Journal of Non-Crystalline Solids 476 (2017) 128–136

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Investigations on the optical properties of Dy^{3+} ions doped potassium aluminiumtelluroborate glasses for white light applications

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ARTICLE INFO

Keywords:
Dysprosium
Glasses
Laser
CIE
Energy transfer

ABSTRACT

Dy^{3+} doped potassium aluminiumtelluroborate glasses with the chemical composition $55H_3BO_3 + (20 - x)TeO_2 + 10K_2CO_3 + 15Al_2O_3 + xDy_2O_3$ (where x = 0, 0.05, 0.1, 0.25, 0.5, 1.0 and 2.0 in wt%) were prepared following the melt quenching technique and its structural and optical behavior were analyzed through recording FTIR, UV–Vis-NIR, luminescence and decay spectra. The FTIR spectra confirm the presence of different stretching and bending vibrations of B—O and Te—O network in the prepared glasses. The nephelauxetic ratios (β) and bonding parameter (δ) values were determined from the absorption spectra and these values confirms the increasing covalent nature. The Judd-Ofelt (JO) intensity parameters (Ω_2, Ω_4, Ω_6) have been determined and the Ω_2 parameter value is found to increase with the increase in Dy^{3+} ions concentration thus indicates the increasing asymmetry nature. The luminescence spectra exhibits three distinguishable peaks at around 483 nm, 575 nm and 662 nm corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions while exciting at 388 nm. The Y/B ratio which signifies the local field environment was found to increase with the increase in the concentration of Dy^{3+} ions in the present glasses. The luminescence intensity of these transitions is found to quench beyond 0.5 wt% Dy^{3+} ions concentration which may probably due to the occurrence of possible resonant energy transfer and cross-relaxation mechanisms. The decay measurements were made by monitoring an excitation at 388 nm and emission at 575 nm corresponding to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition and the decay curve exhibit single exponential behavior at lower concentration and turn to exhibit bi-exponential behavior beyond 0.1 wt% of Dy^{3+} ion. Employing the Inokuti-Hirayama model, the type of interaction takes place between the donor-acceptor ions has been identified and the parameters like donor-acceptor interaction parameter (C_{DA}), critical distance (R_0) were also calculated and discussed. Among the prepared glasses, 0.5 wt% Dy^{3+} ions doped glass was found to exhibit higher stimulated emission cross-section pertaining to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition thus suggests its suitability for yellow laser applications. The CIE color chromaticity co-ordinates (x,y) were determined following the standard Commission International de l'Eclairage (CIE) 1931 chromaticity diagram and the values were found to be in close proximity with the standard white light (0.33, 0.33) for all the prepared glasses thus suggests the suitability of the present glasses for white light generation. Further correlated color temperature (CCT) values were found to agree with the cool white light suggesting the suitability of these glasses for operating in schools, offices etc.

1. Introduction

Solid state lighting (SSL) devices such as semiconductor light emitting diodes (LEDs), organic light emitting diodes (OLED), polymer light emitting diode (PLED) find application in many fields due to its low power consumption, ultra-long source life, highly efficient, low maintenance etc., White Light emitting diodes (WLed), a SSL based device provides high luminous efficiency, long operation lifetime reliability, higher shock resistance, safety and environmental friendly compared to other fluorescent lamps. WLeds are prepared following two approaches i.e., by exciting yellow phosphor (yellow YAG:Ce^{3+} phosphor) with blue light emitting diode (GaN-blue chip) or by exciting RGB phosphors with UV excitation [1]. Former suffers from low CRI (Ra–60–75 range), high CCT (~7750 K) while latter suffers from low luminescent efficiency due to reabsorption of light [2,3]. In both the approaches, phosphors were mixed with epoxy resin to enable coating on the chip. Due to the large difference in refractive index, high scattering takes place resulting in low heat resistance and change in

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http://dx.doi.org/10.1016/j.jnoncrysol.2017.09.038
Received 6 July 2017; Received in revised form 14 September 2017; Accepted 20 September 2017
Available online 26 September 2017

Table 1
Physical properties of Dy^{3+} ions doped Potassium aluminiumtelluroborate glasses.

