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Spectroscopic characteristics of Sm^{3+} doped alkaline earth potassium titanium phosphate glasses

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The paper reports on the preparation and characterization of Sm^{3+} doped alkaline earth potassium titanium phosphate (RKTP) glasses with molar composition of $24(NaPO_3)_6 + 30KH_2PO_4 + 25TiO_2 + 20RCl_2 + 1Sm_2O_3$ (R=Mg, Ca & Sr). Optical absorption spectra in the UV-VIS-NIR region reveal twelve absorption bands and are assigned to different transitions arising from the $^6H_{5/2}$ ground state. The energy level structure of Sm^{3+} ($4f^5$) has been analyzed using the free-ion Hamiltonian model. The root mean square deviations between the experimental and calculated energies of Sm^{3+} doped MgKTP, CaKTP and SrKTP glasses are 44, 35 and 56 cm^{-1} respectively and are comparable with the earlier reports. By measuring the areas under the absorption peaks, the experimental oscillator strengths are calculated and the phenomenological JO-intensity parameters (Ω_2, Ω_4 and Ω_6) have been determined with the help of least-squares fitting approach. These parameters exhibit a similar trend as $\Omega_2>\Omega_6>\Omega_4$ in all the three glasses. The evaluated JO parameters are then used to calculate the excited $^4G_{5/2}$ level radiative properties such as radiative transition probabilities (A_R), branching ratios (β_R) and lifetimes (τ_R). The emission spectra recorded by exciting with 476 nm shows four peaks at 563, 599, 649 and 714 nm and are assigned to $^4G_{5/2} \rightarrow {^6H_{5/2}}, {^6H_{7/2}}, {^6H_{9/2}}, {^6H_{11/2}}$ respectively. The experimentally observed decay profiles of the $^4F_{5/2}$ level of Sm^{3+} are found to be single exponential yielding the lifetimes (τ_{mes}) 2330, 1750 and 2320 µs in MgKTP, CaKTP and SrKTP glasses respectively, which are comparable with the calculated lifetimes (τ_R) obtained from the Judd-Ofelt theory.

Glasses doped with rare-earth (RE) ions are well known as fluorescent materials with high luminescence behaviour for potential applications in for fiber amplifiers, lasers, sensors, quantum electronic devices etc.[1]. The luminescence signal from these materials provides characteristic lines determined by the electronic structure of the RE^{3+} energy levels, which are almost independent of the host matrix. However, the linewidth and the relative intensities of these lines are frequently affected by the nature of the matrix; in such a way that some lines are present while others are inactive. This feature can be used to tune the emission of radiation of the material depending on its practical applications. Thus, it is important to pursue research studies on RE luminescence hosts in different types of matrices.

Experimental Procedure

The glass composition used in the present study is 24 $(NaPO_3)_6$ + 30 KH_2PO_4 + 25 TiO_2 + 20 RCl_2 + 1 Sm_2O_3 (R=Mg, Ca and Sr) in mol %. Commercial reagent grade chemicals were grinded thoroughly and melted in an electric furnace at 975°C for 45 min. Then the melt was carefully quenched onto a brass plate at 425°C and pressed with another plate and kept for annealing for 4 h. Densities of the glasses were measured using Archemedie's principle and refractive indices with Abbe refractometer using 1-bromonapthalene as contact liquid. The physical properties[2] measured for these glasses are presented in Table 1.

The optical absorption spectra were measured in the region 350-800 nm using Varian Cary 5E UV-VIS-NIR spectrophotometer. The fluorescence spectrum in the wavelength region 500-750 nm was obtained by exciting the samples at 476 nm wavelength of a Xenon flash lamp using Hitachi F-3010 fluorescence spectrophotometer. Lifetime measurements were done by exciting the glass samples at 476.5 nm line of an Ar^+ laser. Decay curves were obtained using a mechanical chopper with a multi channel scalar interfaced to a personal computer which records and averages the signal at room temperature.

