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Sm³⁺-DOPED MOLYBDENUM GADOLINIUM BORATE GLASSES FOR ORANGE EMISSION LASER ACTIVE MEDIUM

Room temperature visible and near infrared optical absorption and emission spectra of Sm³⁺-doped molybdenum gadolinium borate (MGB) glasses with molar composition 25MoO₃-20Gd₂O₃-(55-x)B₂O₃-xSm₂O₃ (x = 0.05, 0.1, 0.5, 1.0, 2.0 mol.%) have been analyzed. The experimental oscillator strengths of absorption bands have been used to determine the Judd-Ofelt (J-O) parameters. Fluorescence spectra were recorded by exciting the samples at 402 nm. Using the J-O parameters and luminescence data, the radiative transition probabilities (A_R), branching ratios (β_R), and stimulated emission cross-sections σ_e are obtained. The decay curves of the ⁴G_{5/2}-⁶H_{7/2} transition exhibit a non-exponential curve fit for all concentrations. The concentration quenching has been attributed to the energy transfer through the cross-relaxation between Sm³⁺ ions. ⁴G_{5/2} level and its relative quantum efficiencies are measured. Intense reddish-orange emission corresponding to the ⁴G_{5/2}-⁶H_{7/2} transition has been observed in these glasses at the 487-nm excitation. From the values of the radiative parameters, it is concluded that the 1.0-mol% Sm³⁺-doped MGB glass may be used as a laser active medium with the emission wavelength at 599 nm. The analysis of the non-exponential behavior of decay curves through the Inokuti-Hirayama model indicates that the energy transfer between Sm³⁺ ions is of dipole-dipole type. The quantum efficiency for the ⁴G_{5/2} level of MGBSm10 glass is found to be 67%. The co-related color temperature obtained from CIE (Commission International de L'Eclairage) for these glass samples is ~1620 K for the indicated orange emission at the 402-nm excitation.

Keywords: trivalent samarium, molecular structure, borate glasses, optical properties, fluorescence spectrum, CIE chromaticity.

1. Introduction

Glasses containing rare-earth (RE) ions such as Sm³⁺ and Gd³⁺ ions have received much attention, because such materials have high potential for practical applications. For instance, Sm³⁺-doped borate glasses have been used as amplifying optical fibers. Because the fluorescence performance of RE ions in glasses depends largely on their site environments (crystal fields), it is of importance to clarify the coordination and bonding states of RE ions in glasses. So far, numerous papers on the optical properties of RE ions in glasses have been reported, and it has been recognized that the Judd-Ofelt analysis is one of the good methods to get information on site environments of

RE ions. MoO₃ is a transition metal oxide, belonging to the intermediate class of glass forming oxides, which may participate in the glass network forming in the presence of modifying oxides with poor metals, but it may also act as a modifier MoO₃, which is well known as a conditional network former and it is not able to form a glass itself at slow cooling rates. The main problem of the preparation of glasses without involving the network formers is related to a high crystallization tendency of the components. Many binary and more complex molybdate glasses can be obtained by introducing the modifiers or other glass network formers [1-4]. The molybdenum ions exist at least in two stable valence states, viz., Mo(V) and Mo(VI), in the glass network; Mo(VI) ions act as network formers with MoO₄²⁻ structural units, alternate with BO₄ structural units, and make the glass network more

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Table 1. Physical properties of the MGB glass system

Sample Composition	Code	Density (g/cm ³)	Mol Vol (cm ³ /mol)
25MoO ₃ -20Gd ₂ O ₃ -(55 - x)B ₂ O ₃ -0.05Sm ₂ O ₃	MGBSm0.0	3.9539	37.156
25MoO ₃ -20Gd ₂ O ₃ -(55 - x)B ₂ O ₃ -0.1Sm ₂ O ₃	MGBSm0.1	3.9685	37.055
25MoO ₃ -20Gd ₂ O ₃ -(55 - x)B ₂ O ₃ -0.5Sm ₂ O ₃	MGBSm0.5	3.9747	37.278
25MoO ₃ -20Gd ₂ O ₃ -(55 - x)B ₂ O ₃ -1.0Sm ₂ O ₃	MGBSm1.0	4.0054	37.341
25MoO ₃ -20Gd ₂ O ₃ -(55 - x)B ₂ O ₃ -2.0Sm ₂ O ₃	MGBSm2.0	4.0878	37.270

stable. However, Mo(V) ions may act as modifiers with Mo⁵⁺O³⁻ complexes [5–10].

