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RESEARCH ARTICLE

OPTICAL INVESTIGATIONS ON Dy^{3+} ION DOPED HEAVY METAL CHLOROBORATE GLASSES FOR LASER APPLICATIONS

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ABSTRACT

Glasses have been prepared by melt-quenching technique. Optical absorption and emission spectra of 0.5 mol% Dy^{3+}doped lithium– sodium and lithium-potassium chloroborate glasses havebeen recorded. The amorphous nature of glass matrix was confirmed by XRD. Free-ion Hamiltonian model and Judd - Ofelt theory have been used to analyze the energy level scheme and the spectral intensities of Dy^{3+} ion in these glasses. The intensities of f-f transitions are parameterized in terms of Judd-Ofelt (JO) intensity parameters Ω_λ (λ = 2, 4 and 6). The JO parameters obtained have been further used to predict radiative propertiessuch as total radiative transition probabilities (A_T), radiative lifetimes (τ_R), branching ratios (β_R) and integrated absorption cross-sections (Σ)forall the excited states of theseDy^{3+}doped glasses. Photoluminescence spectra consist of two bands due to $^4F_{9/2}\rightarrow$ $^6H_{15/2}$(blue) and $^4F_{9/2}\rightarrow$ $^6H_{13/2}$(yellow). The stimulated emission cross-sections(σ_p)are also evaluated for all theobserved emission transitions. Optical band gaps (Eopt) for both direct and indirect transitions are reported. The rare-earth doped glasses with variousvisible emissions are useful for developing new color light sources, fluorescent display devices, UV-sensor and tunablevisible lasers.

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INTRODUCTION

Rare earth doped glasses in recent years are found to be more attracting, due to their potential application in optical devices, solid-state lasers, optical fibers and optical memory devices (Pisarski *et al*., 2005; Lakshminarayana and Buddhudu, 2006; Eraiah and Bhat, 2007). Over the past few years, in the study of borate based glasses there has been enhanced interest due to their structural and optical properties. The suitable interesting characteristic of the borate glasses is the appearance of variations in its structural properties when alkaline or alkaline-earth cations are introduced (Kamitsos and Karakassides, 1989; Motke *et al*., 2002; An *et al*., 2008). The characteristics desired for good laser performance are high gain, energy storage capacity and low optical losses. Gain and stored energy depends on the stimulated emission cross-section, fluorescence lifetime and coupling efficiency of the pumping. Heavy metal oxide based glasses are very attractive hosts for RE ions with important characteristics for photonic application because of low transition temperature, large spectral transition window and low phonon energy (Kamitsos *et al*., 1987). The addition of PbO is expected to make these glasses more moisture resistant and also modifiers have the ability to form stable glasses due to its dual role (Srinivasa Rao and Veeraiah, 2002; Raghavaiah *et al*., 2004). The infrared (IR) harmonic and anharmonic electron–phonon modes are expected to contribute significantly to the nonlinear optical susceptibilities in these glasses (Raghavaiah *et al*., 2004). The phenomenon of mixed alkali effect is useful for preparation of low loss electrical glass and in understanding the chemical strengthening of glass (Dietzel, 1983). Among the RE ions, trivalent dysprosium (Dy^{3+}) doped glasses have been considered as promising materials for two-color phosphors and white light emission. The photo luminescencespectrumofDy^{3+} consists of two relatively intense bands in the visible spectral region that correspond to $^4F_{9/2}\rightarrow$ $^6H_{15/2}$ (blue) and $^4F_{9/2}\rightarrow$ $^6H_{13/2}$ (yellow) transitions and another red luminescence band which corresponds to $^4F_{9/2}\rightarrow$ $^6H_{11/2}$ transition. The optical absorptionandfluorescencestudiesofDy^{3+} doped lead telluroborateglasses were reported by Vijaya Kumar *et al*. (2012). Luminescence quenching of Dy^{3+}ions inlead bismuth glasses were studied by Pisarski *et al*. (2012). The luminescence spectraofDy^{3+} ions in heavy metalglasses and

