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Pr^{3+} ions doped single alkali and mixed alkali fluoro tungsten tellurite glasses for visible red luminescent devices

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ABSTRACT

The present work illustrates the optical absorption and fluorescence properties of Pr^{3+} ions doped single alkali and mixed alkali fluoro tungsten tellurite glasses prepared by using melt quenching technique. The prepared glasses were characterized by using absorption, excitation and photoluminescence (PL) spectral measurements. The energies of the absorption spectral features called oscillator strengths were calculated using area method and in turn used to evaluate the Judd-Ofelt (J-O) intensity parameters (Ω_2, Ω_4, Ω_6). Such J-O parameters are used to estimate various radiative parameters such as radiative transition probabilities (A_R), branching ratios (β_R), and radiative lifetimes (τ_R) for the prominent fluorescent levels of Pr^{3+} ions in these glasses. The PL spectra of the as prepared glasses show three prominent peaks at wavelengths 488, 646 and 670 nm related to the transitions $^3P_0 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3F_2$ and $^1D_2 \rightarrow {}^3H_5$ respectively for which emission cross-sections and branching ratios were evaluated. The variations in the spectral parameters with the variation of glass matrix composition have been examined in detailed. The decay profiles of the prepared glasses have been recorded to evaluate quantum efficiency of present series of glasses. From the measured branching ratios, emission cross-sections and quantum efficiency, it was concluded that the tungsten tellurite glasses added with potassium fluoride and doped with 1 mol% of Pr^{3+} ions (TeWK glass) are quite suitable to produce visible red emission at 670 nm suitable to fabricate red luminescent devices.

1. Introduction

Recently Rare Earth (RE) ions doped oxide glasses are playing vital role in diversified fields such as photonics, optoelectronic devices, wavelength conversion devices, optical fiber amplifiers, fiber lasers and compact microchip lasers [1–4]. Glassy materials have got so much of attention when compared with crystalline materials for the aforementioned applications because of their low cost and simple manufacturing procedure. Over and above the bulk samples of glassy materials can be prepared easily when compared with single crystalline materials [5]. Many researchers have investigated the lasing potentialities of RE ions doped fluoride, borate, fluoroborate and tellurite glasses to understand the effect of the host material and doped RE ion concentration [6–10]. Among the various types of oxide glasses, tellurite based oxide glasses have gained so much of attention in recent years because of their unique properties such as low phonon energy and low melting point ($800^0 \pm$ C); which are in fact the key points to get relatively higher quantum efficiency [11,12]. Tellurite glasses doped with RE ions have dragged so much attention for spectroscopic investigations, due to their potential applications in diversified areas like biochemical studies, telecommunications and optical sensors etc. [13–16]. Tellurite host matrices have several interesting features like low phonon energy ($< 800\ cm^{-1}$), high refractive index, large dielectric constant, broad transmission window (~0.4–5 μm), large RE ion solubility and higher stability among various other oxides hosts [17–26]. The above characteristics prompted us to choose tellurites as host matrix for the present investigation. On the other hand tellurite based glasses are conditional glass formers; i.e., independently they can't form a glass without the support of intermediates/modifiers such as WO_3, Ti_2O, Bi_2O_3, Li, Na and K [21]. Addition of tungsten oxide to tellurite's makes them non-hygroscopic and transparent in the visible and NIR regions. One of the special features of tungsten ions is that they show strong influence on luminescence properties of RE ions in the tellurite glasses because of their various valency states (W^{6+}, W^{5+} and W^{4+}). The

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thermo-reversible disproportionate reaction of these ions is represented as $W^{5+} + W^{6+} \Leftrightarrow W^{4+} + W^{6+}$ [27–29]. Each valency state of tungsten ion has a unique importance depending upon the formation of bonds with tellurium oxide. Tungsten ions with 5+ valence state (W^{5+}) form the complexes of $W^{5+}O^{3-}$. Due to these complexes, structural changes happen in tellurite network because TeO_4 structural units changes to TeO_{3+1} structural units [30,31]. The 6+ valence state of tungsten ions entered into the network of glasses as WO_4 and WO_6. Due to these units, new networks/linkages formed between Te ions and tungsten ions such as Te-O-W with TeO_4 and TeO_3 structural units [30,31]. In addition to the above, addition of WO_3 to a tellurite glass enhances the chemical stability and devitrification resistance. This loosens the glass network and increases the solubility of RE ions in the host glass [32–34].

The present series of tungsten tellurite glasses have been prepared in combination with different alkali fluorides (RF; where R stands for Li, Na and K metals) which act as network modifiers (NWM) and increase the stability of the glasses [35]. Moreover alkali fluorides can avert the moisture in glasses more effectively than alkali oxides and iodides [36]. The fluoride ions in alkali fluorides act as co-activators and replace the activators in the lattice. Due to the addition of these alkali fluorides, the mixed alkali effect (MAE) raised which can change various physical properties such as dielectric loss, ionic conductivity and alkali diffusion coefficient due to cation movements [37–40]. In addition to the above, fluorides addition to the glasses can lower the phonon energy (300-600 cm^{-1}) which in turn reduces non-radiative decay losses due to multiphonon relaxations. If non-radiative losses are reduced, the quantum efficiency of RE ion doped glass will increase. Due to these low non-radiative decay rates near maximum infrared (IR) cut-off edge will occur, which can lowers the non-linear refractive index. Hence transmission ability enhances from UV to IR. Addition of alkali fluorides to these glasses decreases OH absorption because fluoride ions reacting with OH group will form HF [41–43]. Fluoride content added to these glasses can also decrease the phonon energy and enhance the emission cross-section and quantum efficiency. This has been reported by many researchers in Pr^{3+} ions doped host glasses [44,45].

