

SPECTROSCOPIC PROPERTIES OF SAMARIUM DOPED POTASSIUM ALUMINIUM PHOSPHATE GLASSES

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Abstract

In this work, potassium aluminium phosphate ($K_2O-Al_2O_3-P_2O_5$) glasses doped with various concentrations of samarium oxide (Sm_2O_3) were prepared by melt-quenching technique. The structural, optical and luminescence properties of the glass samples were characterized through the molar volume, absorption and emission spectra measurements, respectively. The absorption spectra were investigated in the ultraviolet - visible light - near infrared (UV-Vis-NIR) region from 250 to 2,000 nm. The emission spectra were observed four prominent emission bands centered at 561, 597, 643, and 704 nm by excitation at 402 nm. From the Judd-Ofelt (J-O) analysis, the J-O parameters (Ω_2 , Ω_4 and Ω_6), oscillator strength (f), radiative transition possibility (A_R), stimulated emission cross section ($\sigma(\lambda_p)$) and branching ratio (β_R) were determined to investigate the local structure and bonding in the vicinity of Sm^{3+} ions, including quality of a glass host for using as the optical device application.

Keywords: Samarium oxide, Judd-Ofelt analysis, luminescence and optical properties

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Introduction

Oxide glasses containing trivalent rare earth (RE^{3+}) ions are the promising luminescent materials for optical and photonic device applications due to their intense emissions in the visible light and near infrared regions under suitable excitation (Linganna and Jayasankar; Nanda *et al.*, 2016). Trivalent samarium (Sm^{3+}) ion is one of the most interesting RE^{3+} ions to analyze the spectroscopic and radiative properties because of its luminescent $^4\text{G}_{5/2}$ level exhibiting relatively high quantum efficiency and its can be used in the compact fiber lasers, high-density optical storage, planner waveguides, under sea communication and color displays (Srinivasa Rao and Jayasankar, 2013; Rajaramakrishna *et al.*, 2014).

Among the available glasses, phosphate glasses are regarded as better hosts for Sm^{3+} ions compared to silicate glasses due to their excellent properties such as high thermal expansion coefficient, lower melting temperature, high transparency and more solubility of RE^{3+} ions (Srinivasa Rao and Jayasankar, 2013; Vijayakumar and Marimuthu, 2015), but it possesses the poor chemical durability and corrosion. To enhance the chemical durability of phosphate glasses, it was added with metal oxide such as lithium oxide (Li_2O), sodium oxide (Na_2O), potassium oxide (K_2O), barium oxide (BaO) and aluminium oxide (Al_2O_3), which lead to the formation of new bonds (Praveena *et al.*, 2008; Srinivasa Rao *et al.*, 2011; Cherbib *et al.*, 2016). Many researchers (Srinivasa Rao *et al.*, 2011; Vijaya *et al.*, 2013; Nanda *et al.*, 2016; Deopa *et al.*, 2018; Yuliantini *et al.*, 2018) have studied and reported the optical and luminescence properties of Sm^{3+} doped glasses to evaluate their potential for using as the solid-state lighting and laser medium applications. In this work, potassium aluminium phosphate glasses doped with various concentrations of Sm_2O_3 have been fabricated. The physical, optical, luminescence properties and Judd-Ofelt analysis of the glass samples were studied to determine the potential for laser medium applications in the visible region.

Experiment

Sm^{3+} doped potassium aluminium phosphate (KASm) glasses with chemical compositions of $15\text{K}_2\text{O}:20\text{Al}_2\text{O}_3:(65-x)\text{P}_2\text{O}_5:x\text{Sm}_2\text{O}_3$, where x is 0.00, 0.05, 0.10, 0.50, 1.00 and 2.00 mol% (here after called as KASm000, KASm005, KASm010, KASm050, KASm100 and KASm200 glasses) were prepared by melt-quenching technique. The starting batch was prepared by mixing appropriate ratio of K_2CO_3 , Al_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and Sm_2O_3 as powders, about 20 g of batch compositions. The chemical batches were kept in an electric furnace for melting at $1,200^\circ\text{C}$ for 3 h. Then the melt samples were poured on to a preheated graphite mold and annealed at 500°C for 3 h. Afterwards, the glass samples were cut and finely polished to a dimension of $1.0 \times 1.5 \times 0.3$ cm to achieve good optical surfaces for the optical and spectroscopic investigations, these glass samples are presented in Figure 1.