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glass ceramics were investigated by Mohanbabu *et al*. (2011) and Babuetal, (2010). Optical absorption and photoluminescence properties of Dy^{3+} doped heavy metal borate glasses-effect of modifier oxides was studied by Sasi kumar *et al*. (2013). Optical absorption and luminescence characteristics of Dy^{3+} doped zinc alumino bismuth borate glasses for lasing materials and white LEDs were investigated by Swapna *et al*. (2013). The structural and photoluminescence properties of Dy^{3+} doped different modifier oxide-based lithium borate glasses were reported by Balakrishna *et al*. (2012). In this contribution, the author is interested to ascertain the characteristic spectroscopic properties of Dy^{3+} doped lithium sodium and lithium potassium heavy metal mixedalkali chloroborate glasses. J- O parameters ($\Omega_{2,}$ Ω_4 and Ω_6) have beencalculated from f_{exp} and f_{cal} values of absorption spectra. From these three parameters, various radiative properties like total radiative transition probabilities (A_T), radiative lifetimes (τ_R), branching ratios (β_R) and peak emission cross-sections (σ_P) are measured. Variation of these parameters with the glass composition has been reported and discussed.

MATERIALS AND METHODS

Heavy metal oxide (PbO)based highly transparent glass systems in the generalcomposition of65.5B_2O_3. x LiCl.(30-x) NaCl. 5 PbO. 0.5 Dy_2O_3 (lithium-sodium) and 65.5B_2O_3.xLiCl. (30-x) KCl. 5PbO. 0.5 Dy_2O_3 (lithium- potassium) Where x=5, 10, 15, 20 and 25) have recently been developed.The starting materials used in the preparation are H_3BO_3, LiCl, NaCl, KCl, PbO and Dy_2O_3. About 6 grams of the batch composition was powdered in an agate mortar. This fine powder was taken into porcelain crucible and placed in a furnace at a temperature of 900-1000^{0}C for 1-2 h. After that melt was poured between two well polished brass plates and samples were obtained. Furhter, these samples were polished for optical studies. The densities of the glasses were determined by Archimedes' principle using xyline as immersion liquid. Absorption spectra were recorded on a JASCO-V570 spectrophotometer in the wavelength range 400-1800 nm. The luminescence spectra were obtained under excitation wavelength348nm for Dy^{3+} using SPEX Fluorolog – 2 fluorometer (Model –II). All these measurements are taken at room temperature.

RESULTS AND DISCUSSION

Optical absorption Spectra

The room temperature optical absorption spectra of Dy^{3+} ion doped lithium-potassium heavy metal chloroborate glasses for different x values are shown in Fig.1. In the present work, seven absorption peaks are obtained and their assignments for Dy^{3+} ion are shown in Fig. 1. The characteristic feature of J-O parameter (Judd, 1962; Ofelt, 1962), Ω_2 is that it is sensitive to the local environment of the RE ion. The Ω_4 and Ω_6 parameters represent the rigidity of the medium. The values of Judd-Ofelt intensity parameters are presented in Table 1 for all the glass matrices. It is observed that Ω_2 parameter is minimum at x=15 mol% in both lithium-sodium and lithium-potassium glass matrices indicating lower covalency of RE-O bond at equal mol%. Ω_6 parameter is also minimum at x=15 mol% in both the glass matrices indicating lower rigidity of the glass matrices. For Dy^{3+} ion, in the case of lithium-sodium glass matrix, Ω_2, Ω_4 and Ω_6 decreased at x=10-15 mol% and then increased at x=20-25 mol%. For lithium-potassium glass matrix these parameters increased at x=10 mol% and then decreased at x=15 mol% and further increased at 20-25 mol%.

