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Judd-Ofelt Parameters of Sm^{3+}-doped Alkali Telluroborate Glasses

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Abstract: Alkali borotellurite glass (ABTe) doped with concentration of 0.5 mol% Sm^{3+} ions was prepared by melting method. The absorption, luminescence spectra and lifetime of ABTe:Sm^{3+} have been measured at room temperature. The results were analyzed using Judd–Ofelt (JO) theory, that gives the Ω_λ intensity parameters, transition probabilities (A_R), calculated branching ratios (β_R), measured branching ratios (β_{mes}) and stimulated emission cross-sections ($\sigma_{\lambda p}$) for $^4G_{5/2} \rightarrow {}^6H_J$ transitions.

Keywords: Alkali borotellurite glass, Judd-Ofelt theory.

1. Introduction

Samarium with $4f^5$ electron configuration usually exists in triply ionized (Sm^{3+}), which is a quite popular rare earth element. The optical properties of Sm^{3+} ions doped glasses have been extensively investigated due to their wide applications in many optical devices like: lasers, sensors, high-density memories, undersea communications and optical amplifiers [1,2]. Recently there have been many reports on optical properties of Sm^{3+} doped glasses to which TeO_2 component was added. Besides, the authors also gives the application prospects of these glasses [1-4].

In this work, the optical properties of Sm^{3+} in borotellurite glass with co-former B_2O_3 and TeO_2 (TeO_2-B_2O_3-Na_2O-CaO-Al_2O_3-Sm_2O_3) being a low phonon energy and high refractive index material [1-4] have been investigated by using Judd-Ofelt theory. The different types of network_modifier like Na_2O, CaO and Al_2O_3 were added to borotellurite glass to improve their chemical durability and alter the physico-chemical properties. Al_2O_3 has received significant consideration as the most likely useful matrix composition due to its high solubility of the RE^{3+} ions.

2. Experiments

Alkali-borotellurite glass (ABTe) with the composition of $44.5TeO_2$+$30B_2O_3$+$5Al_2O_3$+$10Na_2O$ +10CaO+$0.5Sm_2O_3$ was prepared by conventional melt quenching. The optical absorption spectrum

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was obtained between wavelengths 300 and 2000 nm using Jascco V670 spectrometer. The photoluminescence spectrum was recorded by Fluorolog-3 spectrometer, model FL3-22, Horiba Jobin Yvon. Luminescence lifetime was measured using a Varian Cary Eclipse Fluorescence Spectrophotometer. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Absorption spectra and Judd-Ofelt parameters

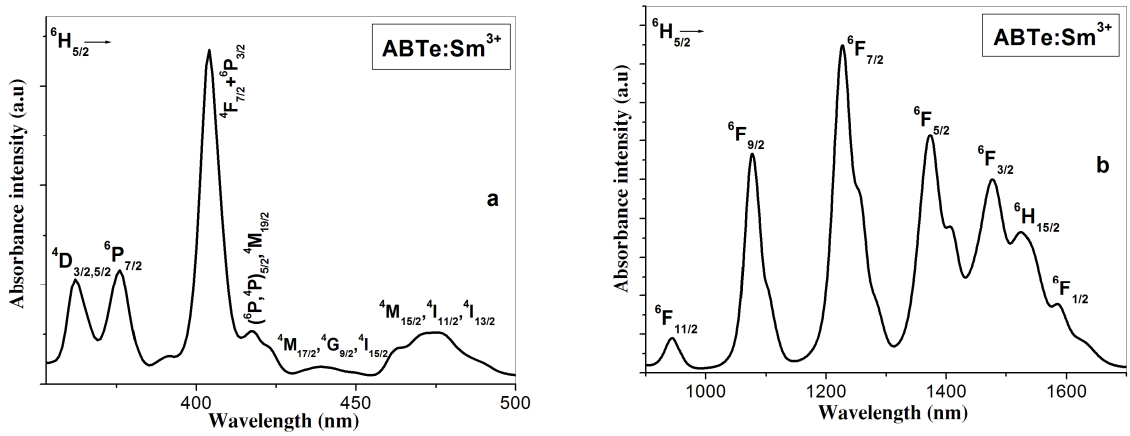

Fig. 1. The absorption spectra of ABTeSm^{3+} glasses (a) in the range of UV.Vis and (b) in the range of NIR.

