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Oxyfluorotellurite glasses doped by dysprosium ions. Thermal and optical properties

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ABSTRACT

The paper shows results of investigation of thermal and optical properties of oxyfluorotellurite $(65-x)TeO_2$–$20ZnF_2$–$12Pb_2O_5$–$3Nb_2O_5$–xDy_2O_3 ($x = 0.5$, 2 and 5) glass systems. Thermal stability and the onset of crystallization of the materials were monitored by differential thermal analysis (DTA). It was found that characteristic parameters, namely glass transition temperatures (T_g), onset of crystallization temperatures (T_c) and thermal stability criteria ΔT and H' increased with increasing Dy_2O_3 content indicating that the incorporation of dysprosium ions improves substantially thermal stability of glass system under study.

Optical absorption and emission spectra of Dy^{3+} ions in oxyfluorotellurite glass were investigated at room temperature in the visible (VIS) and near-infrared (NIR) region. Oscillator strengths, phenomenological Judd–Ofelt (JO) intensity parameters $\Omega_{2,4,6}$, radiative transition probabilities, branching ratios and radiative lifetimes of luminescent levels were determined. Decay curves of the $^4F_{9/2}$ luminescence of incorporated Dy^{3+} ions were recorded and analysed. Lifetimes and the luminescence dynamics were studied as a function of the Dy_2O_3 concentration. It was concluded that good thermal stability combined with desirable spectroscopic parameters of investigated dysprosium-doped oxyfluorotellurite glass point at the suitability of this material for the design of UV-excited visible phosphors.

1. Introduction

Oxyfluorotellurite glasses combine advantages of the two (fluoride and tellurite) glass systems and that is reason why they were subject of scientific and technological interest [1–6]. Due to their good thermal stability [1–6] and chemical durability [1–5], non hygroscopicity, high refractive index [1–4,6], low phonon energies [1–3,5,6], wide optical transmittance region [1,2,4], good transparency in the mid-infrared [3,5,6] and also high solubility for rare earth ions [3,6] oxyfluorotellurite glasses are good candidates for application and development of optoelectronics (colour displays), photonics (fibre amplifiers), telecommunications (fibre-optic communications, optical amplifiers) or laser techniques (solid-state lasers, laser fibres) [1–6].

Rare earth (RE) ions play an important role in modern technology as active ions in many optical materials. It is common knowledge that the optical properties of rare-earth ions in glasses depend on the chemical composition of the glass matrix, which determines the structure and nature of the bonds [7]. Among different lanthanides, dysprosium ion (Dy^{3+}) is of interest ions because it is able to show emissions in the visible (VIS) and near infrared (NIR) regions. The visible fluorescence of Dy^{3+} ion consists of two strong emission transitions: one in the yellow (∼560–600 nm, $^4F_{9/2} \rightarrow {}^6H_{13/2}$) and the other one in blue (∼470–500 nm, $^4F_{9/2} \rightarrow {}^6H_{15/2}$) regions. As a consequence dysprosium-doped glasses are promising for application in solid state visible lasers [8,9], up converters and optical amplifiers [9], commercial display devices [10] and through appropriately combination of yellow to blue emission could result in white light emission [8–11]. Knowledge on their thermal behaviour and spectroscopic features is thus relevant to the practice.

In the present paper we report on the synthesis, thermal stability and fundamental spectroscopic properties of Dy^{3+}-doped oxyfluorotellurite glass with chemical composition $(65-x)TeO_2$–$20ZnF_2$–$12PbO$–$3Nb_2O_5$–xDy_2O_3 where $x = 0.5$, 2 and 5 mol%. The thermal stability parameters, oscillator strength, Judd–Ofelt intensity parameters, branching ratios and radiative transition probabilities were calculated and compared with available literature data. As far as we know, thermal and spectroscopic features of this system have not been reported before. Detailed investigation of the undoped glass matrix has been reported by Guihua Liao et al. [2] and the information gathered therein was used as a reference point for the present work.