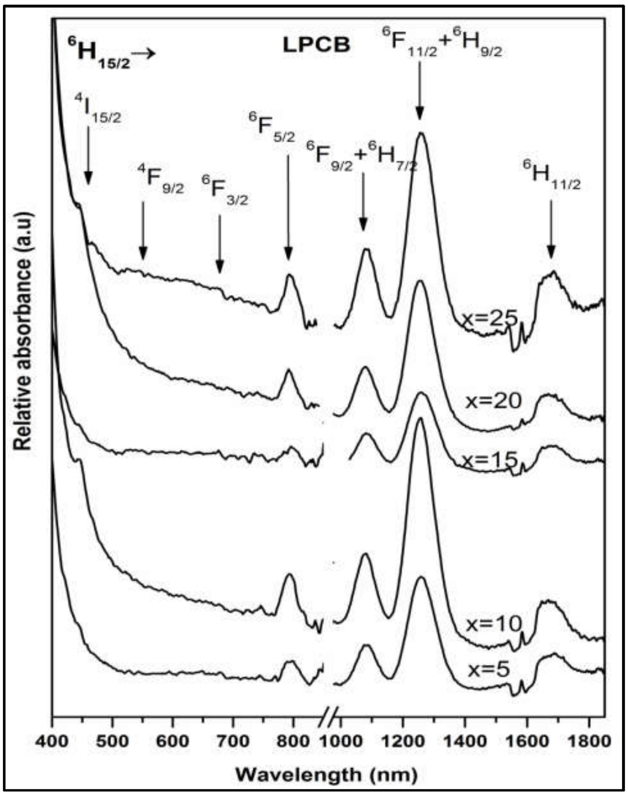

Fig. 1. Optical absorption spectra of Dy^{3+} doped lithium–potassium heavy metal chloroborate glass matrices

XRD profile

The XRD patterns of Dy^{3+} doped glass samples do not contain any sharp peaks which conforms the amorphous nature of the glass samples as shown in Fig.2. The diffract grams of other samples are also similar in shape.

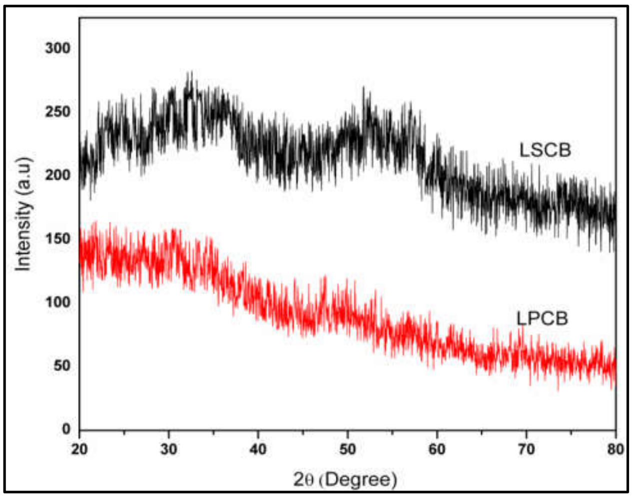

Fig. 2. XRD spectra of LSCB and LPCB host glass matrices

Hypersensitive transitions

$^6H_{15/2}\rightarrow(^6F_{11/2},^6H_{9/2})$ is the hypersensitive transition for Dy^{3+} ion. The position and spectral intensity of the hypersensitive transition is sensitive to the environment of the rare earth ion (Tanabe *et al*., 1992). In this contribution, from the variation of shift in peak wavelength of the hypersensitive transition and Ω_2 parameter with x in the glass matrix, it is observed that there are some structural variations at x=5-10 mol% in Dy^{3+} doped lithium- sodium glass matrix. But in lithium-potassium glass matrix, the structural changes are influencing the covalency of Dy-O bond at x=5-10, 10-15 and 15-20 mol%.

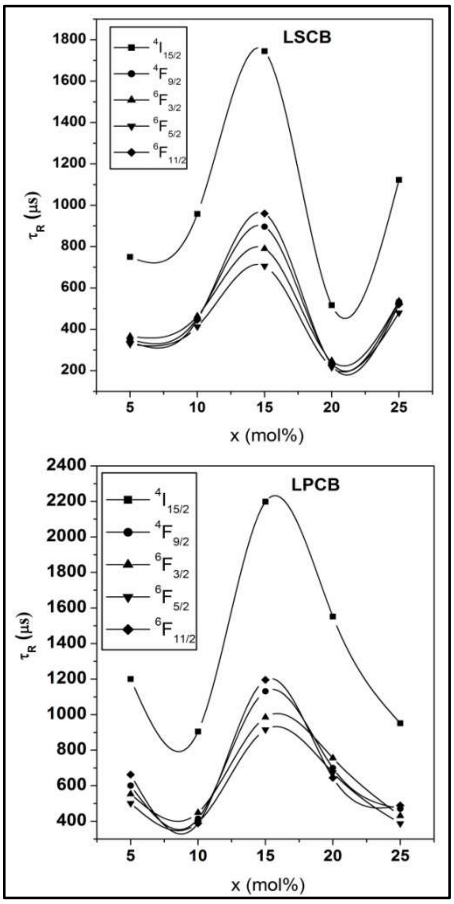

Fig. 3. Variation of radiative lifetimes (τ_R) with the variation of x in lithium- sodium and lithium-potassium heavy metal chloroborate glass matrices