However, the interest in these glasses is limited as laser hosts due to their high phonon energy. Nevertheless, the addition of a transition metal oxide like MoO₃ to Gd₂O₃-B₂O₃ glass makes it more moisture-resistant, and the phonon losses can also be minimized to a large extent. Further, MoO₃-Gd₂O₃-B₂O₃ glasses are expected to foster a variety of fluorescence centers, which can be used for the modeling of typical glass applications such as a sensor for the investigation of structural aspects of the amorphous materials [11–12]. MoO₃-containing glasses have been the subject of many investigations due to their catalytic properties. The ions of molybdenum inculcate high activity and selectivity in a series of oxidation reactions of practical importance in the glass matrices [13]. Gd₂O₃ has become a material of much interest within the glass matrix because of the highly efficient energy transfer from Gd³⁺ ions to incorporated activators, at an affordable cost [14]. While, Gd₂O₃ has been a popular oxide for photonic materials due to the efficient energy transfer from Gd³⁺ ions to luminescence activators, high thermal neutron capture cross-section, and high light yield of emission [15, 16]. Glass scintillators with a high Gd₂O₃ content are concentrated in various silicate, borosilicate, phosphate, and germanate glasses with fast decay time and/or relative high light yield [17]. The Gd³⁺-RE³⁺ energy transfer also can enhance the photoemission, which improves the laser ability. Therefore, it can be said that RE³⁺-doped molybdate gadolinium borate glass is very interesting for using in photonic applications such as a scintillation material and a laser medium. The aim of this investigation is to obtain new molybdate glasses with high concentration of rare-earth oxide Gd₂O₃ and small concentration of Sm³⁺ to make conclusions on the luminescence properties on such concentration inclusions.

2. Experimental

The glasses with the compositions of 25MoO₃-20Gd₂O-(55 - x)B₂O₃-xSm₂O₃ (x = 0.05, 0.1, 0.5, 1.0, 2.0 mol.%) corresponding sample codes are given in Table 1. The samples were prepared by using the conventional melt quenching technique. The high pure chemicals, MoO₃, Gd₂O₃, H₃BO₃, and Sm₂O₃ with high purity were totally weighted to 30 g, were mixed thoroughly in an alumina crucible, and melted at 1400 °C for 3 h in an muffle furnace. After the melting, the glassy liquid was quenched in preheated graphite mold. The obtained glasses were annealed at 550 °C for 3 h in order to remove thermal strains and then cut and polished for a dimension of 1.0 cm × 1.5 cm × 0.3 cm. The densities of glasses were measured by applying the Archimedes principle. The samples were weighted in air and water on a 4-digit sensitive microbalance (AND, HR 200). The optical spectra were measured with a UV-VI-NIR spectrophotometer (Shimadzu UV-3600) in the ultraviolet, visible, and near-infrared regions. The excitation and emission spectra and the lifetime were collected, by using a spectro-fluoro-photometer (Cary-Eclipse) with a xenon lamp as a light source. The refractive indices (n) were measured by an Abbe refractometer, by using light with a wavelength of 589 nm and 1-Bromonaphthalin as a contact liquid. The absorption spectrum, emission spectrum, and refractive indices were used to analyze the lasing ability of glass via Judd-Ofelt (JO) theory.

3. Physical Properties

Density is an effective tool to explore the degree of structural compactness [18], modification of the geometrical configurations of the glass network, change in coordination, and the variation of dimensions of the interstitial holes [19]. It can be seen from Fig. 1 that the density increases with the Sm₂O₃

concentration. Eraiah *et al.* (2006) proposed that the addition of a small amount of Sm₂O₃ which enters into the glass network may resist the creation of nonbridging oxygen [20]. Hence, the density increases with the Sm₂O₃ content. However, the prepared MGBSm glasses show a decrease in the molar volume under the addition of a very low amount of Sm₂O₃, and then it increases along with the density, as the dopant amount increases. This effect suggests an increase of the free space in the glass network. However, the trend of r_i (interatomic radius) in the prepared glasses decreases the available volume per atom [21]. This implies that the atoms are more tightly packed, resulting in a denser glass, as verified by Table 1. Moreover, the global volume of the network slightly loosens with higher amounts of the dopant (2.0 mol% Sm₂O₃). It is expected that the substitution of boron atoms by RE ions with bigger radii, such as samarium, would result in an expansion of the rigid glass structure [22]. Moreover, the dopant ions break the bonds on the network, by promoting the formation of non-bridging oxygens (NBO_{s- \emptyset}), thus, resulting in a loosely packed structure [23]. Additionally to this, as shown in Fig. 1, the increase of the molar volume as a function of the Sm₂O₃ concentration can also be attributed to the formation of BO₃ units linked to Mo²⁺ and to the higher bond length of Mo–O than that of the B–O bond.

Table 2. Spectral characteristics of molybdate, gadolinium, and borate groups

Groups	Assignment
Molybdate 760–880 cm ⁻¹	Stretching vibrations of [MoO ₄] anions [24–28]
920–980 cm ⁻¹	Mo–O stretching vibrations of [MoO ₆] [24–28]
Gadolinium 860–970 cm ⁻¹	GdB ₃ O ₆ [29, 30]
Borate [BO ₃] 1240–1350 cm ⁻¹	Boroxol rings [26]
[BO ₄] 900–1100 cm ⁻¹	Di-, tri-, tetra- and penta-borate groups [26]
720–780 cm ⁻¹	Oxygen bridges between one tetrahedral and one trigonal boron atom [26]

4. Structural Studies

The structural studies of MoO₃–Gd₂O₃–B₂O₃ glasses by FTIR reflectance spectra show various reflection bands, which are characteristics of different vibrational modes (see Table 2). The FTIR reflectance spectra of these glasses were recorded in the wavenumber interval 650–1600 cm⁻¹, as shown in Fig. 2. The major reflection band centered at ~970 cm⁻¹ is observed. It arises due Mo–O stretching vibrations and cited as the phonon energy of the present molybdenum glass matrix. The molybdenum

