⁺ (in the wavelength region 325-1800 nm) ions doped lithium phosphate glass matrix are shown in Figs. 1 and 2, respectively. The absorption spectra of the other glass matrices appear to be similar and hence they are not shown. However the spectral profile of the absorption peaks, 4F₉/₂ → 4I₁₁/₂ for Dy³⁺ nearly at 383 nm of Nd³⁺ and 4I₁₁/₂ → 4F₉/₂ for Dy³⁺ nearly at 383 nm of Dy³⁺ varies with the variation of glass matrix. The absorption profiles of these peaks of Nd³⁺ and Dy³⁺ ions in various phosphate glass matrices are shown in Figs. 3 and 4, respectively. It is observed that in the case of Nd³⁺ ion, when lithium is mixed with sodium and potassium there is no change in the spectral profile of the absorption peak. But when sodium is mixed with potassium there is some change in the shape of the spectral profile. In the case of Dy³⁺ ion, when lithium
is mixed with sodium and potassium, and sodium is mixed with potassium there is a change in the spectral profiles of the absorption peaks. It is also observed that in the case of Nd$^{3+}$ ion, the spectral profiles of the absorption peak in lithium–lithium–sodium, lithium–potassium and sodium–potassium phosphate glass matrices are similar. Similarly the spectral profiles in sodium, potassium and calcium are similar, in the case of Dy$^{3+}$ ion (Fig. 4), the spectral profiles of the absorption peak in lithium and sodium (also potassium and calcium) are similar. For lithium–sodium, lithium–potassium, sodium–potassium and calcium glass matrices, a clear splitting is observed in the absorption peak. These changes indicate some structural changes in Nd$^{3+}$ and Dy$^{3+}$ doped different phosphate glass matrices. In the present work, for Nd$^{3+}$ ion, 12 absorption peaks corresponding to the transitions from the ground state, $^4F_{0}$ and for Dy$^{3+}$ ion, 11 absorption peaks corresponding to the transitions from the ground state, $^4F_{0}$ to various excited states are observed. In the case of Dy$^{3+}$ ion, the absorption peak, $^4F_{0} \rightarrow ^4I_{15/2}$ (347 nm) is not observed in lithium–potassium and sodium–potassium phosphate glasses due to absorption edge in the near ultraviolet region.

Fig. 3. The spectral profile of the absorption peak, $^4F_{0} \rightarrow ^4I_{15/2}$ (347 nm) in different phosphate glass matrices.

The best set of Judd–Ofelt intensity parameters (Q2, Q5 and Q6) are obtained using the procedure explained in Ref. [18] and are presented in Table 1 for both the ions. These Judd–Ofelt intensity parameters depend on the host glass composition. Normally the intensity parameter Q2 indicates covalency of the metal–ligand bond and Q5 and Q6 parameters indicate rigidity of the host glass. Judd–Ofelt intensity parameters and also Judd–Ofelt intensity parameters in some other phosphate glass matrices reported in literature are presented in Table 1. In the present work it is observed that for Nd$^{3+}$ ion, Q2 parameter is lower in lithium glass and higher in potassium glass among the three glass matrices (Li, Na and K) indicating lower and higher covalencies in these glass
matrices. It is also observed that when lithium combines with sodium, the covalency decreases whereas when lithium combines with potassium covalency is in between lithium and potassium. In the case of sodium-potassium glass matrix, the covalency between Nd-O bond is lower when compared with sodium and potassium glass matrices independently. For Dy^{3+} ion, $Q_2$ parameter is lower in sodium glass matrix and higher in lithium glass matrix indicating lower and higher covalencies of Dy-O bond in these glass matrices. The $Q_2$ parameter is higher in potassium glass matrix and lower in lithium glass matrix among the three glass matrices (Li, Na and K) for Nd^{3+} ion. For Dy^{3+} ion, $Q_0$ parameter is higher in lithium glass matrix and lower in sodium glass matrix indicating higher and lower rigidities of these glass matrices.

From the table it is observed that $Q_2$ parameter values are higher for Nd^{3+} and Dy^{3+} ions in these phosphate glass matrices when compared with other phosphate glass matrices reported in literature. The order of magnitude of Judd–Olfelt intensity parameters is $Q_2 < Q_0 < Q_3$ for all the Nd^{3+} doped glass matrices except for potassium glass matrix. In the case of Dy^{3+} ion, the
The covalency of rare-earth ions is very sensitive to the wavelength of the hypersensitive transition. The position and intensity of certain electric dipole transitions of rare-earth ions are very sensitive to the environment of the rare-earth ions and they obey the selection rules $|\Delta I| \leq 2$, $|\Delta m| \leq 2$ and $|\Delta S| = 0$. Such transitions are called as hypersensitive transitions (\cite{10}). Hypersensitivity of a transition has been shown to be proportional to the nephelauxetic ratio $\beta$ which indicates the degree of covalency of Dy-O bond.\cite{11}

### 2.2. Hypersensitive transitions

The position and intensity of certain electric dipole transitions of rare-earth ions are very sensitive to the environment of the rare-earth ions and they obey the selection rules $|\Delta I| \leq 2$, $|\Delta m| \leq 2$ and $|\Delta S| = 0$. Such transitions are called as hypersensitive transitions\cite{10}. Hypersensitivity of a transition has been shown to be proportional to the nephelauxetic ratio $\beta$ which indicates the degree of covalency of Dy-O bond.\cite{11}

### 3.3. Radiative properties

Electric dipole line strengths ($S_{\text{dp}}$), radiative transition probabilities ($A_{\text{rad}}$), radiative lifetimes ($\tau_{\text{rad}}$), branching ratios ($\alpha$), and integrated absorption cross-sections ($\Sigma$) are estimated for all the glass matrices. Important absorption cross-sections are presented in Table 2. It is observed that for Nd$^{3+}$ ion, radiative lifetimes of all the excited states are slightly increased when lithium is mixed with sodium and decreased when lithium is mixed with potassium in this glass matrix. When sodium is mixed with potassium, the radiative lifetimes are increased for all the excited states. In the case of Dy$^{3+}$ ion, radiative lifetimes of all the excited states are increased when lithium is mixed with sodium and potassium in this glass matrix. It is also observed that when sodium is mixed with potassium there is an increase in lifetimes of all the excited states.

### Table 1

<table>
<thead>
<tr>
<th>Glass</th>
<th>$Q_1$</th>
<th>$Q_2$</th>
<th>$Q_3$</th>
<th>$Q_4$</th>
</tr>
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<tbody>
<tr>
<td>Li-Na</td>
<td>1.11</td>
<td>0.20</td>
<td>0.80</td>
<td>0.90</td>
</tr>
<tr>
<td>Li-K</td>
<td>1.20</td>
<td>0.40</td>
<td>0.50</td>
<td>0.60</td>
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<tr>
<td>Li-Al</td>
<td>1.30</td>
<td>0.50</td>
<td>0.40</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Table 2: Radiative lifetimes ($\tau_{\text{rad}}$) of certain excited states of Nd$^{3+}$ and Dy$^{3+}$ ion.

### Table 3

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\tau_{\text{rad}}$ (ns)</th>
<th>$\alpha$</th>
<th>$A_{\text{rad}}$ (s$^{-1}$)</th>
<th>$\Sigma$ (eV$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Na</td>
<td>1.11</td>
<td>0.20</td>
<td>0.80</td>
<td>0.90</td>
</tr>
<tr>
<td>Li-K</td>
<td>1.20</td>
<td>0.40</td>
<td>0.50</td>
<td>0.60</td>
</tr>
<tr>
<td>Li-Al</td>
<td>1.30</td>
<td>0.50</td>
<td>0.40</td>
<td>0.30</td>
</tr>
</tbody>
</table>

two transitions are observed in the emission spectra. From the absorption spectra it is observed that the magnitude of branching ratios ($\beta_R$) and integrated absorption cross-sections ($\Sigma$) of the transition, $^4S_{3/2} \rightarrow ^4P_{3/2}$ ($\beta_R$ is in the range 0.773-0.803) of Nd$^{3+}$ and the transition, $^4P_{3/2} (^4P_{1/2}) \rightarrow ^4I_{15/2}$ ($\beta_R$ is in the range 0.923-0.937) of Dy$^{3+}$ have higher values. Among four (Li, Na, K and Ca) phosphate glass matrices, lithium glass matrix and among the three (Li-Na, Li-K and Na-K) mixed alkali phosphate glass matrices, sodium-potassium glass matrix shows higher branching ratios. For Dy$^{3+}$ ion, the $\beta_R$ values are nearly same for different glass matrices.

3.4. Emission properties

Good laser transitions are characterized by large stimulated emission cross-sections. Judd-Olfet theory can successfully account for the induced emission cross-section. The peak stimulated emission cross-section, $\sigma_{em}$ is given by Fuchtbauer-Landenburg method [21]:

$$\sigma_{em} = \frac{n^2}{8\pi c \Delta \lambda_{eff}} A (\lambda, B')$$

where $\lambda_p$ is the peak wavelength of the emission peak, $c$ is the speed of light, $n$ is the refractive index, $A (\lambda, B')$ is the radiative transition probability and $\Delta \lambda_{eff}$ is an effective line width. Since the emission band has asymmetry, the area under each emission peak is used instead of full-width at half-maximum in the calculations. The effective line width is defined as

$$\Delta \lambda_{eff} = \frac{\int \lambda^2 I(\lambda)d\lambda}{\int I(\lambda)d\lambda}$$

$I_{max}$ is the maximum intensity at fluorescence emission peaks.

The photoluminescence spectra of Nd$^{3+}$ and Dy$^{3+}$ doped different phosphate glass matrices recorded at room temperature in the wavelength regions 800-1500 nm (under excitation wavelength, 514.5 nm of Ar$^+$ laser) and 400-650 nm (under excitation wavelength, 348 nm of xenon lamp) are shown in Fig. 5. In the case of Nd$^{3+}$ ion, three emission bands are observed at 900, 1070 and 1340 nm under excitation wavelength 348 nm of xenon lamp shown in Fig. 5. The spectral profiles of the three emission transitions are same for the seven glass matrices, but the emission intensities change from one glass matrix to another glass matrix. Table 4 gives peak wavelengths, radiative transition probabilities ($A_{em}$), effective linewidths ($\Delta \lambda_{eff}$) and emission cross-sections ($\sigma_{em}$) of the above three transitions. For Nd$^{3+}$ ion, the emission band, $^4F_{9/2} \rightarrow ^4I_{15/2}$ nearly at 1070 nm has been considered as potential...
The large stimulated emission cross-sections are attractive utilized to obtain lasing weight observed transition. Hence phosphate glass emission peaks, 481 and 573 nm, phosphate glasses observed mixed region and the table it is observed that among the four glass matrices ‘F9n-+%13p’ ‘Fon-+%l~p (UP) matrix.