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Results and Discussion

Figure 1 shows the absorption spectra of Sm^{3+} doped RKTP glasses in UV-VIS-NIR regions in the wavelength range of 350-1800 nm. Observed twelve energy bands originating from the ground $^6H_{5/2}$ state are indicated with their respective terminal states. The energy levels of Sm^{3+} in RKTP glasses are analysed using free-ion Hamiltonian model as a sum of different interactions[3]. Using the areas under the individual peaks, experimentally measured oscillator strengths (f_{exp}) of the absorption bands are determined. Judd-Ofelt (JO) theory[4,5] has been applied to find JO intensity parameters from the measured oscillator strengths. Since the doubly reduced matrix elements are constant for particular ion and are not dependent on host matrix, we used the reduced matrix elements reported by Jayasankar and Rukmini[6] for Sm^{3+} ions, in our least square fit to find JO parameters.

Table 1—Various physical properties of Sm^{3+} doped RKTP glasses

Physical Property	MgKTP	CaKTP	SrKTP
Optical path length (cm)	0.184	0.188	0.167
Density (g/cc)	2.727	2.806	2.976
Refractive index	1.574	1.580	1.580
Concentration x10^{20} (ions/cc)	1.304	1.405	1.355
Polaron radius (A^o)	7.947	7.752	7.846
Inter nuclear distance (A^o)	19.720	19.240	19.469
Field strength x10^{14} (cm^{-2})	4.750	4.992	4.873
Molecular refractivity of glass	27.81	27.66	29.54
Molecular electronic polarizability factor x 10^{-22}(cm^3)	5.813	5.656	5.859
Dielectric constant	2.476	2.497	2.497
Reflection losses (%)	4.97	5.06	5.06

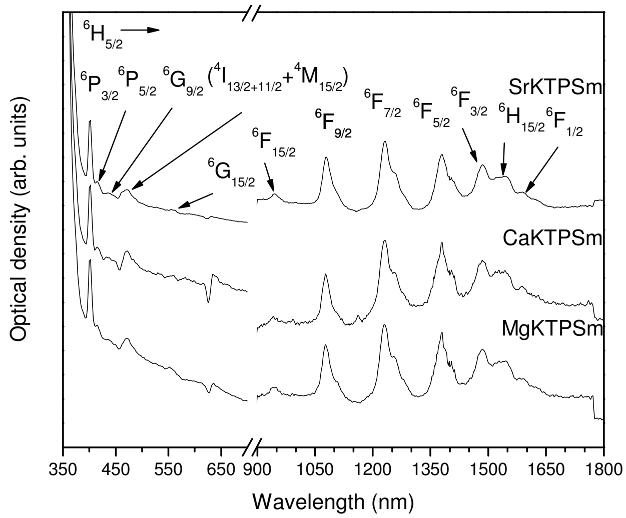

Fig. 1— Absorption spectra of Sm^{3+} doped RKTP glasses in UV-vis-NIR regions

Table 2—Experimental and calculated energy positions (cm^{-1}) and oscillator strengths($\times10^{-6}$) of absorption bands from ground $^6H_{5/2}$ state of Sm^{3+} doped RKTP glasses

Transition	Energy Positions						Oscillator Strengths					
$^6H_{5/2}\rightarrow$	MgKTP		CaKTP		SrKTP		MgKTP		CaKTP		SrKTP	
	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
$^6P_{3/2}$	24876	24857	24876	24863	24876	24865	5.61	5.24	4.93	5.00	5.66	5.13
$^6P_{5/2}$	24160	24142	24160	24148	24160	24133	0.25	0.80	0.43	0.76	0.40	0.78
$^6G_{9/2}$	22936	22942	22936	22937	22936	22921	0.46	0.10	1.06	0.08	0.34	0.10
$^6I_{13/2+11/2}+^4M_{15/2}$	21272	21243	21272	21241	21277	21225	1.92	1.54	2.46	1.25	1.89	1.50
$^6G_{15/2}$	18116	18168	18116	18165	18051	18145	0.47	0.02	0.29	0.15	0.21	0.02
$^6F_{11/2}$	10593	10668	10616	10668	10582	10666	0.61	0.59	0.40	0.48	0.48	0.57
$^6F_{9/2}$	9276	9271	9276	9272	9259	9270	3.31	3.62	2.64	2.94	3.39	3.51
$^6F_{7/2}$	8130	8087	8117	8086	8117	8086	5.36	5.19	4.50	4.38	5.10	5.04
$^6F_{5/2}$	7246	7228	7246	7228	7246	7228	2.42	2.63	2.46	2.48	2.43	2.56
$^6F_{3/2}$	6730	6768	6739	6769	6739	6770	1.51	1.35	1.17	1.18	1.33	1.27
$^6H_{15/2}$	6545	6557	6545	6558	6579	6558	1.16	0.03	1.00	0.02	1.09	0.03
$^6F_{1/2}$	6321	6280	6297	6274	6297	6267	0.17	0.26	0.11	0.10	0.16	0.18
σ_{rms}	±44		±35		±56		±0.45		±0.55		±0.39	

