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Spectroscopic properties of Sm^{3+} doped sodium-tellurite glasses: Judd-Ofelt analysis

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ABSTRACT

Modifying the optical response of rare earth doped inorganic glasses for diverse optical applications is the current challenge in materials science and technology. We report the enhancement of the visible emissions of the Sm^{3+} ions doped sodium-tellurite (TNS) glasses. The impacts of varying Sm^{3+} ions concentration on the spectroscopic properties of such glass samples are evaluated. Synthesized glass samples are characterized via emission and absorption measurements. The UV–Vis–NIR absorption spectra revealed nine absorption peaks which are assigned to the transitions from the ground level ($^6H_{5/2}$) to $^6P_{3/2}$, $^4I_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6H_{15/2}$ and $^6F_{1/2}$ excited energy levels of Sm^{3+} ions. Emission spectra of the prepared glass under 404 nm excitation wavelength consisted of four bands centered at 561 nm, 598 nm, 643 nm and 704 nm which are originated from $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2 and 11/2) transitions. The experimental oscillator strengths, f_{exp} are calculated from the area under absorption bands. Using Judd-Ofelt theory and fit process of least square, the phenomenological intensity parameters Ω_λ ($\lambda = 2, 4, 6$) are obtained. In order to evaluate potential applications of Sm^{3+} ions in telluride glasses, the spectroscopic parameters: radiative transition probability A_R, branching ratio B_R, radiative life time τ_r and stimulated emission cross section σ_λ for each band are calculated. These glass compositions could be a potential candidate for lasers.

1. Introduction

Rare earth (RE) ion activated materials are considered as one of the most interesting research areas due to their various applications, e.g. lasers, sensors, telecommunication, display devices, 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]. In these systems, there are a number of interesting relationships between the active ions and the host glasses. Among these, one important point is that glasses with low phonon energies are of interest as hosts for infrared and infrared to visible upconversion lasers, because the glass host with low phonon energy can reduce the non-radiative loss due to the mutiphonon relaxation and thus achieves strong upconversion luminescence. Consequently, it is important to select a host material for which the maximum phonon energy is as low as possible. In tellurite based glasses, this phonon energy is reasonably large (~700 cm^{-1}). Moreover, tellurite glasses are considered as excellent materials for hosting lasing ions due to their better thermal and chemical stability, low melting temperature, high thermal expansion, good infrared transmission, high refractive index and capable of incorporating large concentrations of rare earth ions into the matrix [5–7]. However, tellurium dioxide (TeO_2) itself is only a conditional glass-former, which requires a special fast-quenching procedures to vitrify. Due to the difficulty of vitrifying TeO_2 alone by traditional method, the high transparent tellurite glasses are obtained by introducing other oxide such as transition metal oxides, alkaline oxides and alkaline-earth oxides or any other glass former [1]. In fact, sodium oxide (Na_2O) is nominated as the best modifier amongst the other alkali oxides. Additionally, Na_2O presents the most glass-forming ability on the basis of stability against crystallization.

Among active RE ions, the trivalent samarium (Sm^{3+}) ions in glassy matrix exhibits efficient fluorescence in a wide spectral

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range from ultraviolet to infrared region which can be used as undersea communications, optical storage materials, in high-density memories, colour displays, medical diagnostics and solid-state laser [8–10]. Glasses doped with Sm^{3+} ions exhibit relatively high quantum efficiency because of the large energy gap between the $^4G_{5/2}$ level and the next lower lying energy level $^6F_{11/2}$, which is approximately 7200 cm^{-1}. Additionally, the Sm^{3+} ions exhibit broad emission bands due to $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) transitions in any host matrix [11,12]. It is also well known that the intensities of emission bands of Sm^{3+} ion in glasses depend on its concentration and glass composition. In order to obtain optimum emission characteristics for device applications, the characteristic features of host as well as concentration dependent studies of Sm^{3+} ions are essential. Over the years, a vast amount of data on the spectroscopic properties of trivalent lanthanide ions in glasses was collected. However, the synthesis and optical analysis of Sm^{3+} ions doped tellurite glasses have seldom been studied. The complicated electronic structure of the $4f^5$ configuration is responsible for this neglect.