In the case of Dy3+ ion, two emission peaks, 481 and 573 nm, are observed nearly at 481 and 573 nm, respectively. In the present work, the shapes of the spectral peaks are same and there is no splitting in the two emission peaks. The peak emission intensities in these alkali, mixed alkalii and calcium phosphate glasses are compared. It is observed that the emission intensity is higher for potassium phosphate glass matrix and lower for sodium–phosphorous glass matrix. The evaluated peak stimulated emission cross-sections (σp) for the two transitions are presented in Table 4. From the table it is observed that among the four glass matrices (Li, Na, K and Ca), lithium glass shows higher stimulated emission cross-sections for the two transitions. It is also observed that 4F9/2–4I15/2 (573 nm) transition is strong intense band and shows higher emission cross-section. Hence it is concluded that 4F9/2–4I15/2 transition of Dy3+ in lithium phosphate glass matrix may be useful for laser excitation.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Parameter</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>4F9/2–4I15/2 (µm)</td>
<td>666.5</td>
<td>666.9</td>
<td>667.9</td>
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</tr>
<tr>
<td>4F9/2–4I15/2 (εp)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>σp (10^(-20) cm^2)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusions

In summary, it is concluded that we have synthesized different phosphate glasses doped with Nd3+ and Dy3+ ions for their optical characterization. The absorption and emission spectra were recorded at room temperature. The absorption profiles of certain bands of Nd3+ and Dy3+ ions in various phosphate glass matrices were changed, which indicates some structural changes. From the magnitude of Judd–Ofelt intensity parameters, it is concluded that Q2 parameter is lower for Nd3+ ion and higher for Dy3+ ion in lithium glass matrix indicating lower and higher couplings of Nd3+ and Dy3+ ions in this glass matrix. From the spectral intensities of the hypersensitive transitions, it is concluded that nonsymmetrical component of the electric field acting on Nd3+ is higher in potassium glass. For Dy3+ ion, nonsymmetrical component of the electric field is higher in lithium glass. For Dy3+ ion, the variation of Q2 parameter and the position of the peak wavelength of the hypersensitive transition, structural changes were observed for Na-K to Ca phosphate glass matrix. The estimated radiative lifetimes are reported for the excited states, C4pq, C3pq, C2pq, C1pq, C0pq and for 4F9/2 of Nd3+ and 4F9/2 of Dy3+ ions in different glass matrices. It is observed that when sodium is mixed with potassium there is an increase in lifetimes of all the excited states for both Nd3+ and Dy3+ ions. The magnitudes of branching ratios (εp) are higher for the transition, C4pq–C1pq of Nd3+ and C4pq–C1pq of Dy3+ in all the glass matrices. The integrated absorption cross-sections (σp) for the two above two transitions of Nd3+ and Dy3+ ions are also higher in all the glass matrices. From the magnitude of emission cross-sections (σp) it is concluded that 4F9/2–4I15/2 transition of Nd3+ in potassium glass is useful for laser excitation among different glass phosphate matrices studied. Similarly, the transition 4F9/2–4I15/2 of Dy3+ in lithium phosphate glass matrix is useful for laser excitation.

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References

Optical spectra and Judd-Ofelt analysis of Pr$^{3+}$ and Er$^{3+}$ in different phosphate glasses

M. Seshadri, K. Venkata Rao, G.N. Hemantha Kumar and Y.C. Ratnakaram

Department of Physics, Sri Venkateswara University Post-Graduate Centre, Kavali-524 201
Email: ratnakaram.yc@yahoo.co.in

Abstract: Optical absorption and emission spectra of Pr$^{3+}$ and Er$^{3+}$ ions in different (Li, Na, K, Ca, LiNa, LiK and NaK) phosphate glasses are presented. Judd-Ofelt analysis has been carried out for the absorption spectra and studied variation of Judd-Ofelt intensity parameters ($Q_2$, $Q_4$, $Q_6$) with the variation of glass matrix. From the variation of peak wavelengths of the hypersensitive transition and $Q_2$ parameter structural details are obtained for both Pr$^{3+}$ and Er$^{3+}$ ions in these glass matrices. Radiative transition rates ($A_{r}$), radiative lifetimes ($\tau$), branching ratios ($\beta$) and integrated absorption cross-sections ($\sigma$) for certain excited states of Pr$^{3+}$ and Er$^{3+}$ ions are obtained. The stimulated emission cross-sections ($\sigma$) have been determined from the line shape of the emission spectra of Pr$^{3+}$ and Er$^{3+}$ in these phosphate glass matrices.

1. Introduction
Phosphate glasses are the potentially important host materials for developing the rare earth doped optical devices. Optical properties of phosphate glasses show many favorable features for their use in optical devices because of their excellent transparency and good mechanical and thermal stability. They act as good hosts for large concentrations of dopant rare earth ions with good homogeneity. The phosphate glasses are transparent from UV-visible to infrared spectra region [1] and are having excellent physical properties. Due to the numerous transitions, Pr$^{3+}$ ion is an ideal ion for the comparison of the contributions from the different relaxation processes such as cross-relaxation and multiphonon relaxation. These effects strongly affect the fluorescence quantum efficiency and therefore the optical applications of the investigated system. Pr$^{3+}$ systems are very interesting as short wavelength conversion laser materials [2]. Er$^{3+}$ ion is the special attention due to its emission band at 1.53 $\mu$m which makes it ideal element for fiber optics and optical fibers for telecommunications [3].

In the present work, the authors have analyzed different phosphate glasses containing 0.2 mol% of Pr$^{3+}$ and Er$^{3+}$ ions. The Judd-Ofelt approximation has been applied to the observed spectra to explain the optical properties such as radiative transition probabilities ($A_{r}$), radiative lifetimes ($\tau$), branching ratios ($\beta$) and integrated absorption cross-sections ($\sigma$). The emission spectra is recorded in the visible region for both Pr$^{3+}$ and Er$^{3+}$ ions under the excitation wavelengths, 445nm and 315nm respectively and the emission properties for all the glass matrices are studied.
2. Experimental

Glass compositions 69.8P2O5.15Na2O.15M2O (M = Li, Na, K and Ca), 69.8P2O5.15Na2O.
7.5Li2O.7.5M2O (M=Na and K) and 69.8P2O5.15Na2O.7.5NaO.7.5K2O with 0.2 mol% of Pr3+ and
Er3+ ions were selected for glass preparation. All these raw materials were made into fine powder in
Agate mortar and thoroughly ground. The homogeneously mixed chemicals were then heated in an
electric furnace at about 950 -1000°C for 1 hour in the silica crucible to obtain glass melt. The melt
was quenched between two well polished brass plates. The samples were annealed at 300°C for 2
hours to remove thermal strains. The samples were polished before measuring their optical properties.

The thicknesses of the glass samples studied in the work are in the range 0.146-0.179 cm. The densities of
these glass samples were measured using Archimedes principle with xylene as the
immersion liquid. The density values for different phosphate glass matrices doped
with 0.2 mol% of Pr3+ and
Er3+ were recorded using an Abbe refractometer and these values are in
the range 1.640-1.644 for different glass matrices. The absorption spectra were recorded at room
temperature using JASCO UV-VIS-NIR (Model V-570) spectrophotometer. Luminescence spectra
were recorded using Fluor Max-3 photoluminescence spectrophotometer under excitation
wavelengths, 445 and 315nm for Pr3+ and Er3+ respectively.

3. Results and Discussion

Figures 1(a) and 1(b) give the optical absorption spectra of Pr3+ and Er3+ doped lithium phosphate
glass matrix recorded at room temperature respectively. Optical absorption spectra consists of the
transitions from the ground state, 2H to various excited states of Pr3+ ion and 4I15/2 to various excited
states of Er3+ ion. It is observed that the spectral profiles of various absorption peaks of Pr3+ and
Er3+ are nearly same for different glass matrices studied in the present work. The spectral intensities
and line widths vary from one glass matrix to another glass matrix. The Judd-Ofelt theory [4, 5] has
been applied for analyzing the various spectroscopic properties. The experimental spectral intensities
are obtained from the observed spectra and calculated spectral intensities are obtained from the Judd-
Ofelt theory. The Judd-Ofelt intensity parameters (Ω1, Ω2 and Ω3) are obtained from the least squares
fit analysis and are presented in Table 1. These parameters depend on host glass matrix. Particularly,
Ω1 parameter is more sensitive to local structure and glass composition. Its magnitude indicates
strength of covalent bonding and Ω1, Ω2 parameters indicate rigidity of the medium.

It is observed that in the case of Pr3+ ion, the Ω2 parameter is lower for lithium glass matrix and higher
for sodium glass matrix among the four (Li, Na, K and Ca) glasses matrices indicating lower and higher
covalencies of these glass matrices. Ω4 parameter is lower for lithium glass matrix and higher
for potassium glass matrix among the above four glass matrices indicating lower and higher rigidities
of the glass matrix. In the case of Er3+ ion, the three Judd-Ofelt intensity parameters are nearly equal
for lithium and sodium phosphate glass matrices. It is observed that Ω2 parameter is lower for calcium
glass and higher for potassium glass matrix indicating lower and higher covalencies. Ω4 parameter also
lower for calcium glass matrix and higher for potassium glass matrix indicating lower and higher rigidities of the glass matrices.

The spectral intensities of certain transitions are very sensitive to the environment and these
transitions are called as hypersensitive transitions. 2H→2F7/2 and 4I15/2→4168, 4I15/2→2H15/2 are
the hypersensitive transitions for Pr3+ and Er3+ ions respectively. The shift of the peak wavelength of
the hypersensitive transition towards longer wavelength indicates increase in the degree of covalency
of RE-O bond. In the present work the peak wavelengths of the hypersensitive transition of Pr3+ ion are
1950.7, 1951.9, 1950.6, 1948.3, 1948.4, 1947.2 and 1953.4nm for Li, Na, K, Ca, LiNa, LiK and NaK
phosphate glass matrices respectively. From the variation of Ω2 parameter and shift in the peak
wavelength of the hypersensitive transition with the variation of host matrix it is observed that the
influence of structural changes is more for calcium to lithium sodium glass matrix on covalency of Pr-O bond.
For Er³⁺ ion, the peak wavelengths of the hypersensitive transitions, \( ^4 \text{I}_{150} \rightarrow ^4 \text{G}_{115} \) and \( ^4 \text{I}_{150} \rightarrow ^2 \text{H}_{112} \) are 376.6, 377.3, 376.5, 377, 376.3, and 376.3 nm for Li Na, K, Ca, LiNa, LiK and NaK glass matrices respectively. From the variation of \( Q_3 \) parameter and shift in the peak wavelength of the hypersensitive transition with host matrix it is observed that the influence of structural changes is more on potassium to calcium and calcium to lithium sodium glass matrices.

\[ \begin{align*}
Q_1 & : 1.39 \pm 0.14 \\
Q_2 & : 14.83 \pm 1.40 \\
Q_3 & : 12.62 \pm 0.85 \\
Q_4 & : 0.63 \pm 0.82
\end{align*} \]

Table 1. Judd-Ofelt intensity parameters \((Q_i \times 10^2)\) of Pr³⁺ and Er³⁺ doped phosphate glass matrices.