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2. Experimental

The glass samples were prepared from a mixture of high purity (4 N or 5 N, Alfa Aesar) powders of tellurium (TeO_2), niobium (Nb_2O_5) and lead (PbO) oxides, anhydrous zinc fluoride (ZnF_2) and 5 N-purity dysprosium oxide (Dy_2O_3). Dy^{3+}- doped glasses have the following chemical compositions (in mol%) $(65-x)TeO_2$–$20ZnF_2$–$12PbO$–$3Nb_2O_5$–xDy_2O_3 with nominal concentrations $x = 0.5$, 2 and 5 mol% of Dy_2O_3.

Thoroughly mixed in dry box 10 g batches of the starting substrates were placed in corundum crucible and then melted in a resistance furnace at 830 °C for 30 min in normal atmosphere. The melt was poured onto a preheated steel plate and then was annealed for a few hours below the glass transition temperature (T_g) in order to eliminate internal stresses.

Differential thermal analysis (DTA) measurement was performed in atmospheric air under normal pressure using a NETZSCH differential scanning calorimeter DSC 404/3/F with Pt/PtRh DSC measuring head and platinum sample pans. An empty platinum crucible was used as the reference. The heating rates of 10 K/min in the DTA measurements were the same for all samples studied.

Optical absorption spectra were recorded with a Varian 5 Absorption Spectrophotometer employing spectral bandwidth of 0.2 nm in UV and visible and of 0.8 nm in near infrared. Emission measurements were carried out in the visible and near infrared spectral range. Luminescence spectra were recorded with an Optron Fluorometer System consisting of 150 W xenon lamp coupled to an excitation monochromator, an emission monochromator with 750 mm focal length equipped with a photomultiplier and InGaAs detector and a signal recovering unit. Luminescence decay curves were recorded following a short pulse excitation provided by an optical parametric oscillator (OPO) pumped by a third harmonic of a Continuum Model Surelite I Nd:YAG laser. Resulting luminescence signal was filtered using a Zeiss model GDM-1000 monochromator, detected by a Hamamatsu R928 photomultiplier and recorded with a Tektronix TDS 3052 oscilloscope. All optical measurements were carried out at room temperature and in atmospheric air under normal pressure.

Values of the density $\rho = 5.76\ g/cm^3$ and refractive index $n = 1.9813$ of the glass have been taken from the literature [2].

3. Results and discussion

3.1. Thermal analysis

In Fig. 1 the DTA curves recorded for $(65-x)TeO_2$–$20ZnF_2$–$12Pb_2O_5$–$3Nb_2O_5$–xDy_2O_3 samples glasses with 0.5, 2 and 5 mol ratio of Dy_2O_3 and for oxyfluorotellurite matrix glass $65TeO_2$–$20ZnF_2$–$12Pb_2O_5$–$3Nb_2O_5$ are compared. The characteristic glass temperatures, namely the glass transition temperatures (T_g) and onset of crystallization temperatures (T_c) were estimated in accordance with the Keavney and Eberlin method [12]. It can be seen in Fig. 1 that the value of T_g indicating initiation of the glass softening is affected by incorporated Dy^{3+} ions. The value of T_g for undoped glass matrix is the lowest and equals to 365.3 °C. In doped samples it grows with increasing Dy^{3+} concentration and amounts to 368.6 °C, 371.3 °C and 378.1 °C for samples containing 0.5, 2, 5 mol% of Dy_2O_3, respectively. Evaluated values of the glass crystallization temperature T_c follow the same trend with a more pronounced increase from 552.3 °C for undoped glass to 830.5 °C for a glass sample containing 5 mol% of Dy_2O_3. For all samples of glasses $(65-x)TeO_2$–$20ZnF_2$–$12Pb_2O_5$–$3Nb_2O_5$–xDy_2O_3 with $x = 0.5$, 2 and 5 mol% of Dy_2O_3 the exothermal crystallization peak T_{pc} values are higher than that for undoped glass matrix and appear between 700 and 860 °C.