Physical properties	BTKA	BTKA0.05D	BTKA0.1D	BTKA0.25D	BTKA0.5D	BTKA1.0D	BTKA2.0D
Density ρ (g/cm^3)	6.023 ± 0.0023	6.145 ± 0.0032	6.233 ± 0.0033	6.433 ± 0.0033	6.566 ± 0.0023	6.892 ± 0.0022	6.988 ± 0.0024
Refractive index n_d (589.3 nm)	1.72 ± 0.01	1.73 ± 0.01	1.74 ± 0.01	1.75 ± 0.01	1.76 ± 0.01	1.77 ± 0.01	1.78 ± 0.01
Dy^{3+} ion concentration N_E (10^{20} ions/cm^3)	0	0.389 ± 0.0015	0.788 ± 0.0003	2.03 ± 0.0024	4.11 ± 0.0028	8.54 ± 0.0043	17 ± 0.0012
Polaron radius r_p (A°)	0	11.9	9.4	6.86	5.42	4.25	3.38
Inter ionic distance r_i (A°)	0	29.5	23.3	17.01	13.44	10.54	8.38
Field strength F (10^{14} cm^{-2})	0	0.3447	0.552	1.04	1.66	2.7	4.27
Molar refractivity R_m (cm^3)	6.23 ± 0.0024	6.18 ± 0.0031	6.16 ± 0.0031	6.05 ± 0.0030	6.02 ± 0.0021	5.86 ± 0.0018	5.96 ± 0.0018
Dielectric constant (ε)	2.96	2.99	3.03	3.06	3.10	3.13	3.17
Reflection losses R (%)	7.01	7.15	7.29	7.44	7.58	7.73	7.87
Molar volume V_m (cm^3/mol)	15.78	15.48	15.28	14.86	14.64	14.10	14.21
Electronic Polarizability α_e (10^{-22} cm^3)	0	24.51	12.22	4.79	2.39	1.16	0.59

luminescence color over a period of time [4]. Although silicon based metals with high thermal resistance have been used for making epoxy in recent days, it reduces the performance of WLed and suffers from thermal shrinking [5]. Thus in order to eradicate these losses, rare earth doped glasses is more favorable for the fabrication of WLed. Generation of white light in glasses is more common due to homogeneous light emission, simple manufacture procedure, lower production cost, better thermal stability, longer lifetime, lower energy consumption and higher reliability [6]. Recently B_2O_3—TeO_2 network was studied by many researchers [7,8] due to its combined property of high thermal stability, high transparency, low melting point, high non-linear susceptibility, broad optical transmission window extending from 350 nm to 5 μm. Addition of aluminium oxide and potassium carbonate increase the insulating strength and the density of glass respectively. Thus in the present system B_2O_3—TeO_2—Al_2O_3—K_2CO_3 has been chosen as the glass host.

Among the RE^{3+} ions, Dy^{3+} ion was chosen in the present study due to the dominant emission from $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) transitions whose ratio (Y/B) can be tuned for white light emission. Swapna et al. studied the Dy^{3+} ions in ZnO—Al_2O_3—Bi_2O_3—B_2O_3 host to explore its suitability for white light generation [9]. Kamel Damak et al. investigated Dy^{3+} ions doped TeO_2—ZnO—PbO—PbF_2—Na_2O host matrix and discussed the impact of blue component in obtaining pure white light [10]. Shanmugavelu et al. described the different energy transfer takes place between Dy^{3+}–Dy^{3+} ions in Bi_2O_3—ZnO—B_2O_3 host and its suitability for white light generation [11]. K. Venkata Rao reported that Dy^{3+} ions in borate glasses with the composition B_2O_3—PbO—MgF_2—NaCl are better for yellow lighting applications [12]. H. H. Xiong et al. studied the quantum yield, spectral distribution of Dy^{3+} ions in alkaline earth borate glass with the chemical composition Li_2CO_3—K_2CO_3—KNO_3—ZnO—$BaCO_3$—Sb_2O_3—H_3BO_3 for developing the fibre lighting sources, display devices, tunable visible lasers and optical signal amplifiers [13]. The present work is aimed to (i) prepare Dy^{3+} ions doped potassium aluminiumtelluroborate glasses by varying the concentration of Dy^{3+} ions following the melt quenching technique (ii) identify the different stretching and bending vibrations (iii) determine the covalent/ionic nature (iv) study the variation of Judd-Ofelt (JO) parameters with the increase in the concentration of Dy^{3+} ions (vi) determine the radiative parameters with these JO parameter values and to explore the suitability of yellow laser applications (vii) determine the Y/B ratio from the luminescence spectra and to analyze the degree of asymmetry in the prepared glasses (viii) analyze the energy transfer mechanism through decay measurements by fitting the IH model and finally (ix) explore the suitability of the prepared glasses for white light generation using standard Commission International de I'Eclairago (CIE) 1931 chromatacity system.

