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Short communication

Optical analysis of samarium doped sodium bismuth silicate glass

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ABSTRACT

Samarium doped sodium bismuth silicate glass was synthesized using the melt quenching method. Detailed optical spectroscopic studies of the glassy material were carried out in the UV–Vis-NIR spectral range. Using the optical absorption spectra Judd-Ofelt (JO) parameters are derived. The calculated values of the JO parameters are utilized in evaluating the various radiative parameters such as electric dipole line strengths (S_{ed}), radiative transition probabilities (A_{rad}), radiative lifetimes (τ_{rad}), fluorescence branching ratios (β) and the integrated absorption cross- sections (σ_a) for stimulated emission from various excited states of Sm^{3+}‡ ion. The principal fluorescence transitions are identified by recording the fluorescence spectrum. Our analysis revealed that the novel glassy system has the optimum values for the key parameters viz. spectroscopic quality factor, optical gain, stimulated emission cross section and quantum efficiency, which are required for a high performance optical amplifier. Calculated chromaticity co-ordinates (0.61, 0.38) also confirm its application potential in display devices.

1. Introduction

Rare earth (RE) ion activated materials find wide applications in display devices, lighting technology, solar cell energy conversion, telecommunications, remote sensing etc. [1]. Recent years have witnessed a tremendous increase in research activities related to glasses doped with rare earth ions in various forms such as network formers, modifiers or luminescent ions [2–4]. Most often, research efforts have concentrated on fluoride, tellurite and chalcogenide glass systems because of their lower phonon energies compared to oxide glasses. Nevertheless, oxide glasses have proven more suitable for practical applications due to their high chemical durability and thermal stability. Among oxide glasses, silicate glasses are the most popular glass hosts for making optical fiber lasers and amplifiers [5–8]. They are also known to be an excellent host matrix for rare earth oxides because of their good glass forming ability when compared to several other conventional systems such as borate, phosphate, germinate, vanadate and tellurite glass families. This makes it an interesting system for experimental and theoretical studies [9–13].

Heavy-metal silicate glasses possess lower phonon energies compared to other silicate glasses and display intense visible and near-infrared fluorescence of the rare-earth ions within the system [14–17]. The trivalent samarium ion (Sm^{3+}) is one of the most important active ions in the RE family due to its closely lying energy level structure [18]. The $^4G_{5/2}$ level of Sm^{3+} has a relatively high quantum efficiency which shows luminescence in the orange and red regions of the visible spectrum via transitions to the ground state $^6H_{5/2}$ or to the higher energy states ^6Hj [(j = 7/2, 9/2, and 11/2) [18]. Although there have been a large number reports on various rare earth doped glassy systems, the synthesis and optical analysis of samarium doped bismuth silicate glasses have seldom been studied. At relatively low Bi_2O_3 content (≤10 mol%), Bi_2O_3incorporates into the interstices of glass as network modifiers which doesn't cause a large-scale structural rearrangement of the local glassy network. At higher concentrations of Bi_2O_3 (>10 mol%), Bi_2O_3 enters into glasses as a network former and a large-scale structural rearrangement of the local glass network takes place, which leads to significant variation of its optical properties[19–21].

In this context, an optical analysis of samarium doped bismuth (10 mol%)sodium silicate glass is deserving of attention which to our knowledge have not been reported so far. Understanding the optical properties of samarium doped bismuth sodium silicate glass is a prerequisite for considering optical applications. The purpose of the present study is to prepare samarium doped bismuth sodium silicate glass and to study various optical properties such as radiative transition

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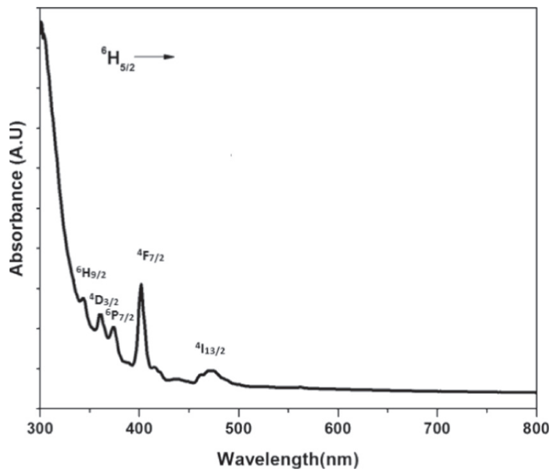
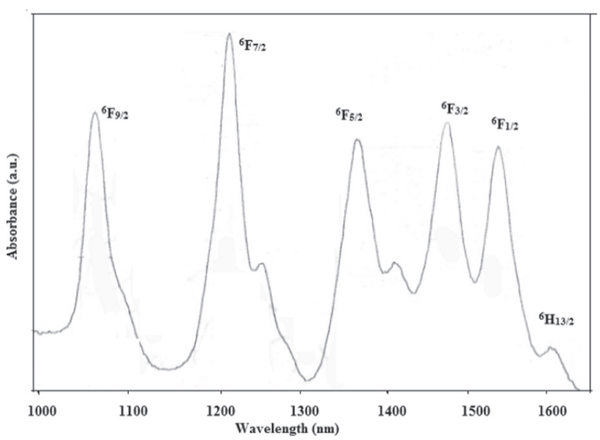


(a) Uv-Vis Absorption spectrum of Sm^{3+} in sodium Bismuth silicate glass



(b) NIR Absorption spectrum of Sm^{3+} in sodium Bismuth silicate glass

Fig. 1. (a) Uv–Vis absorption spectrum of Sm^{3+} in sodium Bismuth silicate glass (b) NIR Absorption spectrum of Sm^{3+} in sodium Bismuth silicate glass.

probability, optical gain, stimulated emission cross section and chromaticity parameters. All derived or observed results are compared with similar systems found in the literature.