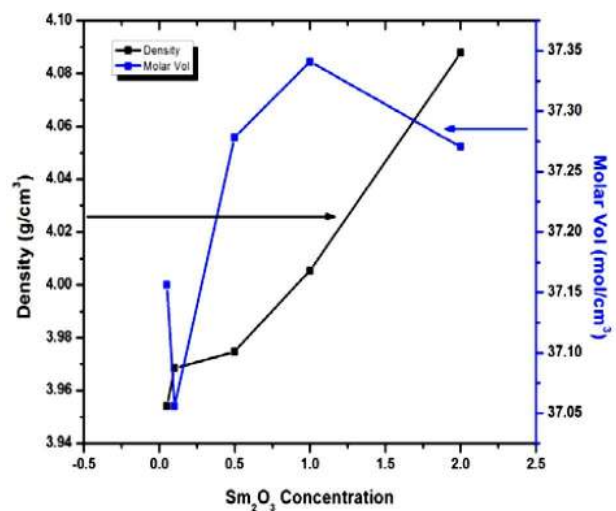


Fig. 1. Density and molar volume versus the concentration of Sm³⁺

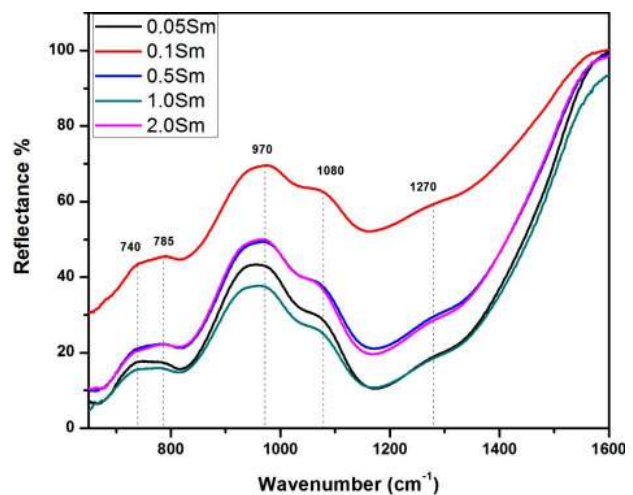


Fig. 2. FTIR reflectance spectra of the Sm³⁺-doped MGB glass system

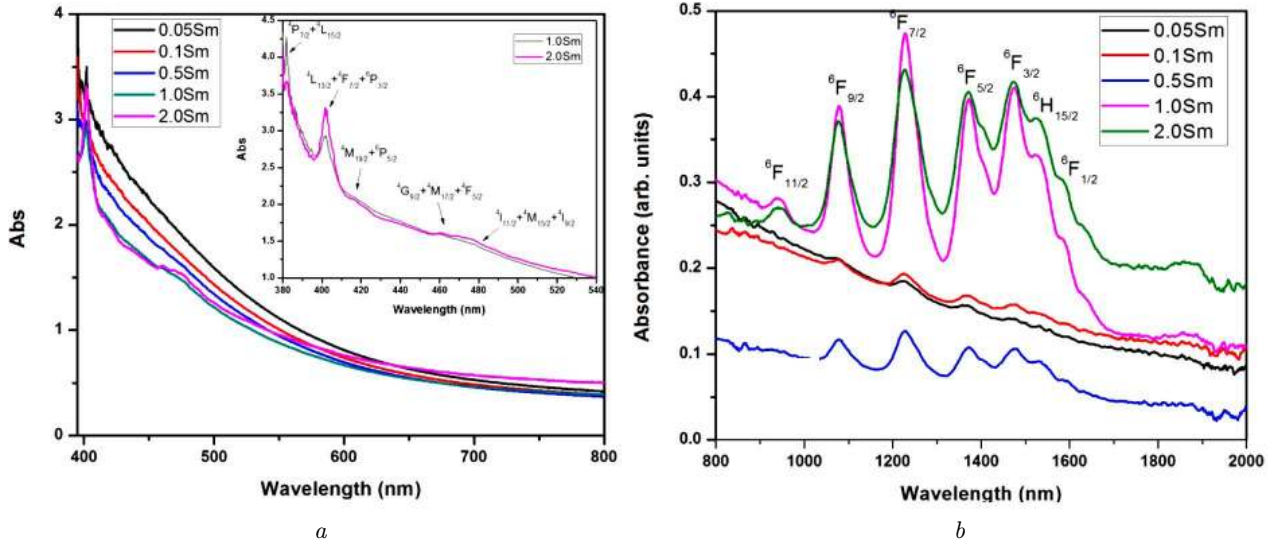


Fig. 3. Optical absorbance spectra for samarium-doped MGB glasses in the UV-Vis region (a) and NIR region (b)

ions can enter the glass network former in position of boron as MoO_4 and as a network modifier in MoO_6 groups. In the present system, it is clear from the reflection band that molybdenum ions exist to a large extent as MoO_6 and are revealed themselves as network modifiers.