2. Experimental

Trivalent Dysprosium doped potassium aluminiumtelluroborate glasses were prepared with the chemical composition $55H_3BO_3 + (20 - x)TeO_2 + 10\ K_2CO_3 + 15Al_2O_3 + xDy_2O_3$ (where x = 0, 0.05, 0.1, 0.25, 0.5, 1.0 and 2.0 wt%) and coded as BTKA, BTKA0.05D, BTKA0.1D, BTKA0.25D, BTKA0.5D, BTKA1.0D and BTKA2.0D respectively. High Purity (99.99%) chemicals from Sigma Aldrich (H_3BO_3, TeO_2, K_2CO_3, Al_2O_3, Dy_2O_3) were used as precursors for the preparation of these glass samples. These precursors were weighed for 15 g batch in a standard weighing balance and grinded in an agate mortar to a well-powdered form. These chemicals were taken in to the porcelain crucible and melted in a furnace at 1100 °C for 90 mins. Then the melt was poured onto a preheated brass plate and annealed for 10 h at 380 °C to remove internal stress, air bubbles and to improve the mechanical strength. These glasses were polished on both sides to meet out the optical quality requirements. All the compounds are correctly weighed to avoid the random errors and more care was given in the materials selection by considering the factors like ionic size, oxidation states and stability of the compounds to prevent the systematic error that occur during the preparation of glass.

The FTIR spectra of the prepared glasses were recorded with JASCO FTIR 460 plus in the mid IR region 400–4000 cm^{-1} with a spectral resolution of ± 1.0 cm^{-1}. The absorption spectral measurements were made using CARY 500 UV–Vis-NIR spectrophotometer in the wavelength region 350–2000 nm with a spectral resolution of ± 1 nm. The Luminescence spectra have been recorded employing JASCO spectrofluorimeter using xenon lamp (450 W) in the wavelength range 400–800 nm with spectral resolution of 1 nm. The decay measurements were made using Edinburgh FLS–900 time resolved fluorescence spectrometer. The density was measured following the Archimedes principle employing xylene as an immersion liquid and the refractive indices were measured through Abbe Refractometer using mono bromonaphthalene as the contact liquid at sodium wavelength. Other physical properties such as electronic polarizability, polaron radius etc., were calculated using the expressions reported in the literature [14] and these values were presented in Table 1. The error analysis for all the measured quantities has been estimated by adopting the basic principle. For example, while considering a relation X = Y/Z whose error have been determined using the equation $\Delta X/X = \Delta Y/Y + \Delta Z/Z$. For some of the parameters, due to its too low significant digits the error value was not mentioned.

3. Results and discussion

3.1. Structural studies

3.1.1. FTIR

Fourier transform infrared spectra of the prepared Dy^{3+} ions doped potassium aluminiumtelluroborate glasses recorded in the region 400–4000 cm^{-1} is shown in Fig. 1 and their band assignments are presented in Table 2. The spectra exhibit nine absorption bands centered at around 3434, 2912, 2854, 1459, 1307, 1187, 1066, 708 and 436 cm^{-1}. The peak around 3434 cm^{-1} indicates the presence of —OH groups in the prepared glasses. The peak positioned at 2912,