Radiative lifetimes

The Judd-Ofelt intensity parameters were used to calculate the radiative lifetimes of the excited states, $^4I_{15/2}$, $^4F_{9/2}$,$^6F_{3/2}$, $^6F_{5/2}$ and$^6F_{11/2}(^6H_{9/2})$of Dy^{3+}ion. Among these states, $^4I_{15/2}$ has higher and $^6F_{5/2}$ has lower lifetimes. It is also observed that for Dy^{3+} ion, the lifetime values are maximum at x=15 mol% in both the glass matrices. Table 2 gives branching ratios (β_R) and integrated absorption cross-sections ($\sum$) of certain transitions for different x values in both the glass matrices. In the case of Dy^{3+} ion, $^4F_{11/2}\rightarrow{}^6H_{15/2}$ transition consists of higher branching ratios at x=5 mol% in LSCB and at x=20 mol% in LPCB glass matrices. Fig. 3 shows the variation of life time values with the variation of x in LSCB and LPCB glass matrices.

Emission spectra

Fig. 4 shows the photo luminescence spectra ofDy^{3+} ion in lithium-potassium glass matrix for different x values in the glass matrix. Due to similar profile of the emission spectra, the spectra Dy^{3+} ions in lithium- sodium glass matrix are not shown. In the emission spectra, two peaks are observed and these are designated as $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$. Peak stimulated emission cross-sections (σ_p) are obtained for all the observed transitions in all the glass matrices and are presented in Table3. For Dy^{3+} ion, $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition shows higher emission cross-section. Among five glass compositions, at x=20 mol% and at x=10 mol%, this transition shows higher cross sections for lithium-sodium and lithium-potassium glass matrices as compared to those reported by Murthy *et al*. (2010) for phosphate glass. Hence this transition is most suitable for laser excitation at these compositions.

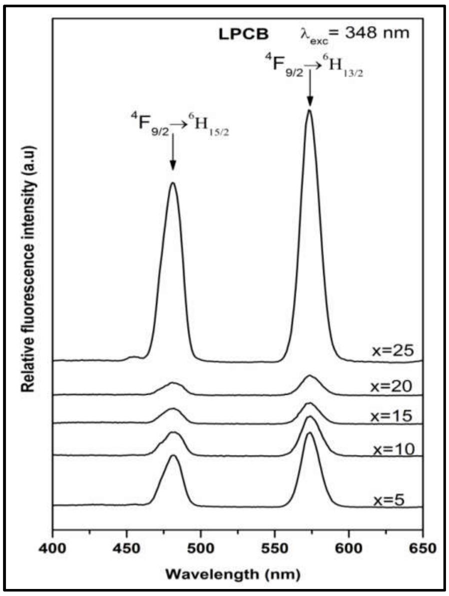

Fig. 4. Emission spectra of Dy^{3+}doped lithium- potassium heavy metal chloroborate glass matrices

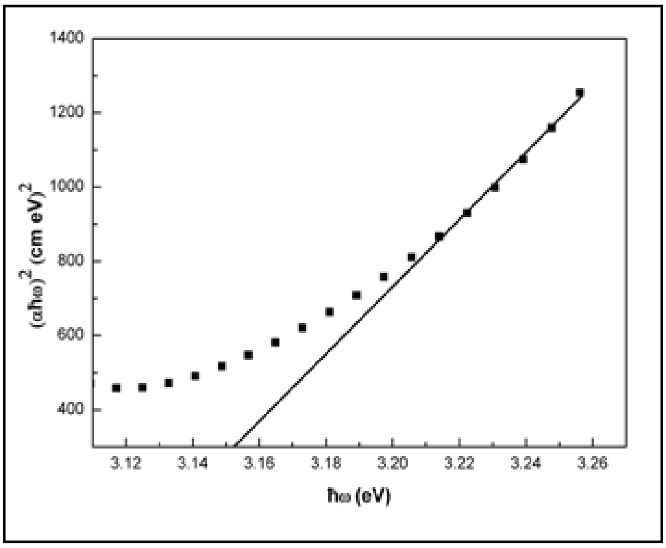

Fig. 5. Variation of $(\alpha\hbar\omega)^2$ with $\hbar\omega$ in Dy^{3+} doped lithium-sodium heavy metal chloroborate glass matrix (X=5 mol%)