5. Judd–Ofelt Intensity Parameters

Figure 3, a, b shows the optical absorption spectra of MGB glasses doped with Sm_2O_3 in the UV-Vis and NIR regions, respectively. We investigated the optically induced transition and determine the structural properties and J–O intensity parameters. The radiative transitions within the $4f^n$ configuration of an Ln^{3+} ion can be analyzed by the J–O theory [31, 32]. According to it, the calculated oscillator strength, f_{cal} , of an induced electric-dipole absorption transition from the initial state (ψJ) to a final state ($\psi' J'$) depends on three J–O intensity parameters (Ω_λ),

$$f_{\text{cal}} = \frac{8\pi^2 m c v}{3h(2j+1)} \frac{(n^2+2)^2}{9n} \times \sum_{\lambda=2,4,6} \Omega_\lambda (\psi J \parallel U^\lambda \parallel \psi' J')^2, \quad (1)$$

where n is the refractive index of the medium, J is the ground-state total angular momentum, v is the energy of the transition in cm^{-1} , Ω_λ ($\lambda = 2, 4, 6$)

are the Judd–Ofelt parameters, and $\| U^\lambda \|^2$ are the squared doubly reduced matrix elements of the unit tensor operator [31–33] of the rank $\lambda = 2, 4$, and 6 , which are calculated from the intermediate coupling approximation for the transition ψJ to $\psi' J'$ at the energy ν (cm^{-1}) and are independent of the host. The experimental oscillator strengths (f_{exp}) of the transitions can be obtained by integrating the molar absorptivity ($\epsilon\nu$) at a wave number ν (cm^{-1}) for each band as [34]

$$f_{\text{exp}} = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu. \quad (2)$$

The Ω_λ parameters have been derived from the electric-dipole contribution of the experimental oscillator strengths, by using the least-square fitting approach. The intensity of an absorption band is determined by its oscillator strength, which is directly proportional to area under the absorption band curve. The experimental oscillator strengths (f_{exp}) obtained from Eq. (2) have been used to determine the J–O intensity parameters by a least-square fit to Eq. (4). The Ω_λ values thus obtained are used to calculate the theoretical oscillator strengths f_{cal} . Table 3 presents the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths of the observed absorption bands along with *rms* deviations. The small Δ_s deviation of $\pm 0.21 \times 10^{-6}$ between the experimental and calculated oscillator strengths of the absorption bands indicates a good fit. The derived J–O parameters are

Table 3. Experimental and calculated oscillator strengths ($\times 10^{-6} \text{ cm}^2$) of Sm³⁺-doped molybdenum gadolinium borate glasses

Transitions	Energy	MGBSm0.05		MGBSm0.1		MGBSm0.5		MGBSm1.0		MGBSm2.0	
		f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
⁶ F _{1/2}	6305.2	0.0364	0.0135	0.0412	0.0245	0.4350	0.3779	0.1900	0.2852	0.1320	0.1864
⁶ H _{15/2}	6553.1	0.1070	0.0050	0.1640	0.0026	0.2030	0.0017	0.5460	0.0026	0.3070	0.0012
⁶ F _{3/2}	6775.1	0.2140	0.2271	0.2080	0.1934	0.3300	0.4086	0.6760	0.5256	0.4420	0.3563
⁶ F _{5/2}	7288.6	0.3970	0.4872	0.2170	0.3941	0.297	0.3126	0.6640	0.7225	0.4690	0.5008
⁶ F _{7/2}	8143.3	0.8130	0.8880	0.4380	0.5412	0.2970	0.3469	0.6540	0.7047	0.3790	0.4122
⁶ F _{9/2}	9276.4	0.6890	0.6011	0.4560	0.3271	0.2720	0.2101	0.4190	0.3566	0.2190	0.1774
⁶ F _{11/2}	10615.7	–	–	–	–	0.1130	0.0040	0.0619	0.0071	0.0513	0.0038
⁴ I _{11/2} + ⁴ M _{15/2} + ⁴ I _{9/2}	21052.6	–	–	–	–	–	–	0.0679	0.0226	0.2660	0.0085
⁴ G _{9/2} + ⁴ M _{17/2} + ⁴ F _{5/2}	21739	0.7260	0.1024	0.3970	0.0578	0.1560	0.0369	0.1458	0.0686	0.3339	0.0351
⁶ M _{19/2} + ⁶ P _{5/2}	23529.4	0.7840	0.1448	0.7280	0.1164	0.0147	0.0711	0.3655	0.1839	0.3065	0.1578
⁴ L _{13/2} + ⁴ F _{7/2} + ⁶ P _{3/2}	24875.6	1.5900	0.9888	1.8800	0.7942	0.9220	0.4867	0.9024	0.1255	1.4710	1.0766
⁴ P _{7/2} + ⁴ L _{15/2}	25974.0	–	–	1.0200	0.0143	0.1840	0.0093	0.1782	0.0155	0.1746	0.0058
Transitions		9		10		11		12		12	
Δ_{ms}		0.364		0.526		0.167		0.211		0.200	
RI (n)		1.65450		1.65320		1.65278		1.65257		1.65348	
N (ions/cm ⁴)		1.59×10^{20}		3.19×10^{20}		1.6×10^{21}		3.22×10^{21}		6.57×10^{21}	
r_p (nm)		0.579		0.602		0.352		0.278		0.219	
r_i (nm)		1.850		1.466		0.857		0.678		0.535	

$\Omega_2 = 0.901 \times 10^{20} \text{ cm}^2$; $\Omega_4 = 1.091 \times 10^{20} \text{ cm}^2$; $\Omega_6 = 0.884 \times 10^{20} \text{ cm}^2$. These J–O parameters are host-dependent and are important for the investigation of the glass structure and the transition rates for rare-earth ion energy levels. The trend of the intensity parameters in the present MGBSm glass is $\Omega_4 > \Omega_2 > \Omega_6$, and they are comparable with other reported values in different hosts [35–38] (see Table 4).