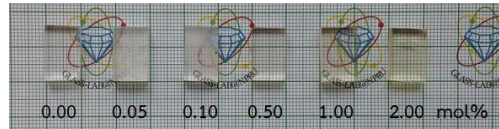


Figure 1. Photograph of glass samples

The density (ρ) of each glass sample was determined by the Archimedes method using a 4-digit sensitive microbalance (AND, HR-200). The density of glasses was calculated from formula

$$\rho = \frac{w_a}{w_a - w_b} \times \rho_b \quad (1)$$

where w_a is weight of the glass samples in air, w_b is weight of the glass samples in water, ρ_b is the density of water. The molar volume (V_m) of glass samples were calculated using the relation

$$V_m = \frac{M_T}{\rho} \quad (2)$$

where M_T is the total molecular weight of the multicomponent glasses system given by

$$M_T = x_{K_2O}Z_{K_2O} + x_{Al_2O_3}Z_{Al_2O_3} + x_{P_2O_5}Z_{P_2O_5} + x_{Sm_2O_3}Z_{Sm_2O_3} \quad (3)$$

where x_{K_2O} , $x_{Al_2O_3}$, $x_{P_2O_5}$ and $x_{Sm_2O_3}$ are the mole fractions of the constituent oxides, and Z_{K_2O} , $Z_{Al_2O_3}$, $Z_{P_2O_5}$ and $Z_{Sm_2O_3}$ are the molecular weights of the constituent oxides. The optical absorption spectra were measured by UV-Vis-NIR spectrophotometer (Shimadzu, UV-3,600) recorded in the wavelength range of 250-2,000 nm. The excitation spectra and emission spectra were measured by fluorescence spectrophotometer (Agilent Technologies, Cary Eclipse) with xenon lamp as a light source. The Judd-Ofelt theory has been used to evaluate the potential for laser applications, which calculated by measuring the area under the absorption and emission bands of glass spectra (Rajaramakrishna *et al.*, 2014; Nanda *et al.*, 2016; Yuliantini *et al.*, 2018).

Results and Discussion

The physical properties of glass samples are shown in Table 1. The result shown that the density, the molar volume and the total molecular weight of glass samples tended to increase with increasing of Sm_2O_3 concentration. This variation is a result from replacement of P_2O_5 via Sm_2O_3 in glass composition, since the higher molecular weight of Sm_2O_3 (349 g/mol) than P_2O_5 (142 g/mol) cause the density of glass samples increased. Also non-bridging oxygen (NBO) increased in the glass network on increasing of Sm_2O_3 content more than 0.10 mol% which can be explained that Sm^{3+} act as glass

modifier causing expansion of the glass molar volume (Wantana *et al.*, 2017).

The optical absorption spectra of KASm glasses are shown in Figure 2. The spectra exhibited absorption bands at 401, 440, 473, 947, 1,080, 1,233, 1,380, 1,485 and 1,537 nm were corresponding to the transitions originated from $^6H_{5/2}$ state to the various excited states, i.e., $^6P_{3/2}$, $^4G_{9/2}$, $^4I_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$ and $^6H_{15/2}$, respectively (Carnall *et al.*, 1968). Among the observed transitions, $^6H_{5/2} \rightarrow ^6F_{7/2}$ transitions are sensitive to the ligand field environment around the Sm^{3+} ion site, obeyed the selection rules of $|\Delta S|=0$, $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$, which termed as hypersensitive transitions (Deopa *et al.*, 2018). In addition, the optical absorption bands show more sharpness with increasing of Sm_2O_3 concentrations.

The excitation spectra of KASm glasses were recorded in the wavelength region 300-550 nm under emission wavelength of 597 nm as shown in Figure 3(a). The excitation spectra

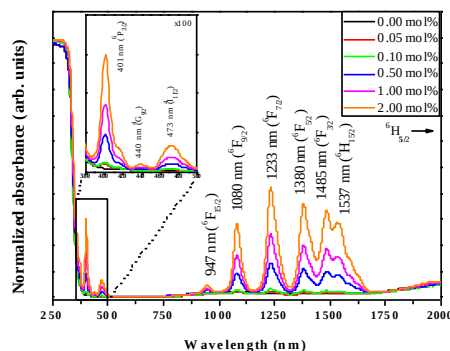


Figure 2. The absorption spectra of the glass samples in UV-Vis-NIR region

Table 1. The physical properties of glass samples

Glass samples	ρ (g/cm ³)	V_m (cm ³ /mol)	M_T (g/mol)
KASm000	2.5843±0.0001	49.0599	126.7854
KASm005	2.5850±0.0015	49.0866	126.8888
KASm010	2.5884±0.0018	49.0620	126.9922
KASm050	2.6040±0.0016	49.0858	127.8193
KASm100	2.6224±0.0023	49.1356	128.8532
KASm200	2.6557±0.0005	49.2981	130.9209