Absorption spectra of the ABTe:0.5 mol%Sm^{3+} glass in two regions of wavelength 350–500 nm and 900–1700 nm are showed in Fig. 2. The observed 13 absorption bands were assigned to transitions from the $^6H_{15/2}$ ground state to the $^6H_{15/2}$ excited states of Sm^{3+} ions by using Carnall's paper [5]. The $^6H_{5/2}\rightarrow{}^6F_{1/2}$ and $^6H_{5/2} \rightarrow {}^6F_{3/2}$ transitions obey the selection rule $\Delta S = 0$, $|\Delta J| \leq 2$ and $|\Delta L| \leq 2$, so these are hypersensitive transitions of Sm^{3+} ions [4]. The position and intensity of these transitions strongly depend on structural and polarization of ligand. In the UV-Vis regions, the various $^{2S+1}L_J$ energy levels are very close to each other. Therefore, the absorption transitions are overlapped and that creates broad bands. The strongest intensity in this region corresponds to $^6H_{5/2}\rightarrow{}^6P_{3/2}$ transition (at the wavelength of 402 nm). This transition is a spin allowed transition which is normally used for fluorescence excitation. The energies of these absorption transitions of Sm^{3+} ion in glass host are also compared with Sm^{3+}-diluted acid solution (aquo-ion) system [5] and show in Table 1. From transition energies, the nephelauxetic ratio ($\overline{\beta}$) and Sm^{3+}-ligand bonding parameter (δ) have been calculated by using the formulas in references [6,7]. For ABTe:Sm^{3+}, the values of $\overline{\beta}$ and δ are 1.0036 and - 0.29, respectively. Thus, the bonding of Sm^{3+} ions with the local host is ionic bond [1-4].

Table 1. Energy transitions (v), bonding parameters (δ), the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths for ABTe:Sm^{3+} glass

Transition $^4H_{15/2}\rightarrow$	v_{exp}(cm^{-1})	v_{aquo} (cm^{-1})	f_{exp}($\times10^{-6}$)	f_{cal}($\times10^{-6}$)
$^6F_{1/2}$	6,302	6,400	0.36	0.92
$^6H_{15/2}$	6,534	6,508	1.54	0.03
$^6F_{3/2}$	6,760	6,630	3.89	3.45
$^6F_{5/2}$	7,181	7,100	6.05	5.93
$^6F_{7/2}$	8,143	8,000	6.45	6.46
$^6F_{9/2}$	9,270	9,200	4.25	4.11
$^6F_{11/2}$	10,558	10,500	0.72	0.67
$^4I_{9/2,11/2,13/2}$, $^4M_{15/2}$	21,262	20,800	3.11	2.89
$^4M_{17/2}$,$^4G_{9/2}$	22,770	22,700	0.59	0.35
(^6P,$^4P)_{5/2}$, $^4M_{17/2}$	23,950	24,050	1.53	1.64
$^4F_{7/2}$, $^6P_{3/2}$	24,743	24,950	12.75	12.71
$^6P_{7/2}$	26,641	26,750	2.98	2.93
$^4D_{3/2}$,$^4D_{5/2}$	27,575	27,700	3.64	2.95
	$\bar{\beta}$ = 1.0036, δ = - 0.29		rms = 0.59×10^{-6}	

3.2. Judd-Ofelt parameters

The Judd-Ofelt (JO) theory [8,9] was shown to be useful to characterize radiative transitions for RE-doped solids, as well as RE-doped aqueous solutions. This theory defines a set of three intensity parameters, Ω_λ (λ = 2, 4, 6), that are sensitive to the environment of the rare-earth ions and can be used to predict a lot of the spectroscopic parameters of the rare earth ions in the host materials. According to the JO theory, the electric dipole oscillator strength of a transition from the ground state to an excited state is given by

$$f_{cal} = \frac{8\pi^2 mc\nu}{3h(2J+1)} \times \frac{\left(n^2+2\right)^2}{9n} \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle \Psi J \left\| U^\lambda \right\| \Psi' J' \right\rangle^2 \quad (1)$$

where n is the refractive index of the material, J is the total angular momentum of the ground state, Ω_λ are the JO intensity parameters and $\left\|U^\lambda\right\|^2$ are the squared doubly reduced matrix of the unit tensor operator of the rank λ = 2, 4, 6, which are calculated from intermediate coupling approximation for a transition $\left|\psi J\right\rangle \rightarrow \left|\psi' J'\right\rangle$. These reduced matrix elements are nearly independent of host matrix as noticed from earlier studies [4].