Usually, the Judd–Ofelt (J-O) theory has been used for the analysis of optical spectra of RE ions in various hosts. J-O theory is a useful tool for characterizing the radiative transition probability for different RE doped materials and to approximate the intensities of transitions in RE [13,14]. Three intensity parameters, Ω_λ ($\lambda = 2, 4, 6$) can be defined by this theory which are very sensitive to RE environment. These parameters are further used to estimate the other radiative parameters such as branching ratio, radiative transition probability and stimulated emission cross-section. Understanding the optical properties of RE doped tellurite glasses are prerequisite for optical applications. Therefore, in present work, a comprehensive analysis of spectroscopic properties of Sm^{3+}:TNS glasses by optical absorption and luminescence spectra were reported. The aim of present study is to synthesize the Sm^{3+}:TNS glasses with varying concentration of Sm_2O_3, to examine the energy levels to calculate the oscillator strength and J-O intensity parameters. Various radiative properties such as radiative transition probability, radiative lifetime, stimulated emission cross-section and optical gain are determined taking the J-O intensity parameters into account. All measured and calculated results were compared with similar Sm^{3+} ions doped glass systems.

2. Experimental procedure

The glass samples have nominal composition (80-*x*)TeO_2-20Na_2O-*x*Sm_2O_3 where $x = 0.0, 0.3, 0.6, 1.0, 1.2$ and 1.5 mol% are prepared using melt-quenching technique. The glass samples code and their compositions ratio are listed in Table 1. The raw materials with required proportion are weighted using a very sensitive weighing machine (Electronic Balance Precisa 205A SCS). The total weight of each batch of glass is 15 g and calculated in mol percent (mol%). A milling machine was used for mixing the chemical compositions before putting inside a Platinum crucible of about 30 ml capacities. Then the batch was preheated at 250 °C for about 20 min in order to reduce the batch blanket coverage on the top of the glass and enlarges the free non coverage glass melt surface [15]. After that, the batch transferred to another controlled electric furnace for melting it at 900 °C for about 40 min. The melts were poured on to a stainless steel mold and annealed at 250 °C for 3 h. After three hours, the furnace is switched off and the samples are allowed to cool down gradually to room temperature (25 °C). Finally, the samples are polished until the appropriate thickness (2.5 ± 0.01 mm) for structural and optical measurements.

Table 1
Glasses samples code and their concentration ratio.

Sample Code	Glass composition (mol%)			Molar Mass [g mol^{-1}]
	TeO_2	Na_2O	Sm_2O_3	
TNS1	80.0	20.0	0.0	140.07
TNS2	79.7	20.0	0.3	140.64
TNS3	79.4	20.0	0.6	141.21
TNS4	79.0	20.0	1.0	141.97
TNS5	78.8	20.0	1.2	142.34
TNS6	78.5	20.0	1.5	142.91

The amorphous nature of glasses are examined via a Bruker D8 Advance X-ray diffractometer (XRD) which uses CuKα radiations (λ = 1.54 A°) at 40 kV and 100 mA. The optical absorption of the prepared samples measured at a room temperature by using UV–Vis–NIR (Shimadzu 1301PC) spectrophotometer and the used wavelength range was 200–1000 nm. Perkin-Elmer LS-55 luminescence spectrometer is used to record the emission and excitation spectra, and pulsed xenon lamp operates as an excitation source, the luminescence spectra in the range of wavelength 200–900 nm under the excitation wavelength 404 nm is used in present research.

3. Results and discussion

3.1. Physical parameter

Density of the glass samples was determined by using Archimedes' method. The weight of the samples was measured by using an accurate 4 digit sensitive analytical electronic balance. Precisa XT220A, toluene was used as an immersed liquid with the density (ρ_t = 0.8669 g cm^{-3}) at room temperature. The density ρ was calculated using the expression [16]:

$$\rho = \left[\left(\frac{W_a}{W_a - W_t}\right) \times \rho_t + \rho_a\right] \quad (1)$$

where W_a and W_t are weight of the glass sample in air and in toluene respectively, ρ_a is the density of air and ρ_t is the density of the toluene. The molar volume (V_M) of the glasses was calculated from density values according to [17]:

$$V_M = \frac{M}{\rho} \quad (2)$$

where M is the molar weight and ρ is the density of the glass. The ionic packing density (V_t) is calculated using Makishima and Mackenzie approach [17,18].

$$V_t = \left(\frac{1}{V_M}\right) * \sum (V_i * x_i) \quad (3)$$

where x_i is the mole fraction (mol%) and V_i is packing density parameter (m^3/mol). For an oxide glass of the form M_xO_Y, the value of V_i yields [18],

$$V_i = \left(\frac{4\pi N_A}{3}\right)\left[X r_M^3 + Y r_o^3\right] \quad (4)$$

where N_A is Avogadro's number (mol^{-1}), r_M and r_o are the Shannon's ionic radius of metal and oxygen, respectively. The refractive index (n) of glass in terms of optical band gap (E_{opt}) is obtained by using [19,20].

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{\frac{E_{opt}}{20}} \quad (5)$$

The molar refractivity (R_M) can be obtained from Ref. [21],