2. Experimental

Samarium (1.5 mol%) doped sodium bismuth silicate glasses (83.5 SiO_2-5Na_2CO_3-10Bi_2O_3-1.5Sm_2O_3) were prepared by the well-known melt quenching method. Appropriate amounts of Bi_2O_3 (99.99% purity, Sigma Aldrich), Na_2CO_3 and SiO_2(99.99% purity, Sigma Aldrich) were mixed and ground continuously using an agate mortar. The powder mixture was placed in proclaim crucible and melted in a box furnace at a temperature of 1200 °C for 3 h before the molten mixture was poured into a stainless steel mold heated to 100 °C. The sample was then annealed at a temperature of 200^{0}Cfor 1 h. The density of the sample was measured by Archimedes' principle. To circumvent any undesired reaction with the synthesized glass, xylene was taken as the immersion liquid. Refractive index of the glasses were measured using Abbe refractometer (accuracy 0.001). Concentration of rare earth ion in the glasses was calculated from the starting batch composition and density of the glass samples. U–Visible-NIR absorption spectra of the sample were measured using a UV–Visible-NIR spectrophotometer Varian Cary 5000 in the wavelength range form250nm to 2000 nm. Fluorescence spectra of the sample were recorded using spectrofluro-photometer Shimadzu RFPC 5301 in the range from 200 to 900 nm. All the measurements were done at room temperature.

Table 1
Doubly reduced unit tensor operators $\langle\psi J\|U^{\lambda}\|\psi' J'\rangle$ for the transitions of Sm^{3+} used for the calculation of JO parameters [27].

Transitions between		$(U^2)^2$	$(U^4)^2$	$(U^6)^2$
$^6H_{5/2}\rightarrow$	$^6F_{1/2}$	0.1947	0.0	0.0
	$^6F_{3/2}$	0.1389	0.1329	0.0
	$^6F_{5/2}$	0.0346	0.2594	0.0
	$^6F_{7/2}$	0.0042	0.1099	0.3939
	$^6F_{9/2}$	0.0001	0.0183	0.3526
	$^6F_{11/2}$	0.0	0.0006	0.0527
$^4G_{5/2}\rightarrow$	$^6H_{5/2}$	0.0002	0.0006	0.0
	$^6H_{7/2}$	0.0	0.0067	0.0081
	$^6H_{9/2}$	0.0112	0.0066	0.0021
	$^6H_{11/2}$	0.0	0.0056	0.0030
	$^6H_{13/2}$	0.0	0.0	0.0022
	$^6F_{1/2}$	0.0008	0.0	0.0
	$^6F_{3/2}$	0.0013	0.0001	0.0

Table 2
Experimentally observed energy, oscillator strength and electric dipole line strength of low energy lying set Sm^{3+} in sodium bismuth silicate glass.

Transition from$^6H_{5/2}$ to	Energy (cm^{-1})	$F_{meas}(10^{-5})cm^2$	$S_{ed}(10^{-22})$
$^6F_{9/2}$	9259	0.12	4.93
$^6F_{7/2}$	8170	0.14	6.52
$^6F_{5/2}$	7289	0.67	35.1
$^6F_{3/2}$	6786	0.51	28.6
$^6F_{1/2}$	6477	0.39	22.9
$^6H_{13/2}$	6329	0.078	4.21

3. Results and Discussions

Fig. 1 shows the optical absorption spectra of samarium in bismuth silicate glass in the NIR region. All absorption bands are due to transitions between the multiplets of $4f^5$ configurations of Sm^{3+} with the ground state $^6H_{5/2}$. The typical absorption peaks of Sm^{3+}result from transitions from the ground state $^6H_{5/2}$ to the excited states $^4H_{9/2}$,$^4D_{3/2}$,$^6P_{7/2}$,$^6F_{7/2}$,$^4I_{13/2}$,$^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6F_{1/2}$ and $^6H_{13/2}$[22].

Indirect but convincing information regarding the RE-ligand bond strength can be obtained from the nephelauxatic ratio(β). The nephelauxatic ratio is given by:

$$\beta = {}^{\nu_m}/_{\nu_a}$$

where ν_m and ν_a are the wave numbers(cm^{-1}) of the particular transitions in the host matrix and aqua, respectively. Larger nephelauxatic ratios indicate a reduction in the strength of the covalent bond between a RE ion and a ligand. The nephelauxatic parameter is directly related to the bonding parameter (δ) by:

$$\delta = {}^{1-\overline{\beta}}\Big/_{\overline{\beta}}$$

where $\overline{\beta}$ is the average value of β for the observed transitions. The positive or negative sign of (δ) indicates the covalent or ionic bonding

Table 3
JO parameters of Sm3+ in sodium bismuth silicate glass and similar glassy systems.

Matrix	Ω_2 (10^{-20}) (cm^2)	Ω_4 (10^{-20}) (cm^2)	Ω_6 (10^{-20}) (cm^2)	Reference
Phosphate	1.65	2.66	2.65	[2]
Tellurite	1.49	5.68	3.33	[18]
Borate	1.28	2.78	1.97	[40]
Fluoride	1.16	2.60	1.40	[33]
Silicate	6.56	5.14	4.08	[3]
ZBLAN	2.15	3.05	1.56	[41]
Bismuth silicate	2.26	3.46	2.09	Present work