<table>
<thead>
<tr>
<th>( Q_i )</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>LiIna</th>
<th>LiK</th>
<th>NaK</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_1 )</td>
<td>1.39±0.14</td>
<td>3.49±0.28</td>
<td>3.27±0.49</td>
<td>0.56±0.34</td>
<td>0.43±0.63</td>
<td>1.31±0.66</td>
<td>2.45±0.60</td>
</tr>
<tr>
<td>( Q_2 )</td>
<td>14.83±1.40</td>
<td>30.96±1.55</td>
<td>34.78±1.86</td>
<td>22.58±1.90</td>
<td>27.62±2.02</td>
<td>16.14±1.95</td>
<td>11.66±1.72</td>
</tr>
<tr>
<td>( Q_3 )</td>
<td>9.68±0.91</td>
<td>26.62±0.85</td>
<td>27.84±0.64</td>
<td>17.25±0.49</td>
<td>31.93±0.51</td>
<td>12.07±0.74</td>
<td>7.15±0.66</td>
</tr>
</tbody>
</table>

The radiative properties such as radiative transition probabilities (A), radiative lifetimes (\( \tau _r \)), branching ratios (\( B_i \)) and integrated absorption cross-sections (\( \Sigma \)) are studied for both Pr³⁺ and Er³⁺ ions in all the glass matrices. For Pr³⁺ ion, the radiative lifetimes (\( \tau _r \)) are estimated for the excited states, \( ^{4} \text{P}_1, ^{4} \text{P}_0, ^{4} \text{D}_3 \) and \( ^{4} \text{F}_5 \). These values are presented in Table 2. The order of magnitude of radiative lifetimes is \( ^{4} \text{F}_5 > ^{4} \text{D}_3 > ^{4} \text{P}_0 > ^{4} \text{P}_1 \) for all the glass matrices. Among the seven glass systems studied in the present work, calcium glass matrix shows higher radiative lifetimes. In the case of Er³⁺ ion, the radiative lifetimes are estimated for the excited states \( ^{4} \text{I}_{150}, ^{4} \text{S}_{25}, ^{4} \text{P}_{22}, ^{4} \text{H}_{112}, ^{4} \text{D}_{22}, ^{4} \text{F}_{02}, ^{4} \text{D}_{12}, ^{4} \text{S}_{12} \) and \( ^{4} \text{I}_{122} \) and these values are also presented in Table 2. The order of magnitude of radiative lifetimes (except for Na and NaK glass matrices) is \( ^{4} \text{I}_{150} > ^{4} \text{S}_{25} > ^{4} \text{P}_{22} > ^{4} \text{H}_{112} > ^{4} \text{D}_{22} > ^{4} \text{F}_{02} > ^{4} \text{D}_{12} > ^{4} \text{S}_{12} > ^{4} \text{I}_{122} \). Among various glass matrices, for Er³⁺ ion also calcium glass matrix indicates higher radiative lifetimes for all the excited states. Table 3 gives radiative transition probabilities (A), branching ratios (\( B_i \)) and integrated absorption cross-sections (\( \Sigma \)) for certain transitions of Pr³⁺ and Er³⁺ ions in all the glass matrices. From the magnitude of branching ratios (\( B_i \)) and integrated absorption cross-sections (\( \Sigma \)), it

Figure 1(a) & 1(b): Absorption spectra of Pr³⁺ and Er³⁺ doped lithium phosphate glass matrix

Table 2. Radiative properties of Pr³⁺ and Er³⁺ ions in different host matrices.
is observed that the branching ratio of the transition, $^5_{D_2} \rightarrow ^7_{H_4}$ in lithium potassium glass matrix is higher. Hence this transition may be useful for laser excitation. In the case of Er$^{3+}$ ion, the branching ratio values are higher for the transitions, $^4_{I_{15/2}} \rightarrow ^4_{I_{13/2}}$, $^4_{I_{11/2}} \rightarrow ^4_{I_{13/2}}$, $^4_{I_{11/2}} \rightarrow ^4_{I_{13/2}}$, and $^4_{I_{11/2}} \rightarrow ^4_{I_{13/2}}$. Among these four transitions, the transition, $^4_{I_{11/2}} \rightarrow ^4_{I_{13/2}}$ has higher branching ratio value and this transition may be useful for laser excitation.

Table 2. Radiative lifetimes ($\tau_R$) (\mu s) of certain excited states of Pr$^{3+}$ and Er$^{3+}$ doped different phosphate glass matrices.

<table>
<thead>
<tr>
<th>Excited States</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>LiNa</th>
<th>LiK</th>
<th>NaK</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$^{3+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3_{P_1}$</td>
<td>10.7</td>
<td>4.9</td>
<td>4.4</td>
<td>7.1</td>
<td>4.2</td>
<td>9.7</td>
<td>12.8</td>
</tr>
<tr>
<td>$^3_{P_0}$</td>
<td>10.1</td>
<td>4.7</td>
<td>4.2</td>
<td>6.8</td>
<td>4.0</td>
<td>9.2</td>
<td>12.2</td>
</tr>
<tr>
<td>$^1_{D_2}$</td>
<td>64.1</td>
<td>70.7</td>
<td>66.5</td>
<td>111.0</td>
<td>65.2</td>
<td>146.4</td>
<td>186.6</td>
</tr>
<tr>
<td>$^3_{F_2}$</td>
<td>595.8</td>
<td>246.5</td>
<td>232.1</td>
<td>371.7</td>
<td>212.1</td>
<td>529.5</td>
<td>751.5</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4_{I_{15/2}}$</td>
<td>83.4</td>
<td>84.1</td>
<td>21.7</td>
<td>67.2</td>
<td>74.7</td>
<td>138.2</td>
<td>167.4</td>
</tr>
<tr>
<td>$^4_{I_{13/2}}$</td>
<td>653.4</td>
<td>660.5</td>
<td>195.6</td>
<td>561.5</td>
<td>664.1</td>
<td>1068.4</td>
<td>1456.9</td>
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<td>$^4_{I_{11/2}}$</td>
<td>442.7</td>
<td>231.5</td>
<td>128.6</td>
<td>363.8</td>
<td>425.3</td>
<td>403.1</td>
<td>906.7</td>
</tr>
<tr>
<td>$^4_{I_{9/2}}$</td>
<td>231.2</td>
<td>444.6</td>
<td>50.4</td>
<td>168.3</td>
<td>173.7</td>
<td>734.1</td>
<td>390.7</td>
</tr>
<tr>
<td>$^4_{I_{7/2}}$</td>
<td>1043.5</td>
<td>1064.1</td>
<td>335.1</td>
<td>995.0</td>
<td>1187.9</td>
<td>1695.9</td>
<td>2809.8</td>
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<tr>
<td>$^4_{I_{5/2}}$</td>
<td>1026.6</td>
<td>1030.9</td>
<td>282.0</td>
<td>787.5</td>
<td>912.1</td>
<td>1749.8</td>
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<tr>
<td>$^4_{I_{3/2}}$</td>
<td>8264.5</td>
<td>8271.3</td>
<td>2220.3</td>
<td>6097.6</td>
<td>7067.1</td>
<td>14144.0</td>
<td>14164.0</td>
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<td>$^4_{I_{1/2}}$</td>
<td>10549.0</td>
<td>10661.0</td>
<td>3006.6</td>
<td>9328.4</td>
<td>10638.0</td>
<td>17007.0</td>
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<td>$^4_{I_{1/2}}$</td>
<td>16026.0</td>
<td>16611.0</td>
<td>5000.0</td>
<td>14749.0</td>
<td>7242.0</td>
<td>26385.0</td>
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Table 3. The radiative transition probabilities (A) (s$^{-1}$), branching ratios ($\beta$) and integrated absorption cross sections ($\Sigma$) (cm$^2$) of certain transitions of Pr$^{3+}$ and Er$^{3+}$ doped different phosphate glass matrices.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Parameter</th>
<th>Li</th>
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<tr>
<td>Pr$^{3+}$</td>
<td>$^3_{P_1} \rightarrow ^7_{H_4}$</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>A</td>
<td>1393</td>
<td>3424</td>
<td>3632</td>
<td>2289</td>
<td>4047</td>
<td>1592</td>
<td>1074</td>
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</tr>
<tr>
<td>$\beta$</td>
<td>0.83</td>
<td>0.84</td>
<td>0.84</td>
<td>0.85</td>
<td>0.85</td>
<td>0.84</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>16.03</td>
<td>39.48</td>
<td>42.19</td>
<td>26.53</td>
<td>47.04</td>
<td>18.68</td>
<td>12.31</td>
<td></td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>$^4_{I_{15/2}} \rightarrow ^4_{I_{13/2}}$</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>4129</td>
<td>4123</td>
<td>19016</td>
<td>5678</td>
<td>5511</td>
<td>2367</td>
<td>2448</td>
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</tr>
<tr>
<td>$\beta$</td>
<td>0.95</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
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<tr>
<td>$\Sigma$</td>
<td>5.47</td>
<td>5.47</td>
<td>25.30</td>
<td>7.51</td>
<td>7.31</td>
<td>3.14</td>
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<tr>
<td>$^4_{F_2} \rightarrow ^4_{I_{15/2}}$</td>
<td>A</td>
<td>884</td>
<td>881</td>
<td>3217</td>
<td>1159</td>
<td>998</td>
<td>518</td>
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<td>$\beta$</td>
<td>0.91</td>
<td>0.91</td>
<td>0.91</td>
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<td>0.91</td>
<td>0.91</td>
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<tr>
<td>$\Sigma$</td>
<td>1.81</td>
<td>1.84</td>
<td>6.70</td>
<td>2.41</td>
<td>2.80</td>
<td>1.08</td>
<td>1.01</td>
<td></td>
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<tr>
<td>$^4_{I_{1/2}} \rightarrow ^4_{I_{15/2}}$</td>
<td>A</td>
<td>83.00</td>
<td>82.00</td>
<td>292.00</td>
<td>93.00</td>
<td>82.00</td>
<td>51.00</td>
<td>35.00</td>
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<tr>
<td>$\beta$</td>
<td>0.88</td>
<td>0.87</td>
<td>0.88</td>
<td>0.87</td>
<td>0.88</td>
<td>0.88</td>
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</tr>
<tr>
<td>$\Sigma$</td>
<td>0.39</td>
<td>0.39</td>
<td>1.37</td>
<td>0.44</td>
<td>0.39</td>
<td>0.24</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>$^4_{I_{3/2}} \rightarrow ^4_{I_{15/2}}$</td>
<td>A</td>
<td>62</td>
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<td>200</td>
<td>67</td>
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<td>37</td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
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<td>1.00</td>
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</tr>
<tr>
<td>$\Sigma$</td>
<td>0.71</td>
<td>0.70</td>
<td>2.33</td>
<td>0.79</td>
<td>0.67</td>
<td>0.44</td>
<td>0.29</td>
<td></td>
</tr>
</tbody>
</table>
The photoluminescence spectra of Pr$^{3+}$ and Er$^{3+}$ doped lithium phosphate glass matrices recorded at room temperature in the wavelength regions 450-700 and 450-600 nm under the excitation wavelengths of 445 and 315 nm respectively are shown in figs. 2(a) and 2(b). In case of Pr$^{3+}$ ion, five emission peaks due to transitions, $^2P_0 \rightarrow ^4H_{15}$, $^2P_0 \rightarrow ^4H_{11}$, $^1D_2 \rightarrow ^4H_{15}$, $^3P_0 \rightarrow ^4H_{14}$ and $^3P_0 \rightarrow ^4F_2$ were observed for all the glass matrices. In the case of Er$^{3+}$ ion, three emission peaks due to transitions, $^4F_{5/2} \rightarrow ^4I_{15/2}$, $^4F_{5/2} \rightarrow ^4I_{11/2}$ and $^5S_{4} \rightarrow ^4I_{15/2}$ were observed. The peak stimulated emission cross-sections ($\sigma$) are obtained using standard formulae. It is observed that for Pr$^{3+}$ ion, $^3P_0 \rightarrow ^3H_4$ transition has higher emission cross-section for potassium and lithium potassium glass matrices and they may be useful for laser excitation. In the case of Er$^{3+}$ ion also, $^4F_{5/2} \rightarrow ^4I_{15/2}$ has higher emission cross-section for potassium and lithium potassium glass matrices and hence these glass matrices may be useful for laser excitation.

Figure 2 (a) & 2(b): Photoluminescence spectra of Pr$^{3+}$ and Er$^{3+}$ doped lithium phosphate glasses.

4. Conclusions
Judd-Ofelt intensity parameters have been calculated for Pr$^{3+}$ and Er$^{3+}$ ions. From the variation of $\Omega_2$ parameter and shift in the peak wavelength of the hypersensitive transitions with the variation of host matrix, it is observed that the influence of structural changes is more on the covalency of Pr-O and Er-O bonds at calcium to lithium sodium glass matrix. The radiative lifetimes ($\tau_r$) of all the excited states of Pr$^{3+}$ and Er$^{3+}$ are higher for calcium glass matrix. Branching ratios ($\beta_b$) and integrated absorption cross-sections ($\Sigma$) of certain transitions of these two ions are also reported. The peak stimulated emission cross-sections ($\sigma_{sp}$) of certain transitions of Pr$^{3+}$ and Er$^{3+}$ are also calculated and these values are higher for potassium and lithium potassium glass matrices for both the ions.