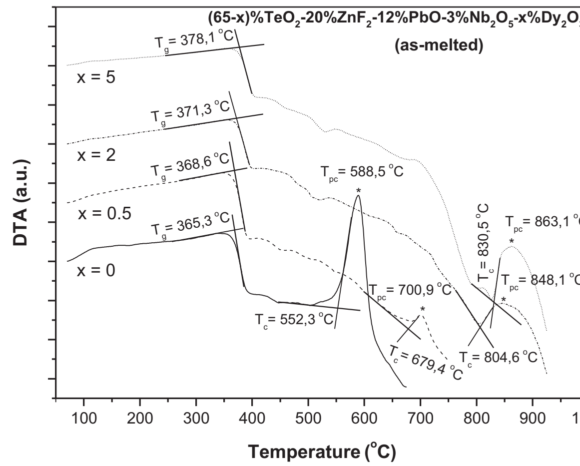

Fig. 1. Differential thermal analysis (DTA) curves recorded for $65TeO_2$–$20ZnF_2$–$12Pb_2O_5$–$3Nb_2O_5$ glass matrix and Dy^{3+}- doped glass samples $(65-x)TeO_2$–$20ZnF_2$–$12Pb_2O_5$–$3Nb_2O_5$–xDy_2O_3 with $x = 0.5$, 2 and 5.

The increase of all characteristic glass temperatures, especially the glass crystallization temperatures (T_c) could be the result of the increased in number of bonds per unit volume and an increased density with the addition of Dy_2O_3 from 0.5 to 5 mol% into TeO_2–ZnF_2–Pb_2O_5–Nb_2O_5 glasses. This behaviour may be connected with a fact that Dy^{3+} ions are capable of breaking existing oxygen bonds (e.g.: Te-O-Te, Te-O-Pb, Te-O-Nb and etc.) linkages and building new bonds with oxygen atoms in the Dy_2O_3 containing glasses like Te-O-Dy, Dy-O-Pb or Dy-O-Nb. Jyothi et al. hint that the increasing the number of bonds per unit volume should be combined with the substitution of TeO_2 by Dy_2O_3 content to provide two dysprosium and three oxygen ions in the place of one tellurium and two oxygen ions [10]. Dy_2O_3 content has greater number of cations per mol and average cross-link density and this consequently leads to an increase of the number of bonds per unit volume [13]. Similar behaviour for both the glass transition and the glass crystallization temperatures have been reported for other oxyfluorotellurite glass systems, e.g.: TeO_2–BaO–BaF_2–La_2O_3–LaF_3, $(60-x)TeO_2$–$20ZnO$–$20LiF$–xEr_2O_3, $(75-x)TeO_2$–$10TiO_2$–$15WO_3$–xDy_2O_3, $80TeO_2$–$5TiO_2$–$(15-x)WO_3$–xA_nO_m (where A_nO_m is Nb_2O_5, Nd_2O_3, and Er_2O_3) or $(1-x)TeO_2$–xWO_3 doped with Nd_2O_3, Er_2O_3, Tm_2O_3 and Yb_2O_3 [1–3,10,13,14].

It follows from these data that incorporated rare earth ions influence the ability of glass formation and thermal stability of the glass. The glass stability can be determined qualitatively based on a difference of thermal stability criteria:

$$\Delta T = T_c - T_g \quad \text{Dietzel factor} \quad [15], \tag{1}$$

$$H' = \frac{T_c - T_g}{T_g} \quad \text{Saad – Poulain factor} \quad [16], \tag{2}$$

$$S = \frac{(T_c - T_g)(T_{pc} - T_c)}{T_g} \quad \text{Saad – Poulain factor} \quad [16], \tag{3}$$

remembering that the larger are values of these parameters the higher is thermal stability of the glass. The ΔT, H' and S values for the systems under study, listed in Table 1, imply that the incorporation of Dy_2O_3 brings about a substantial improvement of thermal stability of the $65TeO_2$–$20ZnF_2$–$12Pb_2O_5$–$3Nb_2O_5$ glass. It should be noticed here that in contrast to ΔT and H' parameters the S parameter values found do not change monotonously with increasing Dy_2O_3 content. In our opinion this is due to high incertitude of T_{pc} values that follow from broad and asymmetric shapes of the matrix crystallization bands. In addition, the T_{pc} value also depends on