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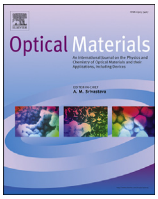

Compositional dependence of red luminescence from Eu^{3+} ions doped single and mixed alkali fluoro tungsten tellurite glasses

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ABSTRACT

Trivalent europium ions doped single and mixed alkali fluoro tungsten tellurite glasses have been prepared via melt quenching method and characterized by using Raman, optical absorption, excitation, emission and time resolved spectral measurements to understand their utility in visible red emission. Raman spectrum is used to identify different functional groups present in the as prepared glasses. The optical absorption spectra recorded for all the glasses show six bands corresponding to the transitions ${}^{7}F_{0}\rightarrow{}^{6}D_{2}$, ${}^{7}F_{0}\rightarrow{}^{6}D_{1}$, ${}^{7}F_{1}\rightarrow{}^{6}D_{1}$, ${}^{7}F_{0}\rightarrow{}^{6}D_{0}$, ${}^{7}F_{0}\rightarrow{}^{7}F_{6}$, and ${}^{7}F_{1}\rightarrow{}^{7}F_{6}$. An excitation spectrum is used to measure the electron-phonon coupling strength 'g' and phonon energy of the glass host 'hω'. The photoluminescence (PL) spectra measured under 464 nm excitation show eight luminescence peaks related to the transitions ${}^{5}D_{1}\rightarrow{}^{7}F_{0}$ (509 nm), ${}^{5}D_{1}\rightarrow{}^{7}F_{1}$ (537 nm), ${}^{5}D_{1}\rightarrow{}^{7}F_{2}$ (556 nm), ${}^{5}D_{0}\rightarrow{}^{7}F_{0}$ (580 nm), ${}^{5}D_{0}\rightarrow{}^{7}F_{1}$ (592 nm), ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$ (614 nm), ${}^{5}D_{0}\rightarrow{}^{7}F_{3}$ (652 nm) and ${}^{5}D_{0}\rightarrow{}^{7}F_{4}$ (701 nm) in all the glasses under investigation. Utilizing the Judd-Ofelt (J-O) parameters evaluated from the PL spectra, various radiative properties have been evaluated. From the decay spectra, experimental lifetimes were measured which are in turn used to evaluate the quantum efficiencies and non-radiatve decay rates in the as prepared glasses. The branching ratios, stimulated emission cross-section, quantum efficiency, colour co-ordinates and confocal images captured to confirm the suitability of these glasses for visible red luminescent devices.

1. Introduction

The necessity of developing solid-state optoelectronic devices, optoelectronic communication devices and white Light Emitting Diodes (w-LEDs) have escalated the research interest in rare earth (RE) ions doped glasses [1–5]. Especially, the demand for materials which are aptly suitable for w-LEDs are increasing day by day as they are playing a crucial role in solid state lighting applications. At present, RE doped phosphors are vigorously used in the production of w-LED. But they are not quite suitable for the excitation of InGaN-based LED chips in near-UV to blue region which finally leads to the low efficiency. Due to this reason, instead of Single w-LED, lots of w-LEDs are required to gain sufficient brightness for general lighting. To unravel this difficulty, so many studies have been done to enhance the output power of LED chips. But due to the increase in the chip temperature, the luminous efficiency and lifetime of the LED's decreases [6]. To avoid this problem, new phosphors without resin such as Ce-doped YAG glass ceramics are proposed [7]. Up to now, the major problem is lack of excellent red phosphors. To get efficient w-LED's, red phosphor is highly required in economic range [8]. But it is very intricate to get bright red colour emitting phosphors because of the sudden drop in quantum yield with increasing Stokes shift.

Europium ions are commonly used RE ions in several devices that can be used for lighting and displays. Europium ions can exist in several oxidation states and is a well-known activator with simple electronic transitions. A very interesting point in europium is, it gives strong visible luminescence in both the oxidation states

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i.e., Blue or green emission under near-UV excitation in Eu^{2+} state and red emission in Eu^{3+} state. Both are acting as efficient luminescent probes. The non-degenerate energy levels of Eu^{3+} ions are very crucial to understand the symmetry and inhomogeneity of the host material. The symmetry of the material depends upon the stark splitting of emission bands ($^5D_0 \rightarrow {}^7F_{1, 2}$). The trivalent europium ions possess prominent laser luminescence in the reddish-orange or bright red region and narrow band emission with higher lifetime [9]. However, the red luminescence of Eu^{3+} usually can't be efficiently excited by near-ultraviolet light because its excitation peaks in this region are due to parity-forbidden f-f transitions [10]. To obtain efficient red luminescence under near-UV excitation suitable host materials are required.

