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Dy^{3+} ions doped single and mixed alkali fluoro tungsten tellurite glasses for LASER and white LED applications

Ch. B. Annapurna Devi [a], Sk. Mahamuda [a], M. Venkateswarlu [a], K. Swapna [a], A. Srinivasa Rao [a, b, *], G. Vijaya Prakash [c]

[a] Department of Physics, K.L. University, Vaddeswaram 522 502, Guntur (Dt), A.P., India
[b] Department of Applied Physics, Delhi Technological University, Bawana Road, New Delhi 110 042, India
[c] Nanophotonics Lab, Department of Physics, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

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ABSTRACT

A new-fangled series of Dy^{3+} ions doped Single and Mixed Alkali Fluoro Tungsten Tellurite Glasses have been prepared by using melt quenching technique and their spectroscopic behaviour was investigated by using XRD, optical absorption, photoluminescence and lifetime measurements. The bonding parameter studies reveal the ionic nature of the Dy–O bond in the present glasses. From the absorption spectra, the Judd-Ofelt (J-O) intensity parameters have been determined and in turn used to determine various radiative properties for the different emission transitions from the $^4F_{9/2}$ fluorescent level. The photoluminescence spectra of all the glasses exhibit two intensified peaks in blue and yellow regions corresponding to the transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (483 nm) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm) respectively. From the photoluminescence spectra, it is observed that the luminescence intensity is maximum for Dy^{3+} ion doped potassium combination of tungsten tellurite glass (TeWK:1Dy). The highest emission cross-section and branching ratio values observed for the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions suggest the possible laser action in the visible region from these glasses. By correlating the experimental lifetimes (τ_{exp}) measured from the decay spectral features with radiative lifetimes (τ_R), the quantum efficiencies (η) for all the glasses have been evaluated and found to be maximum for potassium combination tungsten tellurite (TeWK:1Dy) glass. The CIE colour chromaticity coordinates (x, y), (u, v), colour correlated temperature (CCT) and Y/B ratio were also estimated from the photoluminescence spectra for different compositions of glasses. The chromaticity colour coordinates evaluated for all the glasses fall within the white light region and white light emission can be tuned by varying the composition of the glass. From all these studies, it was concluded that 1 mol% of Dy^{3+} ions doped TeWK glass is more suitable for lasing and white-LED applications.

1. Introduction

Rare earth ions doped glasses are exhibiting applications in diversified fields of science and technology such as bulk lasers, optical fiber amplifiers and waveguide lasers. In recent times, the applications possessed by rare earth doped glasses are not only confined to infrared optical devices, but also spread in the area of visible optical devices, especially for white light emitting diode (w-LED) applications such as indicators, back light, automobile headlights and general illumination [1]. In the current research, white light emitting diodes (w-LEDs) which are also known as next generation of solid state lighting (SSL) technology has become very popular because of their potential applications in diversified fields [2]. The wide spread of SSL is of great importance to reduce significantly the global electricity consumption and the usage of fossil fuels [3]. The w-LEDs have several superior features such as high luminous efficiency, long operation lifetime reliability, safety and environmental friendly characteristics when compared with other conventional sources such as incandescent and fluorescent lights [4]. Currently, these w-LEDs are made up of by the combination of blue light emitting diode (LED) (GaN-blue chip) chip with yellow phosphor (yellow YAG: Ce^{3+} phosphor) [5]. In this method,

* Corresponding author. Department of Applied Physics, Delhi Technological University, Bawana Road, New Delhi 110 042, India. Tel.: +91 85860 39007; fax: +91 01127871023.
E-mail address: drsrallam@gmail.com (A. Srinivasa Rao).

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the desired white light can be produced by exciting the yellow phosphor with blue LED. Due to lack of red component in their spectra, these w-LEDs possess low colour rendering index (CRI) (R_a = 60–75 range) and high correlated temperature (CCT ~ 7750 K). To improve the CRI to the acceptable range (>80) and the light conversion, a small amount of red phosphor will be introduced (YAG:Ce) [6–8]. But, the individual degradation rates of the blue LED chip and the phosphors coated on the chip would cause chromatic aberration and poor white light performance. To overcome this difficulty, it is necessary to develop novel materials which can emit bright white light by ultraviolet (UV) excitation [9,10]. At present w-LEDs, were constructed by mixing the phosphor powder with an epoxy resin that enables its coating on the chip. Due to the large difference between the refractive index of the phosphors and the epoxy resins, the scattering of light becomes high and heat resistance becomes very low which in turn leads to decrease in luminous intensity and a change of luminescence colour over a period. Not only this, the lifetime of LEDs also decreases due to the aging of organic epoxy resins under the long-term irradiation of UV light [11–13]. To overshoot the aforementioned problem, quite recently, the trivalent rare earth ions doped luminescent materials such as glasses and glass-ceramics have been synthesized and tested as an alternative for phosphor powders, since they can be suitably prepared in a plate like shape to ensure the direct encasement of the UV chip [14]. Apart from this, rare earth doped glasses are capable to showcase their superior nature from the perspective of homogeneous light emitting capacity, simple manufacturing procedure, lower production cost and excellent thermal and mechanical stability when compared with their conventional phosphor counterparts such as Li-α-SiAlON:Eu^{2+},Ca-α-SiAlON:Eu^{2+}, $Ba_3MgSi_2O_8$:Eu^{2+}, Mn^{2+} used in w-LEDs [1]. The aforementioned scientific patronages offered by rare earth doped glasses in the field of optoelectronics devices prompted us to take up the present investigation.

