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Optical and radiative properties of Sm^{3+} ions activated alkali-bismuth-germanate glasses

M. Ravi Prakash [a], G. Neelima [b c], Venkata Krishnaiah Kummara [d e], N. Ravi [c], N. Kiran [f], C.S. Dwaraka Viswanath [g], T. Subba Rao [h], V. Venkatramu [i]

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Abstract

Trivalent samarium (Sm^{3+})-doped alkali-bismuth-germanate glasses of a composition (40-x) GeO_2+20 Bi_2O_3+20 Na_2O+10 BaO+10 Gd_2O_3+x Sm_2O_3 (x = 0.05, 0.1, 0.5, 1.0, 1.5 and 2.5 mol%) (GeBiNaBaGdSm) were made from a typical melt-quenching procedure. An optical absorption, photoluminescence excitation, emission and decay curves of GeBiNaBaGdSm glasses were studied. For the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition, an intense orange emission at 601 nm was observed when the Sm^{3+} ions pumped by 405 nm. A high value of 15.59×10^{-22} cm^2 stimulated emission cross-section and 20.59×10^{-28} cm^3 of optical gain bandwidth for the 1.5 mo% Sm_2O_3-doped GeBiNaBaGdSm15 glass were obtained. The experimental lifetime (τ_{exp}) was increased up to GeBiNaBaGdSm05 glass, thereafter diminished with further increase of Sm^{3+} ion concentration. Decay profiles of Sm^{3+} ions were fitted using I-H model. Energy transfer rate (W_{ET}) for GeBiNaBaGdSm10 glass is evaluated to be 554 s^{-1}. The average red to orange (R/O) intensity ratio of these glasses is found to be 0.123. Furthermore, CIE chromaticity coordinates demonstrate that the emission was observed in the orange region and then shifted to red region with the increase of Sm^{3+} ion concentration. All the studies revealed that these glasses could be useful for tunable color display applications.

Introduction

Germanate glasses are of great attention for design and development of luminescent materials owing to their high refractive index, low phonon energies, and sensitivity to UV photon irradiation. Usually, germanate glasses have found applications in nonlinear optical devices, optical waveguides, Bragg gratings and optical fiber telecommunications [[1], [2], [3]]. With a significant addition of alkali metals ions such as

Li^+ and Na^+ to these glasses which acts as mixed glass formers (MGF). The MGF contained glass types of electrolytes are exceptional candidates for next generation solid-state electrolytes. Besides, a better thermal stability and stronger mechanical strength of these glasses because of their sturdy inter-ionic force between Ge^{4+} and O^{2-} ions in comparison with infrared (IR) transmitting glasses that include fluoride, tellurite and chalcogenide glasses [4].

Additionally, neutron scattering studies revealed that the GeO_2–P_2O_5 and K_2O–GeO_2–P_2O_5 glasses have been shown the existence of germanium atoms with a coordination number more than four. As a result, the structure of the GeO_2 has changed from tetrahedral to hexagonal. This higher coordinated germanium would cause a significant modifications in the structure of the binary alkali glasses, especially the alkali concentration less than 20 mol%, where nonlinear trends were noticed in the macroscopic properties that is said to be germinate anomaly [[5], [6], [7]]. The germanate glasses are superior in the optical fiber technology compared to silicate glasses due to their transparency in the mid infrared (mid-IR) region. But the development of these glasses was hindered by Rayleigh scattering losses [8]. These losses can be minimized with the addition of alkali metal ion modifiers in the germanate glass.

Among lanthanide (Ln^{3+}) ions, Gd_2O_3 is a widespread material because of proficient energy transfer occurs to the Ln^{3+} ions from Gd^{3+} ions consequently high thermal neutron capture cross-section that increases the light yield of emission. Addition of alkali metal ions (Li^+, Na^+, K^+) modifies, the Ge network leads to the formation of non-bridging (NBO) oxygens. The high Na^+ ion concentration may decrease ion pair function due to the result of bridging oxygen (BO) to non-bridging where Na–NBO distances are smaller in Na–O–Na bonds compared to Na–O–Bi/Ge that attributed to strong coulomb attractive Ge–O interaction. The addition of Na^+ also decreases defects in solids due to its smaller cation size [[9], [10], [11]].

Samarium (Sm^{3+}) ion is a good choice among the Ln^{3+} ions as its lowest emitting energy state $^4G_{5/2}$ possesses higher quantum efficiency with different quenching channels and exhibits a very small amount of probability for non-radiative decay, which are worthy characteristics of laser applications. Sm^{3+}ions activated glasses have realized in the promising applications as high density optical storage, color displays, solid state lasers (in visible region), photodynamic therapy (PDT) light sources and telecommunication (undersea) [12]. Sm^{3+} -doped glasses show a strong orange-red emission in the visible region. Sm^{3+} ions exhibit broad emission intensity bands in the NIR region due to $^4G_{5/2} \rightarrow {}^6H_J$ transitions (where J = 5/2, 7/2, 9/2 and 11/2). A large energy gap (~7250 cm^{-1}) between meta stable state $^4G_{5/2}$ and lower $^6F_{11/2}$ state in Sm^{3+} ions would cause a reddish orange emission around 600 nm which is not stimulated dreadfully by the phonon energy of the glass matrix [[13], [14], [15]]. For the purpose of energy transfer studies, Sm^{3+} ion can be used as co-doped ion with other Ln^{3+} ions [[16], [17], [18], [19], [20], [21], [22]].