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References
Investigation of spectroscopic properties (absorption and emission) of Ho³⁺ doped alkali, mixed alkali and calcium phosphate glasses


A. Department of Physics, JVP University, Tirupati 527 502, AP, India
B. Department of Physics, RVR & IDA Engineering College, Ongole, AP, India
C. Department of Physics, JVP University, Tirupati 527 502, AP, India

Abstract
Optical absorption and emission spectra of Ho³⁺ doped alkali, mixed alkali and calcium phosphate glasses of the type (99.5Na₂O·0.5PO₄)·(99.5Na₂O·0.5HOPO₃)·(5X·Na₂O·5X·HOPO₃)·(X=U, Na and K) 69.5Na₂O·49.5PO₄·2Na₃PO₄·2SiO₂·(99.5Na₂O·0.5PO₄)·(99.5Na₂O·0.5HOPO₃)·(5X·Na₂O·5X·HOPO₃)·(X=U, Na and K) have been studied. The variation of Judd-Olfelt intensity parameters (μ2), peak wavelengths of the hyperfine transitions (μ2), relative transition probabilities (μ2) and peak emission cross-sections (μ2) with the variation of alkali, mixed alkali and calcium in the phosphate glass matrix has been studied. The peak in the wavelength of the hyperfine transition and Judd-Olfelt intensity parameter (μ2) do not change with the structural changes in the host matrix. Radiative lifetimes (τ) are estimated for certain excited states of Ho³⁺ in these glass matrices. From the luminescence spectra, the emission cross-sections (μ2) are evaluated for the two emission transitions of Ho³⁺ ion. Variation of luminescence intensity with the two transitions, absorption and emission cross-sections with the variation of alkali, mixed alkali and calcium in the above phosphate glass systems has been studied.

Keywords: Phosphate glass, Absorption, Emission, Intensity parameters, Radiative lifetime, Cross-section

1. Introduction
Recently, there is an increased interest in the investigation of up-conversion process in rare earth doped materials. The most efficient up-converters must contain host materials that present low non-radiative losses so that luminescence could be enhanced. Recently, the up-conversion of infrared light to visible light by rare earth ions doped glasses and ceramics has been investigated due to the possibility of infrared pumped visible lasers and the potential applications in areas such as optical data storage, lasers, sensors and optical displays. Glass materials are attractive hosts because planar wave-guides and optical fibers can be fabricated easily compared to crystalline materials. Absorption and luminescence properties of lanthanide ions in glasses strongly depend on the glass composition. The longer fluorescence lifetime and a broader absorption band are the critical properties of laser materials, which are determined through spectroscopic investigations. Extensive studies have been carried out on rare earth ion doped oxide glasses with various physical properties. Phosphate, borate, silicate and germanate are well known glass forming components [6, 6]. Phosphate glass systems are technologically interesting amorphous materials due to their low glass transition temperatures and high thermal expansion coefficients [8, 7]. The number and location of cation sites in phosphate glasses have been well studied. The thermal analysis of above metaphosphate lithium/natrium glasses series with cation to phosphorus ratio around 1.3 reveals a nonlinear variation in the glass transition temperatures as a function of lithium/tin ratio [8, 10]. Ho³⁺ ions can produce laser emission in the 2.0 and 2.9 μm ranges arising from transitions between Stark levels of 7F₅ and 7F₆ states, respectively, and the ground state 7F₄ [9, 11-12]. Pietrassol et al. [13] reported excited state absorption spectroscopy of 28D₅/₂ Ho³⁺ glass. Optical properties of Ho³⁺ doped aluminio-germano-silica glass optical fiber were studied by Waterkey et al. [14]. Recently, Seshadri et al. [15] reported spectroscopic investigations on Sm³⁺ doped similar phosphate glass systems which are studied in the present work. In the present work, the authors reported the spectroscopic and laser properties of Ho³⁺ doped alkali, mixed alkali and calcium phosphate glasses. The Judd-Olfelt theory has been applied to...
interpret the local environment and bond covalency by studying changes in the experimentally fitted $\tilde{j}$-OfeI intensity parameters. The main interest in the present study is to examine the variation of optical band gaps, $\tilde{j}$-OfeI intensity parameters, radiative lifetimes and emission cross-sections with the variation of alkalis, mixed alkalis and calcium in phosphate glass matrix. From these studies, the information related to structural changes and certain transitions of $\text{Ho}^{3+}$ ion for laser excitation in different phosphate glass matrices are reported.

2. Experimental

Glass samples were prepared in our laboratory by taking appropriate amounts of raw materials $\text{Na}_2\text{PO}_4, \text{Na}_2\text{HPO}_4, \text{Li}_2\text{CO}_3, \text{K}_2\text{CO}_3, \text{CaCO}_3, \text{NiO} (99.99\% pure)$, the appropriate proportions of raw materials were thoroughly mixed and ground in an agate mortar in $\text{J} \& \text{J}$ batches. The mixture was then melted in an electrical furnace at a temperature $950-1350^\circ \text{C}$ depending on the chemical composition in a silica crucible for $\text{J}$ batches. The melt was quickly quenched between two well polished graduated brass plates and the samples were annealed at $400^\circ \text{C}$ for $\text{J}$ days in order to remove mechanical stress. The obtained glass samples are in circular-shapes having $\text{J}$ cm in diameter with a thickness of about 0.5–2 mm with good transparency. The optical quality of all the samples was checked with a microscope and bubble free glass samples were chosen for optical measurements. The systems studied in the present work are given below. For convenience these glass systems are designated as $A, B, C, D, E, F$ and $G$ according to the glass compositions in method.

- **Glass A**: $(0.69\text{P}_2\text{O}_5 + 15\text{Na}_2\text{O}) + 13\text{Li}_2\text{O} + 0.5\text{SiO}_2$
- **Glass B**: $(0.69\text{P}_2\text{O}_5 + 15\text{Na}_2\text{O}) + 0.5\text{Li}_2\text{O} + 0.5\text{SiO}_2$
- **Glass C**: $(0.69\text{P}_2\text{O}_5 + 15\text{Na}_2\text{O}) + 15\text{K}_2\text{O} + 0.5\text{SiO}_2$
- **Glass D**: $(0.69\text{P}_2\text{O}_5 + 15\text{Na}_2\text{O}) + 7.5\text{Li}_2\text{O} + 7.5\text{Na}_2\text{O} + 0.5\text{SiO}_2$
- **Glass E**: $(0.69\text{P}_2\text{O}_5 + 15\text{Na}_2\text{O}) + 7.5\text{Li}_2\text{O} + 7.5\text{K}_2\text{O} + 0.5\text{SiO}_2$
- **Glass F**: $(0.69\text{P}_2\text{O}_5 + 15\text{Na}_2\text{O}) + 15\text{K}_2\text{O} + 0.5\text{SiO}_2$
- **Glass G**: $(0.69\text{P}_2\text{O}_5 + 15\text{Na}_2\text{O}) + 15\text{K}_2\text{O} + 0.5\text{SiO}_2$

The optical absorption spectra were recorded using JASCO-V-570 UV–VIS–IR spectrophotometer for the wavelength region 325–700 nm with spectral resolution 1 nm. Emission spectra of $\text{Ho}^{3+}$ doped glasses were measured using a Perkin-Elmer 2 fluorimeter (Model-II) under the excitation wavelength, 484 nm using Xe arc lamp (150 W) as the excitation source in the wavelength region 500–700 nm. The spectral region of the above instrument is 1 nm.

3. Theory

3.1. Optical band gaps

Optical band gaps for both direct and indirect transitions can be obtained from Davis and Mott [118] theory, using the expression:

$$\Delta(E) = \alpha(E) = \frac{\hbar \omega}{\lambda}$$

where $\alpha(E)$ is the absorption coefficient, $\lambda$ is a constant and $\hbar \omega$ is the optical band gap. In the above equation $n = \lambda$ for direct transitions and $n = \lambda + \Delta$ for indirect transitions. From the plots of $\Delta(E)$ versus photon energy $\hbar \omega$, and $\Delta(E)$ versus photon energy $\hbar \omega$, $\Delta(E)$ values can be obtained from extrapolating to $\hbar \omega = 0$ for direct transitions and $\hbar \omega = \Delta$ for indirect transitions.

3.2. Spectral analysis

The interactions primarily responsible for the free ion structure in trivalent rare earth ions are the Coulomb interaction and the magnetic interaction, which is a coupling between their spin and orbital angular momenta. Methods of Racah [17] are used to calculate the electronic interaction and matrix elements. Wybourne [18] calculated approximate electronic and spin–orbit interaction parameters using $\tilde{j}$-OfeI coupling. Using the methods of Wong and Taylor’s series [19] and Taylor’s series [20], using the observed band energies as $\Sigma$, zero order energy $E_0$ and partial derivatives of the rare earth ion, Racah interaction parameters $A^R, B^R, C^R, D^R, G^R$ are evaluated by least squares method. From the known free ion parameters, $A^R, B^R, C^R, D^R$, the parameters $\Sigma, \Delta, \phi$ and $\beta$ in the complex matrix elements, using the correction factors $\Delta^R, \Delta^R_\phi, \Delta^R_\beta$ and $\phi^R$, $\beta^R$ values are obtained. The spectral intensities of the absorption bands are estimated by measuring the areas under the absorption curves using the relation [20]:

$$I = \frac{\text{Area under the curve}}{\hbar \omega \cdot \text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}}$$

where $A$ is the abundance, $c$ is the concentration of the lanthanide ion in mol/l and $I$ is the optical path length. The $\Sigma^2$ transition probabilities are predominantly electric dipole in nature [20]. The magnetic dipole contributions are negligible and hence they are not considered in the present work. The theoretical oscillator strengths $f_{\text{dip}}$ of the dipole transitions, within the $\Sigma^2$ configurations can be calculated using $\tilde{j}$-OfeI [21,22] theory in terms of three intensity parameters $\Omega_0$, $\Omega_1$ and $\Omega_4$ using the relation:

$$f_{\text{dip}}(\text{cm}^{-1}) = 2 \sum \Omega_4 \frac{\Delta_0^2}{(\Sigma^2-1)} - 1 \sum \Omega_0 \frac{\Delta_0^2}{(\Sigma^2-1)}$$

$\Omega_0$ can also be written as

$$\Omega_0 = \left(\frac{2\lambda + 1}{2}\right) \frac{\Delta_0^2}{(\Sigma^2-1)}$$

where $\lambda = 2, 4, 6$ whereas the sum over $\lambda$ includes only the even values 2, 4 and 6 whereas the sum over $\mu$ includes only the odd values 1, 3 and 5. It has been suggested by Reitsch [20] that $\lambda$ correlates to the nephelauxetic parameter $\beta$ which indicates the degree of covalency of the $\Sigma^2$-bond. $\Delta_0^2$ represents the square of the matrix elements of the unit tensor operator $\Sigma^2$ connecting the initial and final states. The matrix elements are calculated in the intermediate coupling approximation [23]. Because of the electronic shielding of the 4f electrons by closed 5p shell electrons, the matrix elements of the unit tensor operator between the two energy manifolds in a given rare earth ion do not vary significantly when it is incorporated in different hosts. Therefore, the squared reduced matrix elements $\Delta^R \Delta^R_{\phi} \Delta^R_{\beta}$ for the LaF$^3+$ ion are used in the calculations. Subtracting $f_{\text{dip}}$ for $\Sigma^2$ and using the squared reduced matrix elements, the three intensity parameters, $\Omega_0$, $\Omega_1$ and $\Omega_4$ characteristics of a given rare earth ion in a given glass matrix are calculated.
These three parameters are related to the radial wave functions of the states $\alpha^s$ and the admixing states $\alpha^s$ of $4P$ and $\alpha^s$ of $5g$ and the ligand field parameters that characterize the environmental field. Generally, $\Omega_g$ parameter or the sum of the intensity parameters ($\Omega_1 + \Omega_2$) is an indicator of the covalency of metal-ligand bond and $\Omega_1$ and $\Omega_2$ parameters related to the rigidity of the host matrix.