In general, the intensity parameter Ω_2 is related to the covalency, structural change, and symmetry of the ligand field around the Sm³⁺ site [39–41]. The Ω_2 parameter is associated with the asymmetry around the Ln³⁺ ion site, while Ω_4 and Ω_6 parameters are long-range parameters that can be related to the bulk properties of the glass such as the viscosity and basicity of the matrix. Moreover, Ω_6 depends on the 6s electron density of Ln³⁺ ions [34]. In the present work, the value of the parameter Ω_4 is higher, refers to the glass matrix viscosity, and is affected by the vibronic transitions of the rare-earth ions bound to the ligand atoms [42].

Table 4. Judd–Ofelt ($\times 10^{-20} \text{ cm}^2$) parameters, trends of Ω_λ parameters of Sm³⁺-doped molybdenum gadolinium borate glasses

Glass composition	JO Parameters			Trends of Ω_λ	Reference
	Ω_2	Ω_4	Ω_6		
MGBSm1.0	0.901	1.091	0.884	$\Omega_4 > \Omega_2 > \Omega_6$	Present
LBTAF	0.27	2.52	2.47	$\Omega_4 > \Omega_6 > \Omega_2$	[35]
ZnBS	0.29	3.82	3.65	$\Omega_4 > \Omega_6 > \Omega_2$	[33]
TeO ₂	3.17	3.65	1.61	$\Omega_4 > \Omega_2 > \Omega_6$	[36]
ZBLAN	2.15	3.05	1.56	$\Omega_4 > \Omega_2 > \Omega_6$	[37]
ZNLAN1	1.95	2.38	1.64	$\Omega_4 > \Omega_2 > \Omega_6$	[38]

The lower Ω_2 for Sm³⁺ ions in these glasses indicates a weaker covalent bonding nature.

5.1. Concentration quenching effect on fluorescence spectra

Figure 4, *a* shows the photoluminescence spectra of MGBSm glasses doped with different concentrations of Sm³⁺ (0.05, 0.1, 0.5, 1.0, and 2.0 mol%) at room

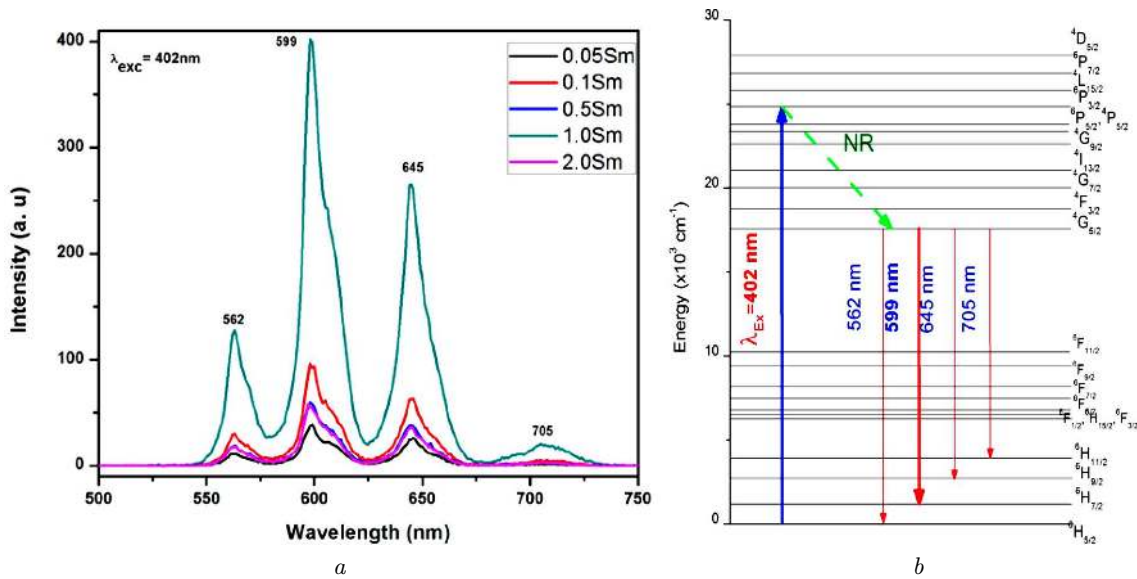


Fig. 4. Room-temperature fluorescence spectra for different concentrations of Sm^{3+} -doped MGB glasses (a). Energy level diagrams of Sm^{3+} -doped MGB glasses (b)