On the other hand, the experimental oscillator strengths, f_{exp}, of the absorption bands are determined experimentally using the following formula [1-4]

$$f_{exp} = 4.318\times10^{-9} \int \alpha(\nu) d\nu \quad (2)$$

where α is molar extinction coefficient at energy v (cm^{-1}). The $\alpha(v)$ values can be calculated from absorbance A by using Lambert–Beer's law

$$A = \alpha(\nu) cd \quad (3)$$

where c is RE^{3+}concentration [dim: L^{-3}; units: mol/dm^3], d is the optical path length [dim: L; units: cm]

By equating the measured and calculated values of the oscillator strength (f_{cal} and f_{exp} and solving the system of equations by the method of least squares, the JO intensities parameters Ω_λ (λ = 2,4 and 6) can be evaluated numerically. In the case of ABTe:0.5mol%Sm^{3+} glass, $\Omega_2 = 2.95\times10^{-20}$ cm^2, $\Omega_4 = 10.99\times10^{-20}$ cm^2 and $\Omega_6 = 5.26\times10^{-20}$ cm^2. The Ω_2 is more sensitive to the local environment of the RE^{3+} ions and is often related with the asymmetry of the local crystal field and the valency of RE^{3+}–ligand bond. The value of Ω_2 in ABTe:Sm^{3+} glass is smaller than that in TRZNB glass ($6.81\times10^{-20}cm^2$) [4] but is larger in B4TS glass (0.06×10^{-20} cm^2) [4], PTBS glass ($0.21\times10^{-20}cm^2$) [2] and LGT10 glass ($0.73\times10^{-20}cm^2$) [1]. Thus the asymmetry of crystal field at the Sm^{3+} ions site and covalency of Sm^{3+}-ligand bond in ABTe glass is lower than that in the TRZNB glasses but higher in B4TS, PTBS and LGT10 glasses

3.4. Emission spectrum

The emission spectrum of the ABTe:Sm^{3+} glasses was recorded using 402 nm excited wavelength and is shown in Fig. 2, the spectrum consists of 5 observed emission bands at wavelengths of 560, 600, 645, 710 and 795 nm which correspond to the $^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2, 13/2) transitions, respectively. Among emission transitions, the $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition has the most intense intensity whereas the $^4G_{5/2}\rightarrow{}^6H_{13/2}$ transition is very weak in intensity. The $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ transitions are purely electric dipole transitions, whereas the $^4G_{5/2}\rightarrow{}^6H_{5/2}$ and $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transitions include both electric and magnetic dipole transitions.

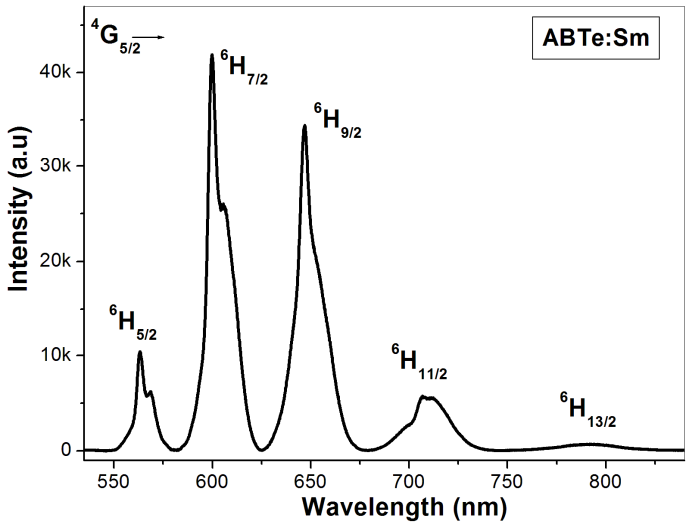

Fig. 2. The emission spectrum of the ABTe:Sm^{3+} glass.

3.4. Radiative parameters

From the JO parameters and emission spectrum, the radiative properties of Sm^{3+} ion such as: transition probabilities (A_R), radiative lifetime (ι_R), branching ratios (β_{cal} and β_{exp}), effective line width ($\Delta\lambda_{eff}$), stimulated emission cross-section ($\sigma(\lambda_P)$) and integrated emission cross section (Σ_{ij}) have calculated for $^4G_{5/2}\rightarrow{}^6H_J$ radiative transitions. The detail formulas for these parameters have been given in previous reports [6,7]. The results are displayed in Table 2.