3.3. Radiative properties

The $g (L = 2, 4, 6)$ values thus obtained from the absorption measurements are used to calculate the radiative transition probabilities. The radiative lifetimes and radiative transition probability, $A_{\text{rad}}(\alpha^s, \beta^s)$ for transition from an initial state $\alpha^s$ to a final ground state $\beta^s$ is given by Peacock [25].

$$A_{\text{rad}}(\alpha^s, \beta^s) \propto \frac{\text{nc}^2 (\text{nc}^2 + 1)}{\text{nc}^2} \sum_{\alpha^s, \beta^s} \frac{\Omega_1 (\alpha^s, \beta^s) \Omega_2 (\alpha^s, \beta^s)}{\Omega_1 (\alpha^s, \beta^s) + \Omega_2 (\alpha^s, \beta^s)}$$

(6)

The total radiative transition probability, $A_{\text{rad}}(\alpha^s)$ involving all the intermediate terms between $\alpha^s$ and $\beta^s$ is given by the sum of the $A_{\text{rad}}(\alpha^s, \beta^s)$ terms calculated over all terminal states $\beta^s$.

$$A_{\text{rad}}(\alpha^s) \propto \sum_{\beta^s} A_{\text{rad}}(\alpha^s, \beta^s)$$

(7)

The radiative lifetime, $\tau_{\text{e}}$ of the emission state is

$$\tau_{\text{e}} = \frac{1}{A_{\text{rad}}(\alpha^s)}$$

(8)

The fluorescence branching ratio, $\beta$ of the emission transition is defined as

$$\beta(\alpha^s, \beta^s) = \frac{A(\alpha^s, \beta^s)}{A_{\text{rad}}(\alpha^s)}$$

(9)

The integrated absorption cross section, $\Sigma$ for the stimulated emission is [26]

$$\Sigma = \frac{1}{\text{meV}^2 \text{cm}^2}$$

(10)

4. Results and Discussion

4.1. Optical band gaps

Optical band gaps for both direct and indirect transitions are obtained using the formulae given in the theoretical part. These values are 3.55, 3.56, 3.56, 3.57, 3.57, 3.58 and 3.85 eV for indirect transitions and 3.61, 3.61, 3.61, 3.61, 3.65, 3.65 and 3.80 eV for direct transitions of Ho$^3+$ doped glass (Li-Na, U-Kb-Na-K and Ca). The change in optical band gaps for both direct and indirect transitions among all the glass matrices studied, it can be observed that there is no much change in optical band gap values by mixing the alkalis in the glass matrix.

4.2. Energy levels

The absorption spectra of Ho$^3+$ doped different alkali, mixed alkali and calcium phosphate glasses are shown in Fig. 1. Though the observed spectra appear similar for different Ho$^3+$ doped glass matrices, the spectral intensities vary, particularly for the hypersensitive transitions. Also spectral profiles of certain absorption bands change with the environment. In the present work, eight absorption transitions are observed clearly. The observed bands and their band positions of Ho$^3+$ in seven different phosphate glass matrices are presented in Table 1. Racah $g (\alpha^s, \beta^s)$ spin-orbit ($\alpha^s$) and configuration interaction ($\alpha^s$) parameters of Ho$^3+$ doped different phosphate glass matrices are obtained and are presented in Table 1. The hydrogenic ratios $g (\alpha^s, \beta^s)$ and $g (\alpha^s, \beta^s)$, which indicate the radial properties, are also presented. It is observed that hydrogenic ratios are nearly equal for different glass matrices indicating that the radial properties remain unchanged. Using the procedure explained in the theory, energy values are calculated for all the observed bands. The rms deviations between experimental and calculated energies (in cm$^{-1}$) are presented in the table. It is observed that the rms deviation is very small indicating the validity of full matrix diagonalization procedure. It is observed that among the four phosphate glass matrices (Li-Na, U-Kb-Na-K and Ca), potassium glass and among the mixed alkali phosphate glass matrices (Li-Kb-Na-K and Ca) lithium phosphate glasses shows higher absorptions indicating a strong electron–phonon interaction in the absorption matrices.

4.3. Spectral intensities and intensity parameters

The spectral intensities (both experimental and calculated) are obtained for all the observed absorption bands of Ho$^3+$ in all the phosphate glasses using the expressions given in the theory. The experimental spectral intensities ($I_\text{exp}$) of all the observed bands of $\alpha^s$ and $\beta^s$ of the glass matrices are presented in Table 2. It is observed that $I_\text{exp}$ of all the bands are low in lithium phosphate glass and high in potassium phosphate glass matrix. It indicates that non-symmetric component of electric field acting on $\text{Ho}^3+$ ion is weak in sodium glass matrix and strong in potassium glass matrix. It is also observed that the spectral intensities of all the bands in mixed alkali glasses are lower when compared with single alkali phosphate glasses. The rms deviations
between experimental and calculated spectral intensities is also presented in Table 2.

The best set of Judd-Ofelt intensity parameters (Q values) obtained from a least square analysis of the observed spectral intensities and the sum of the intensity parameters (S values) for all the Ho-doped phosphate glass matrices along with other glass matrices are presented in Table 3. It is observed that among all the glass systems studied, potassium phosphate glass shows higher Gq parameter and sodium glass shows lower Gq parameter indicating higher and lower covalencies of the glass matrices. It is also observed that among the three combinations studied, lithium-potassium phosphate glass shows higher Gq parameter and lithium-sodium glass shows lower Gq parameter indicating higher and lower covalencies. Similar trend has been observed from the magnitude of the sum of intensity parameters (\(\sum \Omega\)). Gq and \(\Omega\) parameters are higher for potassium glass matrix and lower for sodium glass matrices indicating higher and lower rigidities for these two glass matrices, respectively. Among the three mixed alkali phosphate glass matrices (Li-Na, Li-K and Na-K), Gq and \(\Omega\) parameters are higher for lithium-potassium glass matrix and lower for sodium-sodium glass matrix indicating higher and lower rigidities of the glass matrices. From Table 3, it is also observed that except for sodium phosphate glass matrix, all the Ho-doped phosphate glass matrices (the present work) show higher \(\sum \Omega\) values when compared with borate and silicate glass matrices indicating higher covalency of Ho-O bond in phosphate glass matrices. Variation of Gq, \(\Omega\), and \(\sum \Omega\) parameters with glass matrix is shown in Fig. 2. From the figure, it is observed that Gq, \(\Omega\), and \(\sum \Omega\) parameters increase for potassium glass matrix and also for lithium-potassium glass matrix. Similar trend has been observed in the case of Sm3+ doped different phosphate glass systems [15].
towards longer wavelengths indicates that the degree of covalency of Ho–O bond increases. In the present work, it is observed that there is no change in the peak wavelength of the hypersensitive transition, $\Delta^2 \nu = \nu_0^2$, with the variation of alkali metal alkalis and calcium in the glass matrix. But for $\Delta^2 \nu = \nu_2^2$ transition, the peak wavelengths for Li, Na, K, Li–Na, Li–K, Na–K and Na–K–Ca phosphate glasses are 451.5, 451.3, 451.8, 451.7, 451.5, 451.9 and 451.8 nm, respectively. From the spectral profiles of the hypersensitive transition, it is observed that some splitting is visible between the small peaks for Ca and Ca glass matrices when compared with other matrices.

There is no change in the shape or the spectral profile of the other hypersensitive transition, $\Delta^2 \nu = \nu_0 \nu_2$, with the variation of alkali, mixed alkalis and calcium in the phosphate glass matrix. The analysis of the present work with Eq. (5) indicates that the increase in the magnitude of the parameter $\mu$ with the glass matrix is in the same order with the shift in the peak wavelength of the hypersensitive transition towards longer wavelength side or shorter wavelength side. It indicates that the structural changes are not influencing the covalency of metal ligand bond for lithium to sodium, sodium to potassium, potassium to lithium–sodium, lithium–sodium to lithium–potassium and sodium–potassium to calcium in the glass matrix. But for lithium–potassium to sodium–potassium glass matrix the peak wavelength of the hypersensitive transition, $\Delta^2 \nu = \nu_2^2$, shifts towards longer wavelength (from 451.3 nm to 451.9 nm) but the $\Delta^2 \nu$ parameter decreases from $10.46 \times 10^{-20}$ to $5.38 \times 10^{-20}$ cm$^3$ indicating some structural changes for lithium–potassium to sodium–potassium in this glass matrix.

**4.5. Radiative properties**

Using Judd–Ofelt intensity parameters, $Q_i$ ($i = 2, 4$ and $6$) obtained from the measured spectral intensities of the absorption bands and using the formulae given in the theory, the total radiative transition probabilities $\beta_i$ and the radiative lifetimes $\tau_i$ of the excited states $\mu_0$, $\mu_2$, $\mu_0 \mu_2$, $\mu_1$, $\mu_2$, $\mu_0 \mu_2$ and $\mu_0 \mu_2 \mu_1$ have been calculated. The calculated radiative lifetimes of all the excited states are presented in Table 4. It is observed that the order of magnitude of lifetimes for different excited states are

$\tau_2 > \tau_4 > \tau_6 > \tau_3 > \tau_1 > \tau_5$. It is also observed that the radiative lifetimes of all the excited states are higher for sodium phosphate glass and lower for potassium phosphate glass among the four glass matrices (Li, Na, K and Ca). It is also observed that when sodium combines with lithium and potassium the radiative lifetimes of all the excited states decreases. When potassium combines with lithium there is no change in the radiative lifetimes of all the excited states except small change in $\tau_2$ and $\tau_6$ excited states. Branching ratios $\beta_i/\beta_6$ and integrated absorption cross-sections of certain transitions of Ho$^{3+}$ are calculated for all these glass matrices. It is observed that among various transitions of Ho$^{3+}$ ion, the transitions $\mu_0 = \mu_2$, $\mu_0 \mu_2 = \mu_1$, $\mu_0 \mu_2 = \mu_6$ and $\mu_0 \mu_2 \mu_1 = \mu_6$ have higher branching ratios and integrated absorption cross-sections. The branching ratios are in the range $0.880$ to $0.884$, $0.881$ to $0.885$, $0.745$ to $0.785$ and $0.730$ to $0.741$ for the above four transitions, respectively, for different glass matrices studied in the present work. It is observed that among the four glass matrices studied (Li, Na, K and Ca), Ca glass and among the three mixed alkali glass matrices (Li–Na, Li–K and Na–K; Na–K glass matrix have higher branching ratio values for most of the transitions.
Table 4
Total radiative transition probabilities (A<sup>r</sup>) and radiative lifetimes (T<sub>r</sub> ps) of certain excited states of Ho<sup>3+</sup> doped alkali, mixed alkali and calcium phosphate glass matrices.

<table>
<thead>
<tr>
<th>Excited Level</th>
<th>Class A</th>
<th>Class B</th>
<th>Class C</th>
<th>Class D</th>
<th>Class E</th>
<th>Class F</th>
<th>Class G</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U&lt;sup&gt;L&lt;/sup&gt;</td>
<td>Na&lt;sup&gt;L&lt;/sup&gt;</td>
<td>K&lt;sup&gt;L&lt;/sup&gt;</td>
<td>U&lt;sup&gt;Na&lt;/sup&gt;</td>
<td>Na&lt;sup&gt;Na&lt;/sup&gt;</td>
<td>K&lt;sup&gt;Na&lt;/sup&gt;</td>
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</tr>
<tr>
<td>Ho&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>59830</td>
<td>50000</td>
<td>50000</td>
<td>50000</td>
<td>50000</td>
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</tr>
</tbody>
</table>

Fig. 4. Fluorescence spectra of Ho<sup>3+</sup> doped alkali, mixed alkali and calcium in phosphate glasses.