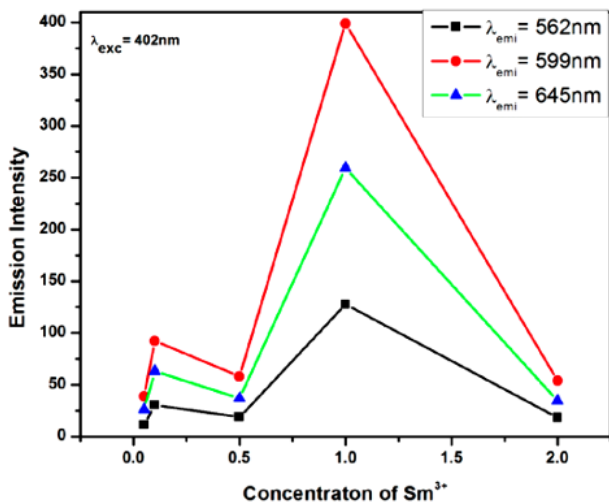


Fig. 5. Fluorescence quenching effect for different concentrations of Sm^{3+} -doped MGB glasses

temperature in the spectral interval 500–750 nm with an excitation wavelength of 402 nm corresponding to the ${}^6\text{H}_{5/2}$ – ${}^4\text{L}_{13/2}$ transition. The fluorescence spectra have been obtained for all the excitation energies higher than 17.724 cm^{-1} . The reason for this is that when any of the energy levels above ${}^4\text{G}_{5/2}$ is excited, there is a quick non-radiative relaxation to this excited level due to the small energy gaps between them. This can be seen from the energy level diagram

of Sm^{3+} shown in Fig. 4, b. The ${}^4\text{G}_{5/2}$ level possesses a purely radiative relaxation rate, since this level has a sufficient energy gap $\sim 7150 \text{ cm}^{-1}$ with respect to the next lower level ${}^6\text{F}_{11/2}$ [43]. The fluorescence spectra consist of four peaks and are assigned to the ${}^4\text{G}_{5/2}$ – ${}^6\text{H}_J$, $J = 5/2, 7/2, 9/2,$ and $11/2$, transitions at 562, 599, 645, and 705 nm, respectively. Among these four transitions, ${}^4\text{G}_{5/2}$ – ${}^6\text{H}_{7/2}$ (599 nm) exhibits the intense orange luminescence, and ${}^4\text{G}_{5/2}$ – ${}^6\text{H}_{11/2}$ (705 nm) is a feeble one. The other two transitions, ${}^4\text{G}_{5/2}$ – ${}^6\text{H}_{5/2}$ (562 nm) and ${}^6\text{H}_{9/2}$ (645 nm), show a moderate luminescence in the visible region. From Fig. 5 presenting the emission intensity, it is very clear that the fluorescence intensity increases with the concentration from 0.05 to 1.0 mol%. Beyond the 1.0-mol%, the concentration quenching is observed. It is also found that the emission peak positions are unchanged for all concentrations.

By the relative areas under the emission peaks, the measured branching ratios (β_{exp}) have been estimated for the ${}^4\text{G}_{5/2}$ – ${}^6\text{H}_J$ ($J' = 5/2, 7/2, 9/2,$ and $11/2$) transitions, and the results are presented in Table 5. There is a reasonable agreement between measured and calculated branching ratios (β_{cal}). As can be seen from Table 5, the ${}^4\text{G}_{5/2}$ – ${}^6\text{H}_{5/2}$ and ${}^6\text{H}_{7/2}$ transitions contain the magnetic dipole interaction due to the selection rule $\Delta J = 0, \pm 1$ [43]. The stimulated emission cross-section (σ_e) of $1.19 \times 10^{-22} \text{ cm}^2$ estimated

Table 5. Radiative properties such as the peak emission wavelength (λ_p), electric and magnetic dipole line strengths (S_{ed} , S_{md}), transition probability rates (A_r), measured branching ratios, and stimulated emission cross-section ($\sigma_e \times 10^{-22} \text{ cm}^2$) for the ${}^4G_{5/2}$ emission level of the 1.0-mol% Sm³⁺-doped MGB glass

Transition	λ_p , nm	S_{ed} , $\times 10^{22} \text{ cm}^{-1}$	S_{md} , $\times 10^{22} \text{ cm}^{-1}$	A_r , S ⁻¹	Branching ratios		Stimulated emission cross-section (σ_e in cm ²)
					β_{cal}	β_{exp}	
${}^6H_{11/12}$	705	2.43	17.62	10.45	0.0743	0.0069	3.55×10^{-23}
${}^6H_{9/2}$	645	39.55	14.60	34.84	0.2478	0.0710	1.01×10^{-22}
${}^6H_{7/2}$	599	34.84	0.00	54.15	0.3852	0.1062	1.19×10^{-22}
${}^6H_{5/2}$	562	0.00	10.45	20.05	0.1426	0.0282	4.07×10^{-23}

for the ${}^4G_{5/2}$ - ${}^6H_{7/2}$ intense emission band of the 1.0-mol% Sm³⁺-doped MGB glass is comparable with the other reported values [42, 45]. Reasonably high values of σ_e suggest that the present glasses can be used for high-gain laser applications [46–47]. As the intensity of the transition ${}^4G_{5/2}$ - ${}^6H_{7/2}$ (599 nm) is the highest among all the observed emission transitions, these glasses have inherent favorable local environment to emit the laser output at ~ 599 nm, which is the most prominent and important characteristic of Sm³⁺ ions. The support for this viewpoint can be derived from the ratio between the emission state (EM) intensity and the excited state absorption (ESA) intensity. This ratio is calculated in terms of the J–O parameters:

$$\frac{A_{EM}}{A_{ESA}} = 0.21\Omega_6 / (0.11\Omega_2 + 0.063\Omega_4)$$

A_{EM}/A_{ESA} values are found to be 1.106 for MGBSm1.0 glass. As the ratio is higher than unity (this means that $A_{EM} > A_{ESA}$), a light amplification can occur most significantly in the present glasses.