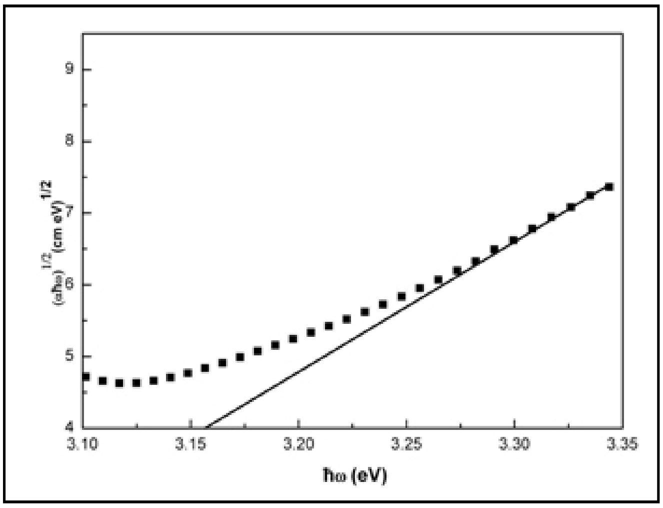

Fig. 6. Variation of $(\alpha\hbar\omega)^{1/2}$ with $\hbar\omega$ in Dy^{3+} doped lithium-sodium heavy metal Chloroborate glass matrix (X=5 mol%)

Optical band gaps

Optical band gap (Eopt) values for both direct and indirect transitions of Dy^{3+}doped lithium sodium and lithium potassium heavy metal mixed alkali chloroborate glasses are obtained. The variation of $(\alpha\hbar\omega)^2$ with $\hbar\omega$ and $(\alpha\hbar\omega)^{1/2}$ with $\hbar\omega$ for x=5 mol % glass composition of LSCB glass matrixis shown in Figs.5 and 6 respectively. The optical band gap values (Eopt) (eV) for both direct and indirect transitions of Dy^{3+} doped LSCB and LPCB glasses for different x values in the glass matrices are given below.

x	Direct band gap		Indirect band gap	
(in mol%)	LSCB	LPCB	LSCB	LPCB
5	3.15	2.87	3.15	2.81
10	3.07	3.05	2.97	2.97
15	2.77	2.80	2.75	2.80
20	2.94	2.89	2.86	2.83
25	3.16	3.06	3.16	2.91

Table 1. Judd-Ofelt intensity parameters ($\Omega_\lambda \times 10^{20}$) ($cm^2$) of Dy^{3+} doped Lithium-Sodium and lithium potassium heavy metal chloroborate glasses (x in mol%)

S.No.	Parameter	Lithium-sodium					Lithium-potassium				
		x = 5	x = 10	x = 15	x = 20	x = 25	x = 5	x = 10	x = 15	x = 20	x = 25
1	Ω_2	18.13	13.79	6.15	26.63	11.70	9.73	15.46	5.03	9.13	12.21
2	Ω_4	4.79	3.80	1.82	7.75	3.22	1.69	4.75	1.34	3.09	3.45
3	Ω_6	4.48	3.59	2.29	6.63	3.07	3.37	3.45	1.78	1.94	4.01

Table 2. Branching ratios (β_R) and integrated absorption cross-sections (∑) of certain transitions of Dy^{3+} doped lithium sodium and lithium potassium heavy metal chloroborate glasses (x in mol%)