This study is aimed to synthesize the Sm^{3+}-doped alkali bismuth-germanate (GeO_2+Bi_2O_3+Na_2O+BaO+Gd_2O_3, GeBiNaBaGd) glasses and to investigate their optical, photoluminescence and radiative properties with the variation of Sm^{3+} ion concentration. The radiative transition probabilities (A), branching ratio (β) and stimulated emission cross-sections (σ_{SE}) of GeBiNaBaGdSm15 glass were evaluated with the help of Judd-Ofelt (JO) theory. Inokuti and Hirayama (IH) model is employed to fit the non-exponential decay profiles of Sm^{3+} ions in these glasses, with an aim to know the multipolar interactions among Sm^{3+} ions and explore the energy transfer processes.

Section snippets

Glass fabrication procedure

A batch of 10 gm from high purity chemical composition of (40-x) GeO_2+20 Bi_2O_3+20 Na_2O+10 BaO+ 10 Gd_2O_3+ x Sm_2O_3 (x = 0.05, 0.1, 0.5, 1.0, 1.5 and 2.5) (GeBiNaBaGdSm) glasses were prepared using conventional melt-quenching technique. These glasses were coded as GeBiNaBaGdSm005, GeBiNaBaGdSm01, GeBiNaBaGdSm05, GeBiNaBaGdSm10, GeBiNaBaGdSm15 and GeBiNaBaGdSm25. The stoichiometrical amounts of chemicals were mixed homogeneously by grinding all the high purity chemicals using agate mortar and …

Optical (UV- visible- NIR) absorption spectrum

The ultraviolet (UV) – visible – near infrared (NIR) optical absorption spectrum of GeBiNaBaGdSm15 glass was recorded in the 350–2500 nm spectral region at room temperature and is shown in Fig. 1. Twelve optical absorption bands from visible and NIR were observed in the absorption spectrum owing to $4f^5$-$4f^5$ transitions. Six absorption bands observed in the range of 400–500 nm are shown in Fig. 1(a), and the rest of the bands noticed in the NIR region in the range of 900–2200 nm for…

Photoluminescence (PL) excitation spectra

The PL excitation spectra of the Sm^{3+}-doped GeBiNaBaGdSm glasses were recorded by monitoring the emission at 601 nm in the range of 350–540 nm at room temperature and are shown in Fig. 2. The spectra consists of twelve excitation bands positioned at 361 nm, 374 nm, 389 nm, 401 nm, 414 nm, 420 nm, 437 nm, 461 nm, 471 nm, 489 nm, 500 nm and 525 nm are ascribed to the transitions from the ground state, $^6H_{5/2}$ to $^4D_{3/2}$, $^6P_{7/2}$, $^4L_{5/2}$, $^6P_{3/2}$, $^6P_{5/2}$, $^4M_{19/2}$, $^4G_{9/2}$, $^4I_{13/2}$, $^4I_{11/2}$ + $^4I_{9/2}$, $^4M_{15/2}$, $^4G_{7/2}$ …

PL spectra

PL spectra of GeBiNaBaGdSm glasses with variation of Sm^{3+} ion concentration were recorded upon excitation of 405 nm in the spectral range of 530–740 nm, as shown in Fig. 3. The spectra revealed four emission bands of yellow, orange, orange-redand red were positioned at 561 nm (17825 cm^{-1}), 597 nm (16750 cm^{-1}), 644 nm (15527 cm^{-1}) and 707 nm (14144 cm^{-1}), which are ascribed to $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ transitions, respectively. Similar emissions were noticed in the reported…

Photoluminescent decay curves of $^4G_{5/2}$ level of Sm^{3+} -doped GeBiNaBaGdSm glasses were recorded upon the excitation of 405 nm. The decay curve of GeBiNaBaGdSm005 glass reveal the exponential behaviour, as shown in Fig. 5 and is analysed by using a single exponential equation. The non-exponential behaviour was observed for the glasses from GeBiNaBaGdSm01 to GeBiNaBaGdSm25, which analysed by using a double exponential equation and Inokuti and Hirayama (I-H) model. The I-H model is used to fit the…

CIE chromaticity diagram

CIE chromaticity diagram was used for evaluating the color representation of the visible emission of Sm^{3+} -doped GeBiNaBaGdSm glasses. The chromaticity coordinates are found to be (0.53, 0.39), (0.54, 0.38), (0.56, 0.36), (0.56, 0.35), (0.55, 0.36), and (0.62, 0.35) for the Sm^{3+} concentration of 0.05, 0.1, 0.5, 1.0, 1.5 and 2.5 mol%, respectively, by following the procedure has been described elsewhere [42]. The locations of all the coordinates were shown in Fig. 7. The emission from the CIE…

Conclusion

Alkali bismuth germanate glasses doped with different Sm^{3+} ions concentration have been fabricated using melt quenching technique and studied their optical and spectroscopic properties. Nephelauxetic ratio and bonding parameters of the GeBiNaBaGdSm15 glass were determined and revealed the ionic bond nature of the Sm^{3+} ion – ligand. Judd-Ofelt (JO) parameters have been carried out to find the radiative properties for the excited states of Sm^{3+} ions in the GeBiNaBaGdSm15 glass. Upon 405 nm…

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...The transitions of 4G5/2 → 6H9/2 and 4G5/2 → 6H11/2 are pure electric dipole in nature (ΔJ ≤ 6 and ΔL = 2) and they are hypersensitive to the environment. Moreover, the intense transition of 4G5/2 → 6H7/2 is both electric dipole and magnetic dipole in nature following the selection rule ΔJ = ±1.31,32 The emission intensity got improved for heat-treated glasses compared to that of precursor glass....

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