6. Lifetime Measurement

Decay curves of the ${}^4G_{5/2}$ level for different Sm³⁺ ion concentrations are shown in Fig. 4. The decay curve is a non-exponential fit for all the samples obtained. The experimental lifetime (τ_{exp}) of the fluorescent ${}^4G_{5/2}$ level has been determined from the non-exponential decay curves by finding the average or effective lifetime, by using the formula [46, 47]

$$\tau_{exp} = \frac{\int tI(t)dt}{\int I(t)}$$

The measured lifetime (exp) can be expressed as [46, 47]

$$\frac{1}{\tau_{exp}} = \frac{1}{\tau_{rad}} + W_{MPR} + W_{ET},$$

where τ_{rad} is the radiative lifetime calculated from the J–O theory, W_{MPR} is the multiphonon relaxation (MPR) rate, W_{ET} is the rate of energy transfer (ET). The MPR in this case is negligible, as there is a large energy gap about 7150 cm^{-1} between the ${}^4G_{5/2}$ level and the next lower level. Hence, the quenching of lifetimes with increase in the concentration may be mainly due to ET through the cross-relaxation (CR). The W_{ET} is given by

$$W_{ET} = \frac{1}{\tau_{exp}} - \frac{1}{\tau_{rad}}$$

W_{ET} (S⁻¹) for the ${}^4G_{5/2}$ level of PPNSm10 glass is found to be 576 s^{-1} . The quantum efficiency (η) of the fluorescent level is given by [48]

$$\eta = \frac{\tau_{exp}}{\tau_{rad}}$$

The quantum efficiency for the ${}^4G_{5/2}$ level of MGBSm10 glass is found to be 67% and is lower than those obtained for fluorozincate (ZnF₂-CdF₂) [49] and higher than those obtained for phosphate PPNSm10 glasses [50]. The luminescence decay curves show the non-exponential nature with the lifetime quenching, when the concentration is increased from 0.05 to 2.0 mol%. The quenching of lifetimes and the non-exponential behavior of decay profiles at concentrations from 0.05 to 2.0 mol% are due to the non-radiative ET between Sm³⁺ ions. The intensity of

Table 6. Experimental (τ_{exp}) & radiative (τ_{rad}) lifetimes (ms) and the quantum efficiency (η) of the Sm³⁺:MGB glasses

Sample	τ_{exp} ms	τ_{rad} ms	η	Reference
MGBSm0.05	1.071	0.993	1.07	Present work
MGBSm0.1	1.047	1.174	0.89	Same
MGBSm0.5	0.852	0.979	0.87	"
MGBSm1.0	0.571	0.851	0.67	"
MGBSm2.0	0.341	0.892	0.38	"
55P2)5-39PbO-5NbO5-1.0Sm	1.896	2.820	0.69	[50]
49PbO-50GeO2-1.0Sm	1.130	1.653	0.68	[53]
49PbO-30GeO2-20Ga-1.0Sm	1.060	1.740	0.60	[53]
LBSG2	0.736	0.854	0.86	[34]

of lifetimes decrease with increasing the concentration, and the Q values shows 0.30 for MGBSm1.0 and 1.5 for MGBSm2.0 samples. The C_{DA} values were estimated for the present glasses and are found to be 0.11×10^{-41} cm⁶/s and 1.1×10^{-41} cm⁶/s for MGBSm1.0 and MGBSm2.0, respectively. For Sm³⁺-doped PbO-PbF₂ glass, Nachimuthu *et al.* [52] obtained $C_{\text{DA}} = 5.6 \times 10^{-41}$ cm⁶/s for 1.35 wt% of Sm³⁺ ions. V. Venkatramu *et al.* [43] obtained C_{DA} value to be 4.4×10^{-41} cm⁶/s and 5.3×10^{-41} cm⁶/s for 1.5 and 2.5 mol% Sm³⁺ ions. All these values are comparable to those obtained for title glass systems.

Usually, in ET processes assisted by phonons, the transfer probability and the Q parameter are much lower than those in the resonant situation. If the distance between optically active ions decrease (due to an increase in the dopant concentration), then one may expect an increase in the Q parameter and, as a consequence, faster fluorescence decays. As can be seen, the relative quantum yield exceeds 1 for a lower concentration which is within the experimental error and shows that there is no ET at lower concentrations. Beyond the 0.05-mol% concentration of Sm³⁺ ions, ET between Sm³⁺ ions has been observed. This is another evidence of ET between Sm³⁺ ions in these glasses.