S.No	Transition	Parameter	Lithium sodium					Lithium potassium				
			x=5	**x=10**	**x=15**	**x=20**	**x=25**	**x=5**	**x=10**	**x=15**	**x=20**	**x=25**
1	${}^4I_{15/2} \rightarrow {}^6H_{15/2}$	β	0.667	0.669	0.704	0.662	0.671	0.728	0.642	0.705	0.628	0.694
		∑	0.86	0.68	0.39	1.26	0.58	0.59	0.68	0.31	0.39	0.71
2	${}^4F_{9/2} \rightarrow {}^6H_{13/2}$	β_{exp}	0.706	0.701	0.675	0.703	0.701	0.687	0.709	0.680	0.710	0.685
		β_{cal}	(0.632)	(0.615)	(0.608)	(0.599)	(0.609)	(0.580)	(0.628)	(0.587)	(0.602)	(0.584)
		∑	3.10	2.38	1.17	4.59	2.03	1.76	2.62	0.93	1.55	2.24
3	${}^6F_{3/2} \rightarrow {}^6H_{13/2}$	β	0.470	0.474	0.508	0.466	0.474	0.528	0.446	0.507	0.430	0.497
		∑	6.33	5.06	3.21	9.33	4.35	4.74	4.88	2.52	2.76	5.67
4	${}^6F_{5/2} \rightarrow {}^6H_{15/2}$	β	0.494	0.497	0.540	0.486	0.498	0.567	0.462	0.543	0.445	0.526
		∑	4.65	3.73	2.37	6.89	3.20	3.49	3.59	1.84	2.02	4.17
5	${}^6F_{11/2} \rightarrow {}^6H_{15/2}$	β	0.922	0.921	0.911	0.922	0.921	0.914	0.924	0.913	0.925	0.915
		∑	20.91	16.01	7.37	31.23	13.62	10.68	18.29	5.91	11.03	14.45

Table 3. Certain fluorescence properties of Dy^{3+}doped lithium sodium and lithium potassium heavy metal chloroborate glasses (x in mol%)

S. No	Glass	${}^4F_{9/2} \rightarrow {}^6H_{15/2}$				${}^4F_{9/2} \rightarrow {}^6H_{13/2}$			
		λ_P (nm)	A_{rad} (s^{-1})	Δν (cm^{-1})	σ_P (cm^2) $\times 10^{-21}$	λ_P (nm)	A_{rad} (s^{-1})	Δν (cm^{-1})	σ_P (cm^2) $\times 10^{-21}$
	Lithium sodium								
1	x=5	481	434	739	0.667	574	2008	514	6.296
2	x=10	481	346	699	0.563	574	1540	490	5.074
3	x=15	481	212	699	0.345	574	753	500	2.435
4	x=20	481	651	697	1.059	574	2974	489	9.788
5	x=25	481	296	699	0.481	573	1313	489	4.328
	Lithium potassium								
6	x=5	481	301	662	0.518	573	1141	431	4.282
7	x=10	481	350	697	0.569	574	1706	486	5.652
8	x=15	481	164	684	0.272	573	601	471	2.057
9	x=20	481	203	724	0.319	573	1013	477	3.413
10	x=25	481	379	625	0.687	573	1454	435	5.381

It is found that the optical band gap values are minimum at x=15 mol% and maximum at x=25 mol% for direct transition in both LSCB and LPCB glass matrices. For indirect transitions, the optical band gaps are minimum at x=15 mol% and maximum at x=25 mol% in LSCB glass. In LPCB glass, these optical band gaps are found to be the highest at x=10 mol%.

Conclusion

In the high transparent, moisture resistant and stable lithium-sodium and lithium-potassium heavy metal chloroborate glass matrices, the magnitudes of Ω_2 and Ω_6 parameters show minimum at x=15 mol% i.e at equal mol% of alkali contents indicating that covalency of rare earth oxygen bond and rigidity of the glass matrices are minimum. From the variation of shift in peak wavelength of the hypersensitive transition and Ω_2 parameter with x in the glass matrix, it is observed that there are some structural variations in lithium-sodium chloroborate glass matrix. In the case of lithium-potassium glass, structural adjustments are influencing the covalency of Dy-O bond at x=5-10, 10-15 and 15-20 mol%. From the magnitude of peak emission cross sections, the emission transition, $^4F_{9/2}\rightarrow{}^6H_{13/2}$ at x=20 mol% and at x=10 mol% in lithium-sodium and lithium-potassium glass matrices respectively, the corresponding glass are found to be useful for better luminescent material.

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