Among different RE ions, Pr^{3+} ion is one of the optical activator which gives luminescence in blue, green, red and IR regions with numerous applications such as optical devices, up-conversion lasers and fiber amplifiers [46–53]. The Pr^{3+} ions have a number of metastable states which are able to provide the efficient luminescence from visible to infrared region. Recent studies have been focused on 1.3 μm ($^1G_4 \rightarrow {}^3H_4$) emission from Pr^{3+} ions doped glasses which are very useful in telecommunication window [10,11,69]. Pr^{3+} ions also acts as an active luminescent centre, to give red luminescence in 600-720 nm wavelength region [11–25], which locates in the maximum absorption region of the Photo sensitizing currently used in photodynamic therapy or clinical trials [54,55]. Favourable red luminescence from Pr^{3+} ions doped glass fibers with sufficient intensity and suitable directivity are quite suitable for PDT treatment [54,55]. On the other hand, the studies on $^3P_0 \rightarrow {}^3H_6$ (orange-red emission) are not as much focused even though this luminescence is very useful as signal light source in astronomical telescope, in medical therapies (ophthalmology for the treatment of retinal disorders, removal of tissues, tumours and in the treatment of acne and in skin restoration). Various scientific patronages offered by the chemical constituents such as TeO_2, WO_3 and alkali fluorides have prompted us to take up a systematic investigation on Pr^{3+} ions doped different compositions of single and mixed alkali fluoro tungsten tellurite glasses for orange-red luminescent device applications.

2. Experimental

2.1. Synthesis and characterization of glasses

In the present work, the glass samples have been prepared by conventional melt quenching method with the following compositions.

TeWLi: 59TeO_2 - 20WO_3 - 20LiF - 1Pr_6O_{11}
TeWNa: 59TeO_2 - 20WO_3 - 20NaF - 1 Pr_6O_{11}
TeWK: 59TeO_2 - 20WO_3 - 20 KF - 1 Pr_6O_{11}
TeWLiNa: 59 TeO_2 - 20WO_3 - 10LiF - 10NaF - 1 Pr_6O_{11}.
TeWLiK: 59TeO_2 - 20WO_3 - 10LiF - 10KF - 1 Pr_6O_{11}.
TeWNaK: 59TeO_2 - 20WO_3 - 10NaF - 10KF - 1 Pr_6O_{11}.

The analar grade chemicals of TeO_2, WO_3, LiF, NaF, KF & Pr_6O_{11} were used as raw materials to prepare the glass materials. Approximately 10 g of each batch composition was weighed in an electrical balance and crushed in an agate mortar for 2 h to obtain uniform mixture. Then the mixture was collected in a silica crucible and it is sintered at 750 °C for ½ h and kept in a temperature controlled furnace and swirled inside the furnace to obtain homogeneous melt. The bubble free melt was then quenched in between a couple of pre-heated brass plates to get the glass samples with a uniform thickness. Later, these glass samples were annealed at 400 °C for 4 h to avoid the internal stresses generated by rapid cooling and to improve structural stability. The prepared samples are polished with emery paper before using them for absorption and luminescence spectral characterizations. For the prepared samples, densities are measured using standard Archimede's principle, using water as buoyant liquid. Refractive indices of the prepared glass samples were measured using the Brewster's angle method (He-Ne laser at λ = 650 nm) with an accuracy ± 0.01. The optical absorption spectra of the as prepared glasses have been recorded by using a double beam JASCO V-670 UV–vis-NIR spectrophotometer at room temperature with a spectral resolution of 0.1 nm. This is to be noted that the host glass matrix optical band gap is typically about 3 eV (i.e., absorption edge at 400 nm). While calculating the oscillator strengths (from areas under the absorption curve) and corresponding Judd-Ofelt parameters, appropriate background corrections have been made. The PL spectra of these glasses were recorded using RF-5301 PC Spectrofluorophotometer at room temperature. The decay profiles for the present series of glasses have been recorded using Edinburgh FLSP900 with a spectral resolution of 0.1 nm.

3. Results and discussions

3.1. Analysis of optical absorption spectra-measurement of oscillator strengths& J-O parameters

In order to understand the radiative properties possessed by Pr^{3+} ions doped in the as prepared glasses, absorption spectra have been recorded from 400 to 2200 nm. Fig. 1 shows the absorption spectra of Pr^{3+} ions doped alkali and mixed alkali fluoro tungsten tellurite

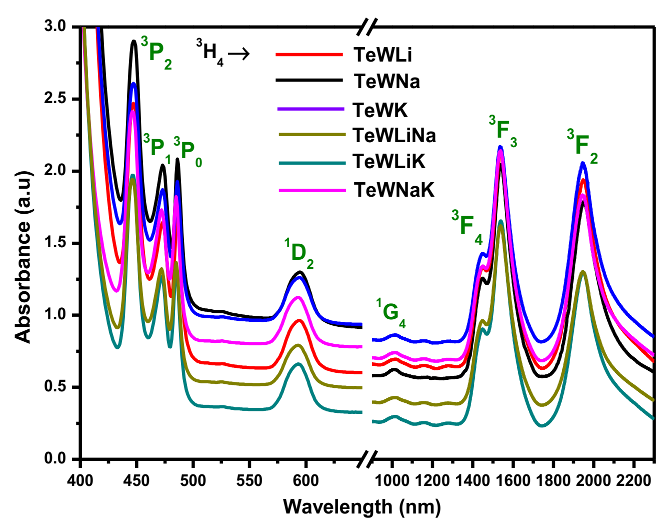

Fig. 1. Absorption spectra of Pr^{3+} ions doped single alkali and mixed alkali fluoro tungsten tellurite glasses.