consists several bands centered at 318, 345, 362, 374, 402, 415, 438, 473 and 527 nm corresponding to the transitions of ${}^6\text{H}_{5/2} \rightarrow {}^2\text{L}_{15/2}$, ${}^4\text{K}_{15/2}$, ${}^4\text{D}_{3/2}$, ${}^4\text{L}_{17/2}$, ${}^6\text{P}_{3/2}$, $({}^6\text{P}, {}^4\text{P})_{5/2}$, ${}^4\text{G}_{9/2}$, ${}^4\text{I}_{11/2}$ and ${}^4\text{F}_{3/2}$, respectively (Carnall *et al.*, 1968). Among these, the ${}^6\text{H}_{5/2} \rightarrow {}^6\text{P}_{3/2}$ (402 nm) transition is found to be more intense than the other transitions. Hence, this wavelength (402 nm) was used as an excitation wavelength to investigate the emission spectra of glass samples as presented in Figure 3(b).

Figure 3(b) shows the emission spectra of KASm glasses in the wavelength range of 500–750 nm under 402 nm excitation wavelength. The emission spectra shows four prominent yellow, orange, reddish orange and red emission bands centered at 561, 597, 643, and 704 nm corresponding to the emission transitions ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$, ${}^6\text{H}_{7/2}$, ${}^6\text{H}_{9/2}$ and ${}^6\text{H}_{11/2}$, respectively. From the emission spectra, glass samples exhibited the strongest emission at wavelength of 597 nm. It is also noticed that the KASm glasses presented luminescence quenching after 0.50 mol% of Sm^{3+} concentration. The quenching in luminescence is mainly due to the Sm^{3+} - Sm^{3+} interactions at high Sm_2O_3 concentration and the increase in non-radiative energy transfer through cross relaxation (Nanda *et al.*, 2016).

From the JO analysis, the experimental and calculated oscillator strength of the glass samples with 0.50 mol% of Sm_2O_3 (KASm050) compared with the other reports

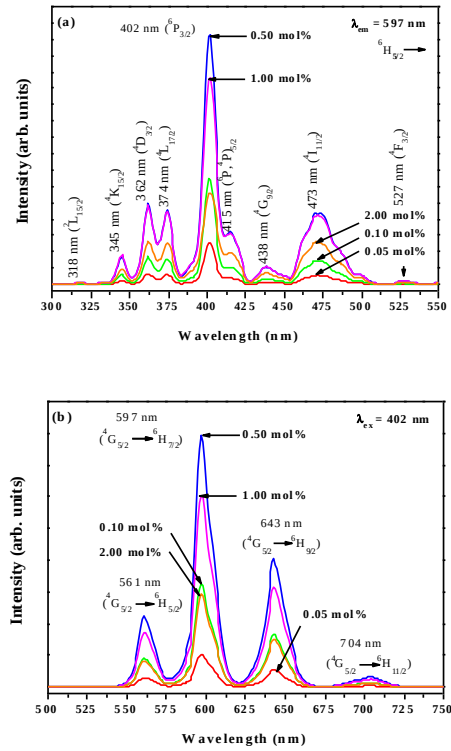


Figure 3. The excitation (a) and the emission spectra (b) of the glass samples

are shown in Table 2. The result shows that, the transition ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{7/2}$ performs the magnitude of f_{exp} and f_{cal} due to the best absorption of 1233 nm in NIR region.

Table 2. Experimental ($f_{\text{exp}} \times 10^{-6}$) and calculated ($f_{\text{cal}} \times 10^{-6}$) oscillator strengths and root mean square deviation (σ_{rms}) between calculated and experimental values of KASm050 glass with the reported Sm^{3+} ion doped glasses