4.6. Non-radiative properties

If the initial states and various states are formed by different multiplets with full Stark splitting <i>ΔE<sub>n</sub></i>, the probability of multimode relaxation can be expressed as (27):

\[ W(n) = \frac{1}{125 N D} \sum_{i=1}^{N} \sum_{j=1}^{D} E_{i} E_{j} \left( |U_{i}| |U_{j}| \right)^{2} \]  

(11)

where \( N \) is the total number of states at the initial level and the summation is taken over all multiplets \( i \) and \( j \) involved in the transition.

From the above expression, the multimode relaxation rate is a product of two factors. The first one depends on the square of the amplitude of lattice ion vibration energy, \( \eta = \frac{2kT}{\hbar} \) (where \( k \) represents a small displacement of the lattice ions from their equilibrium positions, \( \hbar \)), which is in turn determined by the normal coordinates of the vibrational modes. The second factor depends on electronic parameters and it suggests the proportionality of \( W(n) \) to the \( \sum_{i=1}^{N} \sum_{j=1}^{D} \left( E_{i} E_{j} \right)^{2} \) term which is similar to the radiative probability. In this term the intensity parameter \( I_{j} \) of a multiphonon transition includes the parameters of the electronic part of electron-phonon interaction and depends on the ratio of the ligand charge to the unit (electron) charge.

In phosphate glasses, the up-conversion phenomenon is very common, because of the large multiphonon decay rates, due to the high energy stretching vibration of the P-O bond (\( >200 \text{ cm}^{-1} \)). The exponential dependence of the multiphonon relaxation rate, \( W_{\text{up}} \), on the energy gap to the next lower level, \( \Delta E \), has been experimentally established for a number of crystals and glasses and is given by Lifshitz (28):

\[ W_{\text{up}} = C \exp(-\Delta E/n+1)^{2} \]  

(12)

where \( C \) and \( n \) are positive, host dependent constants, which are almost independent of the specific level of trivial rare earth
Table 5
Ceramic emission properties of Nb2O5 doped alkali, mixed alkali and calcium phosphate glass matrices.

<table>
<thead>
<tr>
<th>Glass matrix</th>
<th>( \frac{\lambda_{max}}{\text{nm}} )</th>
<th>( \lambda_{max} ) (nm)</th>
<th>( \Delta \lambda ) (nm)</th>
<th>( \Delta \lambda \text{ (nm cm)}^2 )</th>
<th>( \lambda_{max} ) (nm)</th>
<th>( \lambda_{max} ) (nm)</th>
<th>( \Delta \lambda ) (nm)</th>
<th>( \Delta \lambda \text{ (nm cm)}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass A (K)</td>
<td>464.1</td>
<td>464.1</td>
<td>1.88</td>
<td>0.000</td>
<td>464.1</td>
<td>464.1</td>
<td>1.88</td>
<td>0.000</td>
</tr>
<tr>
<td>Glass B (Na)</td>
<td>454.3</td>
<td>454.3</td>
<td>0.05</td>
<td>0.000</td>
<td>454.3</td>
<td>454.3</td>
<td>0.05</td>
<td>0.000</td>
</tr>
<tr>
<td>Glass C (K)</td>
<td>454.0</td>
<td>454.0</td>
<td>2.22</td>
<td>0.000</td>
<td>454.0</td>
<td>454.0</td>
<td>2.22</td>
<td>0.000</td>
</tr>
<tr>
<td>Glass D (Li-Na)</td>
<td>454.0</td>
<td>454.0</td>
<td>2.22</td>
<td>0.000</td>
<td>454.0</td>
<td>454.0</td>
<td>2.22</td>
<td>0.000</td>
</tr>
<tr>
<td>Glass E (Na-K)</td>
<td>454.0</td>
<td>454.0</td>
<td>2.22</td>
<td>0.000</td>
<td>454.0</td>
<td>454.0</td>
<td>2.22</td>
<td>0.000</td>
</tr>
<tr>
<td>Glass F (Na-Ca)</td>
<td>454.0</td>
<td>454.0</td>
<td>2.22</td>
<td>0.000</td>
<td>454.0</td>
<td>454.0</td>
<td>2.22</td>
<td>0.000</td>
</tr>
<tr>
<td>Glass C (Ca)</td>
<td>452.9</td>
<td>452.9</td>
<td>2.84</td>
<td>0.000</td>
<td>452.9</td>
<td>452.9</td>
<td>2.84</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Fig. 4a. Variation of absorption cross-sections of the transitions, \( \lambda_{max} - \lambda_1 \) and \( \lambda_{max} - \lambda_2 \) with the glass matrix.

Fig. 4b. Variation of emission cross-sections of the transitions, \( \lambda_{max} - \lambda_1 \) and \( \lambda_{max} - \lambda_2 \) with the glass matrix.

4.7. Emission spectra

The photoluminescence spectra of Nb2O5 doped alkali, mixed alkali and calcium phosphate glass matrices recorded at room temperature in the wavelength region 500–700 nm under the excitation wavelength 445 nm are shown in Fig. 4. In the emission spectra, two peaks corresponding to the transitions, \( \lambda_{max} - \lambda_1 \) and \( \lambda_{max} - \lambda_2 \) were observed at 550 and 650 nm, respectively.

Except small splitting in the emission peak, \( \lambda_{max} - \lambda_1 \) of lithium and sodium-potassium glass matrix, the spectral profiles of two transitions in all the phosphate glass systems are nearly same. It is observed that the absorption of these two bands is shifted towards the lower wavelengths for all the glass matrices. It indicates that a relatively low degree of phonon interaction. Variation of emission intensity of the two emission peaks with the glass matrix is shown in Fig. 5. The peak stimulated emission cross-section \( \sigma_{pe} \) is obtained from (24).

\[ \sigma_{pe} = \frac{\Delta \lambda}{6 \pi \Delta \lambda_{max} \lambda_{max}} \]
and lithium–potassium phosphate glass matrices may be useful for the lasting materials when compared with other compositions. Variation of absorption and emission cross-sections with the glass matrix is shown in Figs. 8a and 8b. It is observed that the variation is similar for both the absorption and emission cross-sections for different alkalis, mixed alkalis and calcium in this glass matrix.

5. Conclusions

From the magnitude of Judd–Ofelt intensity parameter (Q4), it is concluded that among the four glass matrices studied (Li, Na, K and Cs), potassium glass shows higher Q4 parameter and sodium glass shows lower Q4 parameter indicating higher and lower covalencies of Si-O bond in these two glass matrices, respectively. Among the three mixed alkali glass matrices (Li–Na, Li–K and Na–K), lithium–potassium glass shows higher Q4 parameter and lithium–sodium glass shows lower Q4 parameter indicating higher and lower covalencies. From the variation of Q4 parameter and shift in the peak wavelength of the hypersensitive transition, some structural changes were observed for lithium–potassium to germanium–potassium in this phosphate glass matrix. For the other glass matrices, structural changes are not influencing the covalency of Si-O bond. Radiative lifetimes of the excited states, H4, H6, H8, H10, H12, H14 and H16 of Ho3+ in different phosphate glass matrices are reported. From the emission spectra, peak stimulated emission cross-sections were reported for the two transitions, F4→F2 and F4→F0 and F2→F0 of Ho3+. It is observed that potassium phosphate glass matrix shows higher peak emission cross-sections among the four phosphate glass matrices (Li, Na, K and Cs) and among the three mixed alkali glass matrices (Li–Na, Li–K and Na–K), lithium–potassium phosphate glass matrix shows higher emission cross-section.

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References

Review

Spectroscopic and laser properties of Sm³⁺ doped different phosphate glasses

M. Seshadri¹, K. Venkata Rao², J.L. Rao², Y.C. Ratnakaram³,*

¹ Department of Physics, S.V. University Post Graduate Centre, Nanded 431 601, AP, India
² Department of Physics, S.V. University, Tirupati 517 502, AP, India
³ Department of Physics, Andhra University, Visakhapatnam 530 003, India

Abstract

Optical absorption and photoluminescence spectra of Sm³⁺ ions in all alkali phosphate [P₂O₅·Na₂O·K₂O·R₂O (R = Li, Na and K)], mixed alkali phosphate [P₂O₅·Na₂O·Li₂O·R₂O (R = Na, K)], [P₂O₅·Na₂O·Li₂O·K₂O], and calcium phosphate [Ca₃(PO₄)₂] glasses doped with 1 mol% of Sm₂O₃ have been investigated using Judd-Oelft intensity parameters (D₀, D₂, and D₄) are obtained using Judd-Oelft theory, which are intern used in studying the radiative properties of Sm³⁺ doped different glass matrices. Absorption cross-sections (σ) and branching ratios (f) of different transitions have been calculated from the absorption spectra. The emission spectra of Sm³⁺ have been recorded under the excitation wavelength 400.0 nm for all the glass matrices. From the emission spectra, emission cross-sections (σₑ) and branching ratios (fₑ) are calculated. From these studies certain transitions have been identified for the suitability of these glasses for laser application. Optical band gaps are also reported for both indirect and direct transitions of all these Sm³⁺ doped glass matrices.

Keywords:
Phosphate glass
Sm³⁺
Absorption
Luminescence

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1. Introduction

Investigation of glasses as host materials for rare earth fluorescence with potential for laser is confined to borate, phosphate, silicate and fluoride glasses [1,2]. The versatility of glasses and the broader emission and absorption spectra they provide, as compared with crystalline hosts, have increasing interest in their properties from both a spectroscopic [3] and a technological point of view [4-5]. Among these glasses, phosphate glass has several advantages over conventional silicate and borate glasses due to their superior physical properties such as high thermal expansion coefficient, low melting and softening temperatures and high ultraviolet transmission [6-7]. The low photon energy of the fluorophosphate glasses yields low non-radiative decay and high radiative emission rates of RE ion energy levels, leading to much higher quantum efficiencies [8]. As Eu³⁺ ions are hypersensitive to local environments...
and microstructures and can be used as fluorescent probe, Yu and Nogari [9] studied photoluminescence cross changes of $\text{Er}^{3+}$ in ZnO-SiO$_2$ glasses induced by femtosecond laser. Among the numerous rare earth doped glasses, samarium doped phosphates glasses are known to have an unusual elastic behavior due to valence instability [10]. Although the trivalent samarium ion exhibits a strong luminescence in the visible range (orange), the complicated electronic structure of the 4f$^2$ configuration is responsible for their neglect.

In the present paper, the absorption and fluorescence studies on $\text{Sm}^{2+}$ doped alkali, mixed alkali and calcium phosphate glasses are reported. Judd–Olfet theory is used in the analysis of the spectra and various optical properties like transition probabilities ($A$), radiative lifetimes ($\tau_\text{rad}$), branching ratios ($\beta$), integrated absorption cross-sections ($\sigma_a$) and stimulated emission cross-sections ($\sigma_s$) for the different glasses. These parameters are obtained by fitting the absorption data with the theoretical expression given by Judd and Ofelt [11] and Sudhakar et al. [12].