Fluoro Tungsten Tellurite glasses with alkali content in mixed and unmixed form were chosen with different compositions as our host glass material because of the unique properties of tellurium, tungsten and alkali fluorides (KF, LiF and NaF) as network modifiers.

The additions of mixed alkalies to these glasses are responsible for the non-linear variation of properties. This is really a remarkable change in the properties related to alkali ion transport. Due to the addition of mixed alkalies internal friction, dielectric loss, viscosity and glass transition etc also varies [15]. Now a days, tellurite glasses become more attractive because of their special physical properties such as high dielectric constant, low melting point (800 °C) and low phonon energies (780 cm^{-1}) [16]. In addition to the above, they are non-hygroscopic in nature and transparent from visible to IR regions. They are also used as nonlinear optical materials due to the unusual glass forming properties of tellurium dioxide (TeO_2). Even it is a four-coordinate; it is only a conditional glass former and by itself it doesn't form any glass but the addition of MO (M = Pb, W, Nb, Zn, Ba, etc.) increases the glass forming ability along with stability. The addition of alkali fluorides to TeO_2-WO_3 glass decreases the phonon energies by modifying the glass structure and by increasing the mechanical strength of the glass.

Among all the trivalent rare earth ions, the luminescent properties of Dy^{3+} ions have attracted special attention because of the interesting wavelengths produced by transitions between its intra 4f levels. The Dy^{3+} doped materials (glasses/phosphors) gained so much of interest among the researchers as it capable of giving two intense emission bands; one in blue (483 nm, $^4F_{9/2} \rightarrow {}^6H_{15/2}$) and the other one in yellow (574 nm, $^4F_{9/2} \rightarrow {}^6H_{13/2}$) region [17]. White light emission is possible with the suitable adjustment of the Y/B luminescence intensity ratio by changing the content of Dy^{3+} and/or composition of the host material [17]. The transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (electric dipole) is a hypersensitive transition ($|\Delta L| \leq 2$ and $|\Delta J| \leq 2$) and its intensity depends upon the host material whereas the intensity of the transition $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (magnetic dipole) is less sensitive to the host environment. In the present work, spectroscopic properties of different compositions of single and mixed alkali fluoro tungsten tellurite glasses doped with dysprosium were studied to check the suitability of these glasses for laser emission and white light generation.

2. Experimental

The glass samples used in the present work were prepared by conventional melt quenching technique with the following compositions.

TeWLi: $59TeO_2 - 20WO_3 - 20LiF - 1Dy_2O_3$

TeWNa: $59TeO_2 - 20WO_3 - 20NaF - 1Dy_2O_3$

TeWK: $59TeO_2 - 20WO_3 - 20\ KF - 1Dy_2O_3$

TeWLiNa: $59\ TeO_2 - 20WO_3 - 10LiF - 10NaF - 1Dy_2O_3$

TeWNaK: $59TeO_2 - 20WO_3 - 10NaF - 10KF - 1Dy_2O_3$

TeWLiK: $59TeO_2 - 20WO_3 - 10LiF - 10KF - 1Dy_2O_3$

Analar grade chemicals such as TeO_2, WO_3, LiF, NaF, KF and Dy_2O_3 were used as the starting materials to prepare the glasses used in the present work. All the chemicals were weighed as per the composition given above and trampled in an agate mortar until a smooth and homogeneous mixture was obtained. Further such homogeneous mixture collected into a silica crucible was heated at 750 °C in an electric furnace for about 30 min to obtain bubble free homogeneous melt. Such melts were then quenched suddenly on a pre-heated brass mould and pressed quickly by another brass mould. The glass samples thus prepared were subsequently annealed at 400 °C for 4 h to remove thermal strains/cracks produced inside and then allowed to cool down to the room temperature. The glass samples prepared thus are polished to a higher degree smoothness before going for the spectral measurements. The densities were measured by employing the Archimedes method using water as an immersion liquid. The refractive indices of these glasses were measured by Brewster's angle method using He–Ne laser (650 nm line) as the source. The optical absorption spectra of the samples were recorded at room temperature in the spectral wavelength range covering 800–2000 nm with a spectral resolution of 0.1 nm using a JASCO model V-670 UV–vis–NIR spectrophotometer. The photoluminescence excitation and emission spectra for all the glasses were recorded using RF-5301PC Spectrofluorophotometer at room temperature. The time-resolved photoluminescence (PL) measurements were carried out using home-built setups with 445 nm (CW laser) laser as an excitation source. The emission from sample was coupled into a monochromator (Acton SP2300) coupled to CCD (charge coupled detector) through the appropriate lenses and filters. For time-resolved photoluminescence, a frequency generator (5 Hz), lock-in amplifier, digital storage oscilloscope and a monochromator (Acton SP2300) coupled to a photomultiplier tube (PMT) were employed.

3. Results and discussion

3.1. XRD spectral analysis

XRD studies have been carried out to differentiate the crystalline

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