7. CIE Chromaticity Analysis

The color chromaticity coordinates $(x, y) = ((0.59808, 0.39475), (0.60179, 0.39553), (0.60134, 0.39648), (0.60154, 0.39756), (0.59872, 0.39796))$ for MGBSm0.05, MGBSm0.1, MGBSm0.5, MGBSm1.0, and MGBSm2.0, respectively, have been calculated from

the emission spectra gained by the CIE (Commission International de l'Eclairage, France) system and are presented in Fig. 7 for various Sm³⁺ concentrations of the doped MGB glasses. The chromaticity coordinates are an evidence supporting the potential analysis of these glasses for the orange emission corresponding to these glass samples. It is not a monochromatic color having a single peak in the spectra, but a mixture of three peaks (562, 599, and 645 nm). The correlated color temperature (CCT) value can be evaluated from the CIE color coordinate, by using the McCamy formula as follows [54–55]:

$$\text{CCT} = -449n^3 + 3525n^2 - 6823n + 5520.33,$$

where $n = (x - 0.332)/(y - 0.186)$. The CCT values obtained from the glass samples are ~ 1620 K for these glasses. From these results, it is suggested that the studied glasses emit the orange emission at the 402-nm excitation. Since the ability to withstand a high temperature is a basic requirement for phosphor applied in LEDs, the thermally stable property of phosphor was investigated, and it turned out to be excellent. So, phosphor is a potential orange component for white light-emitting diodes that based on UV-LEDs.

8. Conclusions

The present paper reports on the photoluminescence properties of MGB glasses containing different concentrations of Sm³⁺ ions. Optical absorption and fluorescence spectra have been recorded at room temperature. The J–O intensity parameters (Ω_λ), radiative transition probabilities (A_R), branching ratios (β_R), and stimulated emission cross-section (σ_e)

have been determined and are found to be comparable with other reported values. From the decay curves, it is concluded that the lifetime of the ${}^4G_{5/2}$ level has been found to depend strongly on the concentration of Sm^{3+} ions and on the glass composition. The decrease in the lifetime with an increase in the concentrations is due to the cross-relaxation between excited Sm^{3+} ions and unexcited Sm^{3+} ions in the ground state. Based on the optical properties, it is concluded that the 1.0-mol% Sm^{3+} -doped MGB glass may be used as a laser active medium for the emission at 599 nm corresponding to the ${}^4G_{5/2}$ - ${}^6H_{7/2}$ transition. The analysis of the non-exponential behavior of decay curves within the Inokuti-Hirayama model indicates that the energy transfer between Sm^{3+} ions is of the dipole-dipole type. The energy transfer parameter (Q) and C_{DA} donor-acceptor interaction parameter increase with the concentration of Sm^{3+} ions. The CIE chromaticity coordinates $(x, y) = (\sim 0.601, \sim 0.395)$ are obtained for these glasses, and the CCT values obtained for these glass samples are around 1663 K corresponding to the orange emission at the 402-nm excitation.

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СКЛО З БОРАТИВ МОЛІБДЕНУ І ГАДОЛІНІЮ,
ДОПІЙОВАНЕ Sm^{3+} , ЯК АКТИВНЕ СЕРЕДОВИЩЕ
ЛАЗЕРА З ЕМІСІЄЮ ПОМАРАНЧЕВОГО КОЛЬОРУ

Резюме

Проаналізовано спектри оптичного поглинання і емісії при кімнатній температурі скла з боратів молібдену і гадолінію (МГБ), допійованих Sm^{3+} з молярним складом $25\text{MoO}_3\text{-}20\text{Gd}_2\text{O}_3\text{-(}55-x\text{)B}_2\text{O}_3\text{-}x\text{Sm}_2\text{O}_3$ ($x = 0,05, 0,1, 0,5, 1,0, 2,0$ мол.%). Експериментальні значення сил осциляторів смуг поглинання використані для визначення параметрів Джадда–Офелта (Дж–О). Записані спектри флуоресценції при збудженні зразків на 402 нм. На основі Дж–О параметрів і даних з люмінесценції, знайдені ймовірності радіаційних переходів (A_R), коефіцієнт розпаду (β_R) і перетини стимульованого випромінювання (σ_e). Криві розпаду пере-

ходу ${}^4\text{G}_{5/2}\text{-}{}^6\text{H}_{7/2}$ мають неекспоненціальну залежність для всіх концентрацій. Концентраційні гасіння відповідають переносу енергії між Sm^{3+} іонами шляхом крос-релаксації. Визначено ${}^4\text{G}_{5/2}$ рівень і виміряні його відносні квантові ефективності. Спостерігалось інтенсивне червонувато-оранжеве випромінювання відповідне ${}^4\text{G}_{5/2}\text{-}{}^6\text{H}_{7/2}$ переходу при збудженні на 487 нм. Виходячи з величин радіаційних параметрів, зроблено висновок про те, що 1,0-мол.% Sm^{3+} -допійоване МГБ скло може бути використано як активне лазерне середовище з довжиною хвилі випромінювання 599 нм. Аналіз неекспоненціальних кривих розпаду в моделі Інокуті–Хираяма показує, що перенесення енергії між Sm^{3+} іонами має дипольний характер. Отримано, що квантова ефективність для ${}^4\text{G}_{5/2}$ рівня МГБ Sm10 скла дорівнює 67%. Колірна температура для цих стекел відповідно до даних МКВ (Міжнародна Комісія з висвітлення) дорівнює ~ 1620 К для оранжевого випромінювання при збудженні на 402 нм.