The end of the last decade is a strong evidence for the regeneration of RE ions doped luminescent materials. Glass materials are excellent option as luminescence materials because of their wide inhomogeneous line width, various compositions and easy mass production. Glasses based on heavy metal oxides like TeO_2 have always been an interesting area because of their typical structural and physical properties such as high refractive index, high density, high thermal expansion, low transformation temperature and excellent infrared transmission in the region 5–11 μm [11]. Comparatively high refractive indices with other glass systems like oxides are due to high polarizability of tellurium ions. Because of this property, the tellurite based glasses also have large values of third order non-linear optical susceptibilities that can be used to make the devices which can give femto second lasers [12]. These glasses are also used to improve the cross-sections because of their low vibrational frequencies which reduce the multiphonon radiations [13]. When these tellurite glasses are prepared in combination with tungsten ions, then these glasses become more suitable for optoelectronic devices because they show signs of photochromism and electrochromism. The main drawback of the TeO_2 is, it does not form a glass by itself and needs other compounds to form the glass. Hence the present system is prepared in combination with the compounds like WO_3, LiF, NaF and KF. The addition of WO_3 to the TeO_2 will improve the glass forming capacity and thermal stability because of conciliatory behaviour of octahedral sites present inWO_3. Tungsten ions can influence the photoluminescence behaviour of rare earth ions in tellurite glasses, because of their various valence states such as W^{6+}, W^{5+} and W^{4+}. These valence states participate in the glass network with different structural units like WO_4 and WO_6 and modify the tellurite network into TeO_4 to TeO_{3+1} structural units due to which remarkable changes can be produced in the photoluminescence behaviour of rare earth ions in a host matrix [14]. In addition, the presence of tungsten in a host matrix lowers their phonon energies and improves the luminescence efficiency or RE ions doped in them [15]. Single alkali and mixed alkali fluorides lend a hand to enhance the solubility of RE ions by creating the non-bridging oxygen ions [16]. They also decrease the melting temperature. They are also capable in reducing the water content in the glasses which in turn elevate the luminescence efficiency by reducing the phonon energies of glasses [16].

In the backdrop of the aforementioned various scientific patronages offered by the chemical constituents such as TeO_2, WO_3, LiF, NaF and KF, in the present work we prepared single and mixed alkali fluoro tungsten tellurite glasses doped with trivalent europium ions to understand their utility in visible red luminescence applications.

2. Experimental

In the present work, the single and mixed alkali fluoro tungsten tellurite glasses doped with trivalent europium ions have been prepared by using melt quenching technique with the following composition.

TeWLi: $59TeO_2$ - $20WO_3$ - 20LiF - $1Eu_2O_3$
TeWNa: $59TeO_2$ - $20WO_3$ - 20NaF - $1Eu_2O_3$
TeWK: $59TeO_2$ - $20WO_3$ - 20 KF - $1Eu_2O_3$
TeWLiNa: 59 TeO_2 - $20WO_3$ - 10LiF - 10NaF - $1Eu_2O_3$
TeWNaK: $59TeO_2$ - $20WO_3$ - 10NaF - 10 KF - $1Eu_2O_3$
TeWLiK: $59TeO_2$ - $20WO_3$ - 10LiF - 10 KF - $1Eu_2O_3$

High quality powders of 15 g for each batch of the composition of glass samples were melted at 750 °C in a silica crucible for about 2 h in an electrical furnace. The molten liquids have been quenched in air by pouring between two preheated brass moulds and later annealed at 400 °C for 4 h to remove internal thermal stresses. The prepared glasses have been polished before moving for characterization. The densities of the prepared glasses have been measured by Archimedes method using distilled water as an immersion liquid. The Raman spectrum of TeWKEu glass has been recorded in the range of 100–1000 cm^{-1} using Renishaw Invia Raman Microscope. The room temperature optical absorption spectra of all the glasses have been recorded in Visible to IR regions in the range of 450–2400 nm using a JASCO V-670 UV–vis–NIR spectrophotometer. The photoluminescence (PL) spectra were recorded using RF-5301PC Spectrofluorophotometer at room temperature. Edinburgh FLSP900 with a spectral resolution of 0.1 nm was used to measure the time resolved photoluminescence (TR-PL) spectra, where a xenon lamp was used as an excitation source.

3. Results and discussion

3.1. Raman spectral analysis

Fig. 1 shows the Raman Spectrum of TeWKEu glass which is recorded in the region 100–1000 cm^{-1}. The inset figure shows the Raman spectra for the remaining as prepared glasses. In all the glasses, nine peaks have been observed at 146, 183, 320, 395, 421, 463, 610, 733 and 924 cm^{-1} respectively. For the present series of glasses, there is no much variation in the intensity and no shifting of Raman peaks is observed. The peaks found in the range of 100–250 cm^{-1} are considered as boson peaks. These boson peaks are related to the scattering of light due to the thermal vibrations of disordered structure [17]. The Raman peaks observed at 320 and 395 cm^{-1} are due to vibrations of Tungsten anions and deformation vibrations of WO_6 octahedron [17,18]. The peaks observed at 421 cm^{-1} and 463 cm^{-1} are due to the bending vibrations of Te-O-Te linkages [17]. The peaks observed at 610 cm^{-1} are due to the vibrations of TeO_2 molecules and TeO_4 units. The peak observed at 733 cm^{-1} is due to the stretching vibrations of TeO_4 and TeO_3 groups or due to the stretching vibrations between Te and non-bridging oxygen (NBO) [19–21]. The peak observed at 924 cm^{-1} is due to the stretching vibrations of $W–O^-$and WO bonds associated with WO_4 and WO_6 units [22].

3.2. Optical absorption spectra

Fig. 2 show the optical absorption spectra of the trivalent Eu^{3+} ions doped single alkali and mixed alkali glasses. The absorption spectra have 6 peaks related to the transitions $^7F_0 \rightarrow {}^6D_2$, $^7F_0 \rightarrow {}^6D_1$, $^7F_1 \rightarrow {}^6D_1$, $^7F_0 \rightarrow {}^6D_0$, $^7F_0 \rightarrow {}^7F_6$, and $^7F_1 \rightarrow {}^7F_6$. Apart from all the trivalent RE ions, Eu^{3+} ions only possess two ground states such as $^7F_0$ and $^7F_1$. The energy gap between these two states is 360 cm^{-1}. Due to this reason, in Eu^{3+} ions doped materials, the absorption not only takes place from the ground level ($^7F_0$) but also takes place from the thermally excited level ($^7F_1$) [9]. Generally for all the