Table 2. Radiative parameters of $^4G_{5/2} \rightarrow {}^6H_J$ transition for Sm^{3+} ions in ABTe:Sm^{3+} glass

$^4G_{5/2}\rightarrow$	ν (cm^{-1})	β_{cal} (%)	β_{exp} (%)	$\Delta\lambda$ (nm)	Σ_{ij} ($\times10^{-18}$ cm)	σ ($\times10^{-22}$ cm^2)
$^6H_{5/2}$	17,746	5.20	6.50	9.33	0.52	0.91
$^6H_{7/2}$	16,674	49.90	45.60	12.85	5.48	14.82
$^6H_{9/2}$	15,457	23.70	34.94	14.94	3.02	8.49
$^6H_{11/2}$	14,158	14.24	10.86	24.12	2.18	4.46
$^6H_{13/2}$	12,623	1.72	2.10	36.68	0.32	0.56

It is noted that there is a good agreement between experimental (β_{exp}) and calculated (β_{cal}) branching ratios. The stimulated emission cross-section, integrated emission cross section and branching ratio are important parameters affecting the potential laser performance. These parameters of $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition gets a maximum value and they are larger than those of some other glasses [1-4]. Thus, the $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition of Sm^{3+} ions in ABTe glass is found to be suitable for developing the visible laser and fiber optic amplifier.

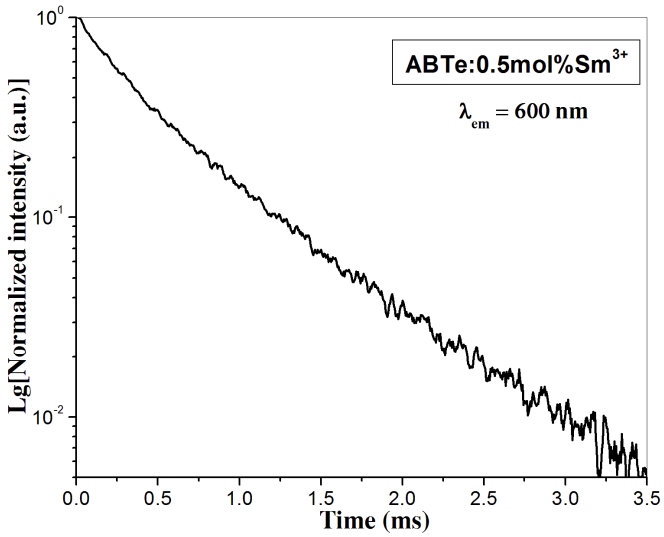

Fig. 3. Luminescence decay profiles of the $^4G_{5/2}$ of Sm^{3+} ions in ABTe glass

The emission decay profile of the $^4G_{5/2}$ excited state of Sm^{3+} ions in ABTe glass was obtained by exciting the sample at 402 nm and was shown in Fig. 3. The measured lifetimes (τ_{exp}) of samples have been determined by the formula:

$$\tau_{exp} = \frac{\int tI(t)dt}{\int I(t)dt} \quad (4)$$

The measured lifetime of $^4G_{5/2}$ level is τ_{exp} = 1.31 ms whereas the calculated lifetime is τ_{cal} = 1.79 ms, respectively. The discrepancy between the measured and calculated lifetime may be due to the nonradiative transitions. The quantum efficiency of the fluorescent level is defined as: $\eta = \tau_{exp}/\tau_{cal}$ [7]. In this case, the luminescence quantum efficiency is 73.2 %. This relatively high value indicates that the nonradiative processes are not too strong at low-doping level of Sm^{3+} ions in ABTe glass.

4. Conclusions

The optical properties of Sm^{3+} -doped alkali borotellurite glass have been investigated. Negative value for the bonding parameter indicates the ionic nature of Sm^{3+}-ligand bond in ABTe glass. Moreover, the small value of Ω_2 shows that the coordination structure surrounding the Sm^{3+} ions has high symmetry. By using JO theory, the radiative properties such as branching ratios, the stimulated emission cross-section and integrated emission cross section have been predicted. The results show that the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of Sm^{3+} ions in ABTe glass is acceptable for one of parameters of laser material emission and fiber optic amplifier.

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