The best-fit free-ion parameters (cm^{-1}) are: E_{avg}=46324, F_2=81250, F_4=52562, F_6=34574, ξ=1144, α=21.55, β=-717 γ=1668, T^2=283, T^3=30, T^4=100, T^6=-231, T^7=265, T^8=319, M_{TOT}=2.34, P_{TOT}=315

Table 2 gives the experimental and calculated energy positions using free-ion Hamiltonian model and oscillator strengths of the absorption bands from ground $^6H_{5/2}$ state of Sm^{3+} doped RKTP glasses. The foot note gives various parameters used while fitting the free-ion Hamiltonion model. The relatively low rms deviations of experimental and calculated values of both the energy positions and oscillator strengths reveal the good fit between the experimental and theoretical values.

JO intensity parameters (Ω_λ) are host dependent. Table 3 gives the list of Ω_λ of RKTP along with other reported systems including Ω_4/Ω_6, the spectroscopic quality factors. It is observed that the magnitude of Ω_λ parameters are in the order $\Omega_4>\Omega_6>\Omega_2$ in all the hosts. In addition, the order of increase of Ω_2 in CaKTP→SrKTP→MgKTP glasses infers that, the site symmetry around Sm^{3+} ion decreases in the same order.

Emission spectra of the Sm^{3+} doped RKTP glasses excited with 476 nm wavelength are shown in Fig. 2. The three spectra exhibit four peaks emitting from $^4G_{5/2}$ level to $^4H_{5/2}$, $^4H_{7/2}$, $^4H_{9/2}$ and $^4H_{11/2}$ levels at 563, 599, 645 and 714 nm respectively. Out of these $^4G_{5/2}\rightarrow{}^4H_{11/2}$ is of very low intensity and $^4G_{5/2}\rightarrow{}^4H_{7/2}$ is of high intensity. Using the Ω_λ parameters radiative properties of RKTP glasses are calculated. These are given in Table 4. The radiative lifetimes for $^4G_{5/2}$ level of RKTP glasses are found to be 2958, 3326 and 3043 µs for MgKTP, CaKTP and SrKTP respectively. The experimental branching ratios are found by dividing the individual area of emission peak by the total area covered under all emission peaks. These are comparable to the radiative branching ratios.

Figure 3 gives the decay curves of $^4G_{5/2}$ level of Sm^{3+} doped RKTP glasses excited at 476.5 nm and emission recorded at 599 nm. All the curves are found to be nearly single exponential. The first e-folding time of the emission intensities are taken as the measured fluorescence lifetimes of the glasses. The measured lifetimes are found to be 2380, 1750 and 2320 µs for MgKTP, CaKTP and SrKTP glasses respectively. This results in quantum efficiencies of 79%, 53% and 76 % for the Sm^{3+} ions in respective

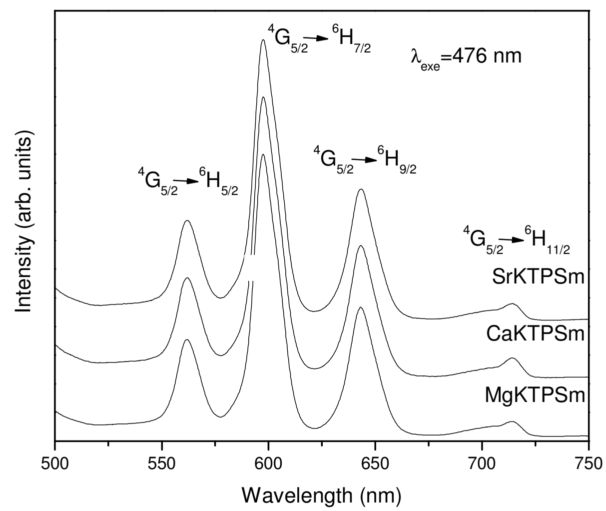

Fig. 2—Visible emission spectra of Sm^{3+} doped RKTP glasses

Table 3—Comparison of JO parameters Ω_λ($\times10^{-20}$ cm^2) of RKTP glasses with different hosts