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### 2. Experimental

The chemical compositions of various glass samples, mixed alkali and calcium phosphate glasses doped with $\text{Sm}^{2+}$ are as follows:

- Glass A: 66P$_2$O$_5$ + 15Na$_2$OPO$_4$ + 15Li$_2$O + 15molO$_3$
- Glass B: 66P$_2$O$_5$ + 15Na$_2$OPO$_4$ + 15Na$_2$O + 15molO$_3$
- Glass C: 66P$_2$O$_5$ + 15Na$_2$OPO$_4$ + 15Na$_2$O + 15molO$_3$
- Glass D: 66P$_2$O$_5$ + 15Na$_2$OPO$_4$ + 7.5Li$_2$O + 7.5Na$_2$O + 15molO$_3$
- Glass E: 66P$_2$O$_5$ + 15Na$_2$OPO$_4$ + 7.5Li$_2$O + 7.5Li$_2$O + 15molO$_3$
- Glass F: 66P$_2$O$_5$ + 15Na$_2$OPO$_4$ + 7.5Na$_2$O + 7.5Na$_2$O + 15molO$_3$
- Glass G: 66P$_2$O$_5$ + 15Na$_2$OPO$_4$ + 15CaO + 15molO$_3$

Calculated quantities of chemicals were taken in an agate mortar and then powdered well to obtain a homogeneous mixture. The mixture is taken in a sterile tube and then heated to about 950 °C in an electric furnace for about 3 h. The melt was quickly quenched between two well-polished brass moulds. Circular shaped glass samples of thickness about 1.5–2 mm having a diameter of 10 mm are obtained. The samples were annealed at a temperature of about 1050 °C for about 2 h for getting the thermal and structural stability and later it was polished to achieve good transparency that appears to be of good optical quality.

Absorption spectra were recorded in the spectral region 300–1100 nm using JASCO V-570 spectrophotometer. Photoluminescence spectra were recorded using Fluoro-Max 3 Fluorospectrophotometer under the excitation wavelength of 460 nm in the spectral region 500–700 nm. The refractive index measurements were performed using an Abbe refractometer with sodium lamp as an adhesive coating with an accuracy of ±0.001 and the density measurements were made using Archimedes principle with xylene as immersion liquid.

### 3. Theory

According to the Judd–Olfet theory [16,17], the oscillator strength, $f_{\text{rad}}$, of an electronic dipole absorption transition from the initial state $|S, L, J\rangle$, to the final state $|S', L', J'\rangle$, depends on the three Judd–Olfet parameters, $\Omega_2$, $\lambda = 2$, 4, 6 as

$$ f_{\text{rad}}(S, L, J; S', L', J') = \frac{\beta_1}{\Omega_2} S_{\text{rad}}^{\text{calc}} \left( \frac{n^2 + 2}{10n^3} \right) \sum_{\alpha,\beta,\gamma} \Omega_{\alpha\beta\gamma}^2 (S', L', J'') (S', L', J') $$

where $\lambda$ is the mean wavelength of the transition, $m$ is the mass of the electron, $c$ is the velocity of light, $n$ the refractive index, $\Omega$ the plank constant and $\bar{\sigma}_\text{rad}$ are the doubly reduced matrix elements of unit tensor operators that are considered to be independent of the host matrix. The experimental oscillator strengths, $f_{\text{exp}}$, of the transitions can be obtained by integrating each absorption band using the formula

$$ f_{\text{exp}} = 6.32 \times 10^{-6} \int \bar{\sigma}(\lambda)d\lambda $$

where $\lambda$ is the molar extinction coefficient. The Judd–Olfet intensity parameter, $\Omega_2$, is obtained from the experimental oscillator strengths using a least squares fitting approach. The radiative transition probability $A_d(q, q')$ is given by

$$ A_d(q, q') = \frac{\pi^4}{64\pi^2 \lambda^2} \frac{m^2 c^2}{8 \hbar} \times \frac{n^2 + 2}{10n^3} \times \sigma_{\text{rad}} \times \pi^2 $$

where electric dipole and magnetic dipole line strengths, $\sigma_d$ and $\sigma_m$ are expressed as

$$ \sigma_d(q, q') = \frac{c^2}{4\pi^2\lambda^2} \sum_{\alpha, \beta, \gamma} \Omega_{\alpha\beta\gamma}^2 (S, L, J) (S, L, J') $$

$$ \sigma_m(q, q') = \frac{c^2}{4\pi^2\lambda^2} \sum_{\alpha, \beta, \gamma} \Omega_{\alpha\beta\gamma}^2 (S, L, J) (S, L, J') $$

The magnetic dipole spontaneous emission probabilities were calculated using the values reported for LaF$_3$ [18] and they are very small. The radiative lifetime, $\tau_\text{rad}$ of an emitting state, $q\ell$ is calculated from

$$ \tau_\text{rad}(q\ell) = \frac{1}{A_d(q\ell, q\ell') \bar{\sigma}(\lambda) d\lambda} $$

The branching ratio of a transition is defined as

$$ \beta(q\ell, q\ell') = \frac{A_d(q\ell, q\ell')}{A_d(q\ell, q\ell') + A_d(q\ell', q\ell')} $$

The integrated absorption cross-section for stimulated emission is evaluated from

$$ \Sigma = \frac{1}{\beta} \times \frac{A}{8\pi c} $$

### 4. Results and discussion

#### 4.1. Spectral intensities and intensity parameters

The room temperature optical absorption spectra of $\text{Sm}^{2+}$ doped different phosphate glass samples investigated in the present work are shown in Fig. 1. A large number of spectral lines are observed and are assigned by analogy with that given in the literature [19,20]. These spectral line characteristics of 4f–4f absorption of trivalent samarium, which corresponds to $^{4}P_{3/2}$ ground state to the different excited states and energy band positions are given in Table 1. The spectral profiles of the absorption spectra of all the glass matrices are similar in shape. The experimental using the Beer–Lambert’s Law [21] and calculated (using the Judd–Olfet theory [16,17]) spectral intensities $I(q\ell)$ of the observed absorption bands of $\text{Sm}^{2+}$ ion are obtained and are presented in Table 2.
The accuracy of the fit is given by the rms deviation between the experimental and calculated spectral intensities, which indicate the validity of Judd-Olfet theory. In the present work, the rms deviations are very small. It is observed that among four glass matrices (Li, Na, K and Ca), the spectral intensities of sodium glass matrix are less. Among the three mixed alkali phosphate glass matrices, lithium sodium glass matrix shows lower spectral intensities.

The \( f_{\text{int}} \) values are used to determine the Judd–Olfet intensity parameters \( (\Omega_{\text{int}}) \) for various excited states and mixed alkali phosphate glass matrices. The values are presented in Table 2 along with the other glass matrix.

**Table 1**

<table>
<thead>
<tr>
<th>Glass Matrix</th>
<th>Mixed Alkali</th>
<th>Sodium</th>
<th>Lithium</th>
<th>Potassium</th>
<th>Calcium</th>
<th>Judd-Olfet Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Na-K-Ca</td>
<td>0.62</td>
<td>0.55</td>
<td>0.58</td>
<td>0.60</td>
<td>0.64</td>
<td>0.59</td>
</tr>
<tr>
<td>Li-Na</td>
<td>0.62</td>
<td>0.55</td>
<td>0.58</td>
<td>0.60</td>
<td>0.64</td>
<td>0.59</td>
</tr>
<tr>
<td>Na-K-Ca</td>
<td>0.62</td>
<td>0.55</td>
<td>0.58</td>
<td>0.60</td>
<td>0.64</td>
<td>0.59</td>
</tr>
<tr>
<td>Li-K-Ca</td>
<td>0.62</td>
<td>0.55</td>
<td>0.58</td>
<td>0.60</td>
<td>0.64</td>
<td>0.59</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Glass Matrix</th>
<th>Mixed Alkali</th>
<th>Sodium</th>
<th>Lithium</th>
<th>Potassium</th>
<th>Calcium</th>
<th>Judd-Olfet Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Na-K-Ca</td>
<td>0.62</td>
<td>0.55</td>
<td>0.58</td>
<td>0.60</td>
<td>0.64</td>
<td>0.59</td>
</tr>
<tr>
<td>Li-Na</td>
<td>0.62</td>
<td>0.55</td>
<td>0.58</td>
<td>0.60</td>
<td>0.64</td>
<td>0.59</td>
</tr>
<tr>
<td>Na-K-Ca</td>
<td>0.62</td>
<td>0.55</td>
<td>0.58</td>
<td>0.60</td>
<td>0.64</td>
<td>0.59</td>
</tr>
<tr>
<td>Li-K-Ca</td>
<td>0.62</td>
<td>0.55</td>
<td>0.58</td>
<td>0.60</td>
<td>0.64</td>
<td>0.59</td>
</tr>
</tbody>
</table>
4.2. Hypersensitive transition

The intensities of certain absorption bands of rare earth ions are very sensitive to the environment and they obey the selection rules $\Delta J \leq 2$, $\Delta L \leq 2$ and $\Delta S = 0$ [23]. These transitions could be called as hypersensitive transitions. Normality, the intensity of the hypersensitive transition is largely dependent on the surroundings and in turn it shows the effect on intensity parameters. $^4H_{4}^{2} \rightarrow ^2F_{2}$ is the hypersensitive transition for Sm$^{3+}$ ion. Hypersensitivity of a transition has been shown to be proportional to nephelauxetic ratio $\beta$ which indicates the covalency of RE-O bonds [23]. In the present work, the hypersensitive band, $^4H_{4}^{2} \rightarrow ^2F_{2}$ clearly shows two peaks corresponding to two transitions $^4H_{4}^{2} \rightarrow ^2F_{2}$ and $^4H_{4}^{2} \rightarrow ^2F_{2}$. Normally the intensity parameter $\Omega_{2}$ (or $\sum \Omega_{i}$), which indicates covalency increases with the increase of intensity of hypersensitive transition. In the present work, $\Omega_{2}$ parameter increases with the increase of the sum of the intensities of the two transitions of hypersensitive transition (except for potassium). It is observed that among the four glass matrices [Li, Na, K and Ca], calcium phosphate glass shows higher spectral intensity; among the three mixed alkali glass matrices, sodium potassium glass matrix shows higher spectral intensity for the hypersensitive transition. It indicates the more covalency of RE-O bond in these glass matrices. The peak wavelengths, spectral intensities of the hypersensitive transition and $\Omega_{2}$ parameter of Sm$^{3+}$ doped different glass matrices are given below.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Peak wavelength (nm)</th>
<th>Spectral intensity ($J \times 10^{-1}$)</th>
<th>$\Omega_{2}$ Parameter ($J \times 10^{-1}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1548</td>
<td>1.649</td>
<td>0.83</td>
</tr>
<tr>
<td>Na</td>
<td>1548</td>
<td>0.736</td>
<td>0.47</td>
</tr>
<tr>
<td>K</td>
<td>1548</td>
<td>1.662</td>
<td>1.18</td>
</tr>
<tr>
<td>Li-Na</td>
<td>1541</td>
<td>0.553</td>
<td>0.43</td>
</tr>
<tr>
<td>Li-K</td>
<td>1541</td>
<td>1.163</td>
<td>0.58</td>
</tr>
<tr>
<td>Na-K</td>
<td>1541</td>
<td>1.708</td>
<td>1.00</td>
</tr>
<tr>
<td>Ca</td>
<td>1544</td>
<td>1.965</td>
<td>1.44</td>
</tr>
</tbody>
</table>

The shift of the peak wavelength of the hypersensitive transition towards longer wavelengths indicates the degree of covalency of RE-O bond increases. In the present work, there is a shift in the peak wavelength of the hypersensitive transition towards shorter wavelengths for Li to Li-Na glass matrix. $\Omega_{2}$ Parameter also decreased and indicates that the structural changes are not influencing the covalency of RE-O bond. For Li to Li-K glass matrix there is a slight decrease in the peak wavelength of the hypersensitive transition, the $\Omega_{2}$ parameter also decreased indicating the influence of structural changes on covalency is very small at this glass composition. Similarly for Na to Li-Na there is a decrease in peak wavelength of the hypersensitive transition, the $\Omega_{2}$ parameter also decreased indicating the less structural changes. For Na to Na-K glass matrix there is a shift of peak wavelength of hypersensitive transition towards shorter wavelengths but the $\Omega_{2}$ parameter increased more indicating more structural changes and the effect of structural changes on covalency is more.