Transition ${}^6\text{H}_{5/2} \rightarrow$	Wavelength (nm)	KASm050 [present work]		ZSBP0.5Sm (Vijayakumar and Marimuthu, 2015)	Borate glass (Deopa <i>et al.</i> , 2018)	ZABBSm (Yuliantini <i>et al.</i> , 2018)
		(f_{exp})	(f_{cal})	(f_{exp})	(f_{exp})	(f_{exp})
${}^6\text{P}_{3/2}$	401	3.05	3.45	-	4.34	-
${}^4\text{G}_{9/2}$	440	0.486	0.07	-	-	-
${}^4\text{I}_{11/2}$	473	1.46	0.15	1.75	0.69	-
${}^6\text{F}_{11/2}$	947	1.01	0.37	0.34	0.68	0.92
${}^6\text{F}_{9/2}$	1,080	2.48	2.29	2.89	2.79	3.21
${}^6\text{F}_{7/2}$	1,233	3.10	3.32	4.38	2.55	4.81
${}^6\text{F}_{5/2}$	1,380	2.16	1.98	1.82	2.38	3.51
${}^6\text{F}_{3/2}$	1,485	1.86	1.90	1.15	2.74	2.86
${}^6\text{H}_{15/2}$	1,537	1.45	0.02	-	-	-
σ_{rms}		± 0.72		± 0.55	± 0.85	± 0.37

Table 3. Judd-Ofelt intensity parameters Ω ($\lambda=2,4,6$) ($\times 10^{-20} \text{ cm}^2$) of KASm050 glass with other reported values

Glasses	Ω_2	Ω_4	Ω_6	Trand	Reference
KASm050	4.78	3.37	2.75	$\Omega_2 > \Omega_4 > \Omega_6$	present work
PKMASm	6.83	2.97	2.03	$\Omega_2 > \Omega_4 > \Omega_6$	(Srinivasa Rao and Jayasankar, 2013)
ZSBP0.5Sm	0.23	3.92	3.38	$\Omega_4 > \Omega_6 > \Omega_2$	(Vijayakumar and Marimuthu, 2015)
Borate glass	3.73	2.79	1.77	$\Omega_2 > \Omega_4 > \Omega_6$	(Deopa et al., 2018)
NbKZFSm10	1.19	6.71	2.48	$\Omega_4 > \Omega_6 > \Omega_2$	(Yuliantini et al., 2018)

Table 4. Comparison of emission peak position (λ_p), radiative transition possibility (A_R), stimulated emission cross-section ($\sigma(\lambda_p) 10^{-22}$), branching ratios (β_R) of KASm050 glass

Transition $^4G_{5/2} \rightarrow$	λ_p (nm)	A_R (s^{-1})	$\sigma(\lambda_p)$ (cm^2)	β_R	
				(β_{Rexp})	(β_{Rcal})
$^6H_{5/2}$	561	4.77	0.25	0.13	0.02
$^6H_{7/2}$	597	137.42	7.88	0.53	0.64
$^6H_{9/2}$	643	64.75	4.41	0.31	0.30
$^6H_{11/2}$	704	6.59	0.06	0.03	0.03

The JO intensity parameter Ω_2 is used to determine asymmetric environment around Sm^{3+} ions and covalency between Sm^{3+} ions and ligands, while the values of Ω_4 and Ω_6 are related to the bulk properties such as viscosity and rigidity of the host medium. From the comparisons of KASm050 glass in this work with other reported glasses indicated that our glass performs the higher asymmetric degree of environment around the Sm^{3+} ions and also higher covalency between Sm^{3+} and ligand than ZSBP0.5Sm (Vijayakumar and Marimuthu, 2015), borate glass (Deopa *et al.*, 2018) and NbKZFSm10 (Yuliantini *et al.*, 2018) glasses and lower than PKMASm (Srinivasa Rao and Jayasankar, 2013). glass as seen from Table 3.

The radiative transition possibility, stimulated emission cross-section and branching ratios from the intensity of emission spectra of KASm050 glass are presented in Table 4. From this table $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition (597 nm) gives the highest stimulated emission cross-section ($7.88 \times 10^{-22} \text{ cm}^2$) and also has the highest branching ratio (0.53) that higher than 0.50. These indicated that KASm050 glass

performs high potential to use as a laser gain medium for 597 nm emission.

Conclusions

Sm^{3+} doped potassium aluminium phosphate glasses were investigated in different concentration of Sm^{3+} ions. The result showed that physical properties of glass samples tended to increase with increasing of Sm_2O_3 concentration. The absorption spectra of glass samples were measured in the wavelength region of 250-2,000 nm. It was found that the intensities of absorption bands increased with Sm_2O_3 contents. The emission spectra, excited with 402 nm excitation wavelength, showed peaks assigned as 561, 597, 643, and 704 nm and the most intense emission was observed at 597 nm. The optimum concentration of Sm_2O_3 for potassium aluminium phosphate glass is 0.50 mol%, which makes the highest intensity of emission spectrum. From the J-O analysis, it is concluded that KASm050 glass performs an interesting potential for using as laser medium with 597 nm emission.

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