Parameter	MgKTP (Present)	CaKTP (Present)	SrKTP (Present)	ZnBS[6]	LiTFP[7]	NaTFP[7]	KTFP[7]	Tellurite[8]	PbO-PbF$_2$[9]	Aquo-ion[10]
Ω_2	0.818	0.334	0.576	0.290	0.042	0.082	0.156	0.006	1.160	0.900
Ω_4	4.889	4.642	4.770	3.820	3.496	3.272	2.443	0.339	2.600	4.100
Ω_6	4.168	3.331	4.032	3.650	2.368	2.469	1.764	0.243	1.400	2.700
Ω_4/Ω_6	1.173	1.394	1.183	1.047	1.476	1.325	1.385	1.395	1.857	1.519

Table 4—Emission peak wavelength (λ_p, nm), radiative transition probabilities (A_R, s^{-1}), stimulated emission cross-sections ($\sigma_e\times10^{-22}$ cm^2) and branching ratios (β) of Sm^{3+} doped RKTP glasses

Transition $^4G_{5/2}\rightarrow$	λ_p	MgKTP				CaKTP				SrKTP			
		A_R	σ_e	β_{exp}	β_{cal}	A_R	σ_e	β_{exp}	β_{cal}	A_R	σ_e	β_{exp}	β_{cal}
$^6H_{5/2}$	563	22.48	0.892	0.165	0.067	22.09	0.836	0.181	0.074	22.42	0.857	0.169	0.068
$^6H_{7/2}$	599	167.02	8.089	0.540	0.494	150.04	6.901	0.581	0.499	164.55	7.767	0.532	0.501
$^6H_{9/2}$	645	77.83	4.465	0.278	0.230	65.09	5.129	0.213	0.217	72.87	4.149	0.279	0.222
$^6H_{11/2}$	714	40.42	6.547	0.017	0.120	37.26	5.634	0.025	0.124	39.82	6.499	0.020	0.121

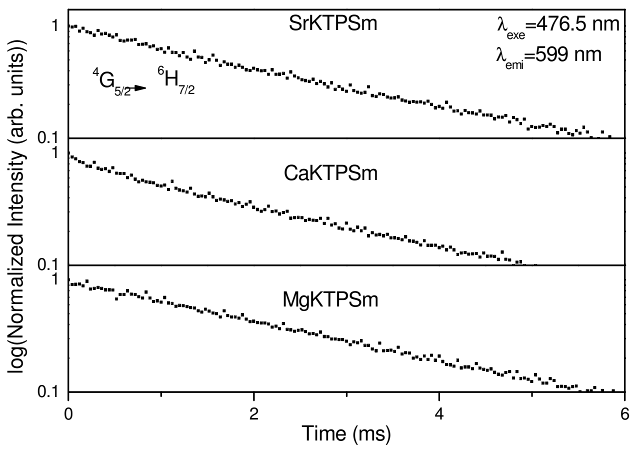

Fig. 3— Fluorescence decay profile of $^4G_{5/2}$ state of Sm^{3+} in RKTP glasses

glasses. As the decay curves are single exponential the difference in the radiative and measured lifetimes may be attributed to the multiphonon relaxation in these glasses. From the lifetime data the estimated multiphonon relaxation rates[11](W_{MP}) are 82, 270 and 102 s^{-1} for Sm^{3+} doped MgKTP, CaKTP and SrKTP glasses respectively.

Conclusions

The present work elucidates the spectroscopic characteristics of Sm^{3+} RKTP glasses by applying free-ion Hamiltonian model and JO theory to the energy level positions and intensities obtained from the absorption spectra. The emission plots show intense red and orange emission in these glasses, which are useful as laser materials in the visible region. These can be used to design lasers for strong orange-red emission.

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