4.3. Radiative properties

Using Judd–Ofelt intensity parameters, the radiative properties such as radiative transition probabilities ($A_{0}$), radiative lifetimes ($\tau_{p}$), branching ratios ($\beta$) and integrated absorption cross-sections ($\Sigma$) of certain transitions of Sm$^{3+}$ doped alkali, mixed alkali and calcium phosphate glasses have been studied using the formulae given in theory and in Ref. [24]. The total radiative transition probabilities ($A_{0}$) for the excited states $^4H_{4}^{2}$, $^2F_{2}$ and $^2F_{2}^{2}$ of all the glass matrices are given in Table 3. It is observed that for all the alkali, mixed alkali and calcium phosphate glass.
phosphate glass matrices, the order of magnitude of A parameter is $6F_{1/2} \rightarrow 6F_{5/2}$, $6F_{3/2} \rightarrow 6F_{9/2}$, $6F_{7/2} \rightarrow 6F_{13/2}$. It is observed that the total radiative transition probabilities are decreased when lithium combined with sodium and potassium in the phosphate glass matrix. In the case of sodium, when it is mixed with potassium the total radiative transition probabilities are increased. Among the four glass matrices studied (Li, Na, K and Ca), calcium glass matrix indicates higher transition probabilities. Among the three mixed alkali phosphate glass matrices, sodium potassium glass matrix indicates higher radiative transition probabilities. Variation of A parameter with the glass matrix is shown in Fig. 3. The estimated radiative lifetimes are lower and higher for $6F_{1/2}$ and $6F_{3/2}$ states, respectively, in all the glass matrices.

From the magnitude of branching ratios ($\beta$), it is observed that among various transitions for different glass matrices, $6F_{3/2} \rightarrow 4F_{5/2}$, $6F_{5/2} \rightarrow 4F_{7/2}$ and $6F_{7/2} \rightarrow 4F_{9/2}$ transitions have higher branching ratio values. For these transitions, the branching ratio values are in the range of 0.509-0.653, 0.391-0.421 and 0.384-0.498, respectively. Among the three transitions, $6F_{3/2} \rightarrow 4F_{5/2}$ transition consists higher branching ratio (0.553) in lithium potassium phosphate glass matrix. Among the four phosphoglass matrices (Li, Na, K and Ca), most of the transitions have higher branching ratio values in lithium glass matrix. The integrated absorption cross-sections ($\sigma$) are higher for $6F_{1/2} \rightarrow 6F_{13/2}$, $6F_{3/2} \rightarrow 4F_{5/2}$ and $6F_{5/2} \rightarrow 4F_{7/2}$ transitions among various transitions. These values are in the range 0.93-3.61, 0.90-3.30 and 0.86-3.32 for the above three transitions, respectively. Among four glass matrices (Li, Na, K and Ca), calcium glass matrix indicates higher absorption cross-sections. Variation of absorption cross-sections ($\sigma$) of the transitions, $4F_{5/2} \rightarrow 4H_{9/2}$, $4F_{7/2} \rightarrow 4H_{11/2}$, $4F_{9/2} \rightarrow 4H_{13/2}$ and $4F_{11/2} \rightarrow 4H_{15/2}$ with the glass matrix is shown in Fig. 4. As we have observed these four transitions in the emission spectra, we have shown the variation of $\sigma$ with the glass matrix. Because of the same reason, electric dipole line strengths ($S_{ep}$), radiative transition probabilities ($A_{R}$), branching ratios ($\beta$) and integrated absorption cross-sections ($\sigma$) from the ground state, $6P_{3/2}$ to various excited states are given in Table 4.

Table 2: Total radiative transition probabilities ($A_{R}$) (s$^{-1}$) of certain excited states of Sm$^{3+}$ doped alkali, mixed alkali and calcium phosphate glass matrices.

<table>
<thead>
<tr>
<th>Glass matrix</th>
<th>$Li$</th>
<th>$Na$</th>
<th>$K$</th>
<th>$Li-Na$</th>
<th>$Li-K$</th>
<th>$Na-K$</th>
<th>$Ca$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{1/2}$</td>
<td>799</td>
<td>795</td>
<td>799</td>
<td>795</td>
<td>795</td>
<td>795</td>
<td>795</td>
</tr>
<tr>
<td>$T_{3/2}$</td>
<td>503</td>
<td>503</td>
<td>503</td>
<td>503</td>
<td>503</td>
<td>503</td>
<td>503</td>
</tr>
</tbody>
</table>

Fig. 4: Variation of integrated absorption cross-section ($\sigma$) with alkali, mixed alkali and calcium in phosphate glasses.

Fig. 3: Variation of $A_{R}$ parameter with alkali, mixed alkali and calcium in phosphate glasses.

Table 4: Energy of the transitions (J) (cm$^{-1}$), electric dipole line strengths ($S_{ep}$ x 10$^{-3}$ lb) (cm$^2$), radiative transition probabilities ($A_{R}$) (s$^{-1}$), branching ratios ($\beta$) and integrated absorption cross-sections ($\sigma$) x 10$^{-19}$ cm$^2$ of $6P_{3/2}$ level of Sm$^{3+}$ in calcium phosphate glass matrix.
4.4. Luminescence spectra

When any of the levels above \( \text{Ce}^{3+} \) is excited, there is a non-radiative relaxation to this fluorescent level and consequently the same emission spectra is obtained with different excitation wavelengths 361.2, 375.1, 400.0 and 419.5 nm. In the present work, for excitation, 400.0 nm wavelength is used. The luminescence spectra of \( \text{Sm}^{3+} \) doped alkali, mixed alkali and calcium phosphate glasses are shown in Fig. 5. The spectrum shows four emission lines, of which three consist strong bands and the other one is a weak band. These could be easily assigned on the basis of the energy level diagram for \( \text{Sm}^{3+} \) given by Dieke [25]. The wavelengths of the four peaks at \(~560, ~597, ~642\) and \(~702~\text{nm}\) are assigned to transitions \( \text{C}_2 \rightarrow \text{H}_2, \text{C}_2 \rightarrow \text{H}_3, \text{C}_3 \rightarrow \text{H}_2 \) and \( \text{C}_3 \rightarrow \text{H}_3 \), respectively. It is observed that the emission intensities of the four transitions are lower for calcium phosphate glass matrix among the four glass matrices (Li, Na, K and Ca). It is also observed that when lithium mixed with sodium and potassium, the emission intensities of the four transitions are increased. The spectral profiles of these strong emission bands are same except the small changes in full width at half maximum (FWHM) for all the glass systems studied. It is observed that, the emission intensities of the four transitions are lower for calcium phosphate glass matrix among the seven glass matrices studied. It may be due to the fluorescence quenching due to nearest neighbor ion interaction (Fig. 6).

Peak wavelengths \( (\lambda) \), radiative transition probabilities \( (\alpha_{\text{RT}}) \), emission linewidths \( (\Delta \lambda) \) and emission cross-sections \( (\sigma_{\text{E}}) \) for the four transitions \( \text{C}_2 \rightarrow \text{H}_2, \text{C}_2 \rightarrow \text{H}_3, \text{C}_3 \rightarrow \text{H}_2 \) and \( \text{C}_3 \rightarrow \text{H}_3 \) of \( \text{Sm}^{3+} \) are obtained using the formulae given in Ref. [26] and are presented in Table 5 for all the glass matrices. It is observed that the effective linewidths vary between 262-428, 407-516, 364-449 and 192-449 cm\(^{-1}\) for the four transitions.

\[ \text{C}_2 \rightarrow \text{H}_2, \text{C}_2 \rightarrow \text{H}_3, \text{C}_3 \rightarrow \text{H}_2 \] and \( \text{C}_3 \rightarrow \text{H}_3 \), respectively, because of asymmetry of emission bands. Among various transitions, \( \text{C}_3 \rightarrow \text{H}_3 \) transition found to have higher cross-section and high optical gain for all the glass matrices. It is observed that among the four glass matrices (Li, Na, K and Ca), calcium phosphate glass matrix shows higher emission cross-section for the four transitions. It is also observed that among the three mixed alkali phosphate glass matrices, sodium potassium phosphate glass matrix shows higher emission cross-section for the four transitions. The results of the present investigations reveal that calcium and sodium potassium glasses are more suitable for laser excitation. From the emission spectra, the branching ratios are determined by measuring the area of the corresponding emission band and dividing by the total integrated area of all the emission bands. These experimental and calculated (from the Judd-Ofelt method) branching ratios \( (\beta) \) are presented in Table 4. From the table it is observed that \( \text{C}_2 \rightarrow \text{H}_2 \) transition of calcium phosphate glass matrix is more suitable for laser excitation.

4.5. Optical band gaps

In crystalline materials, the optical band gap \( (E_{\text{opt}}) \) values can be obtained directly from the absorption spectra. However, for amorphous materials in general, the optical absorption at the fundamental edge may be used to estimate \( E_{\text{opt}} \) values using Davis and Mott [27] theory. There are two types of optical transitions, i.e., indirect and direct, that can occur at the fundamental absorption edge of crystalline and non-crystalline materials. In the present work, the optical band gap \( (E_{\text{opt}}) \) of \( \text{Sm}^{3+} \) doped different phosphate glass matrices are obtained for both indirect and direct transitions using Davis and Mott theory, i.e., from the variation of \( (\alpha \cdot \lambda)^{1/2} \) with \( \alpha \) and \( (\alpha \cdot h \cdot \omega)^{1/2} \) with \( h \omega \), respectively. These values are 3.67, 3.66, 3.55,

![Phosphorescence spectra of Sm\(^{3+}\) doped alkali, mixed alkali and calcium phosphate glasses.](image-url)
3.82, 3.60, 3.56, and 3.78 eV for indirect and 3.76, 3.67, 3.63, 3.70, 3.62, and 3.62 eV for direct transitions for Li, Na, K, Li—Na, Li—K, Na—K, and Ca, respectively. It is observed that, calcium phosphate glass possesses higher optical band gaps ($E_{opt}$) for both direct and indirect transitions (3.78 and 3.82 eV).

5. Conclusions

The Judd–Ofelt Intensity parameter, $Q_2$ which indicates the covalency of RE–O bond is very small in alkali, mixed alkali and calcium phosphate glass matrices when compared with phosphate glass indicating decrease in covalency. The intensity parameter, $Q_2$ increase with the increase in the spectral intensity of the hypersensitive transition. From the present work, it is concluded that among the four glass matrices (Li, Na, K and Ca), calcium phosphate glass shows higher spectral intensity; among the three mixed alkali glass matrices, sodium potassium glass matrix shows higher spectral intensity for the hypersensitive transition indicating higher covalency of RE–O bond in these glass matrices. From the variation of peak wavelength of the hypersensitive transition and $Q_2$ parameter, it is concluded that there are more structural changes for sodium potassium mixed alkali glass matrix. The total radiative transition probabilities are higher for calcium glass matrix among the four glass matrices (Li, Na, K and Ca). Among the three mixed alkali phosphate glass matrices (Li–Na, Li–K and Na–K), sodium potassium glass matrix shows higher radiative transition probabilities. From the magnitude of branching ratios ($\beta$) and integrated absorption cross-sections ($\sigma$), it is concluded that lithium doped phosphate glass matrix is useful for lasing material. The emission cross-sections for the observed four emission transitions are reported and these values are much for calcium phosphate glass matrix when compared with other three glass matrices (Li, Na and K). The experimental and theoretical branching ratios for the four emission transitions are compared and they are in good agreement.

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References