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Review

Thermal and optical properties of oxyfluorotellurite glasses doped with europium ions

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The paper shows some results related to thermal and optical properties of Eu^{3+} -doped (65-x)TeO_2-20ZnF_2-12PbO-3Nb_2O_5-xEu_2O_3 glass systems. Concentration of the Eu_2O_3 was different (x = 0.5, 2 and 5 mol%) so it could determine the influence of active admixture on relevant properties of oxyfluorotellurite glass. Thermal stability and crystalline phases formed by the glass matrix were examined by differential thermal analysis (DTA). The characteristic temperatures (glass transition temperature and oxide glass crystallization temperature) have been determined. Optical absorption and emission spectra of Eu^{3+} ions in oxyfluorotellurite glasses have been investigated at room temperature in the ultraviolet (UV), visible (VIS) and near-infrared (NIR) region. Oscillator strengths, phenomenological Judd-Ofelt intensity parameters $\Omega_{2,4,6}$, radiative transition probabilities, branching ratios and radiative lifetimes of luminescent levels have been also estimated. Lifetimes and the luminescence dynamics were studied as a function of the Eu_2O_3 concentration.

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1. Introduction

Optical properties of rare earth ions in glasses depend on the chemical composition of glass matrix and the nature of a modifier. Over the past several years, research on structural and optical properties of rare earth (RE) doped oxyfluorotellurite glasses gained lot of scientific interest due to their technological applications in the field of telecommunications (fibre-optic communications, optical amplifiers), optoelectronics (colour displays), photonics (fibre amplifiers), or laser techniques (solid-state lasers, laser fibres) [1–6]. This type of glasses characterized by low phonon energies (e.g.: (60-x)TeO_2–20ZnO–20LiF–xEr_2O_3 glasses with different concentrations of Er^{3+} ions were studied in Ref. [1] or glasses TeO_2–ZnO–Na_2O–La_2O_3 and TeO_2–ZnO–ZnF_2–Na_2O–La_2O_3 doped with Er^{3+} and codoped with Er^{3+}/Pr^{3+} [3]). The TeO_2–WO_3–PbO–BaF_2, TeO_2–TiO_2–Nb_2O_5–BaF_2 glasses doped with Er^{3+} ions [4] and fluorotellurite glass system with composition of TeO_2–ZnF_2–PbO–Nb_2O_5 [5] revealed wide optical transmittance region. Oxyfluorotellurite glasses (60-x) TeO_2–20ZnO–20LiF–xEr_2O_3 have investigated by P. Babu at al [6].

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exhibit good transparency in the mid-infrared, possess high refractive index [4–6] and also high solubility for rare earth ions [1,6]. Furthermore, oxyfluorotellurite glasses ensures good thermal stability like oxyfluorotellurite glass systems TeO_2–BaO–BaF_2–La_2O_3–LaF_3 [2], non hygroscopicity, chemical durability [1–6] and they are relatively easy to prepare in various compositions in order to obtain the desired usefulness properties.

It is also known that the optical properties of rare-earth ions introduced into the glass matrix strongly depend on the chemical composition of the glass that defines structure and nature of the bonds [7]. Europium is one of the peculiar ion because of its two oxidation states (Eu^{2+} and Eu^{3+}), energy level structure and high luminescence efficiency of the $^5D_0 \rightarrow {}^7F_2$ emission transition. In addition, it is only one lanthanide ion in which the ground state has $J = 0$ what is related to exceptional restrictions attributed to the induced electric-dipole transitions originating from the ground state. The incorporation of Eu^{3+} ions to oxide glass matrix usually induces significant changes in its magnetic behaviour and relaxation of excited states (relatively weak radiationless transitions) [8]. Study of thermal behaviour and optical properties of the RE ions doped into different glass matrices supply a very important information from a potential application point of view.

In this paper we investigate thermal and spectroscopic properties of the previously prepared Eu^{3+} co-doped oxyfluorotellurite glasses with chemical composition (65-x)TeO_2-20ZnF_2-12PbO-3Nb_2O_5-xEu_2O_3 where x = 0.5, 2 and 5 mol%. Thermal stability parameters, oscillator strengths, Judd–Ofelt intensity parameters, branching ratios and radiative transition probabilities were determined and compared with available literature data.

2. Experimental

The glass samples were prepared from a mixture of high purity (4N or 5N, Alfa Aesar) powders of tellurium (TeO_2), niobium (Nb_2O_5) and lead (PbO) oxides, anhydrous zinc fluoride (ZnF_2) and 5N-purity europium oxide (Eu_2O_3). Eu^{3+}- doped glasses have the following chemical compositions (in mol%) (65-x)TeO_2-20ZnF_2-12PbO-3Nb_2O_5-xEu_2O_3 with nominal concentrations x = 0.5, 2 and 5 mol% of Eu_2O_3 labelled as TZPNEu0.5, TZPNEu2 and TZPNEu5 respectively. For the undoped matrix glass 65TeO_2-20ZnF_2-12PbO-3Nb_2O_5 formula is shortly denoted as TZPN.

Thoroughly mixed in dry box 10 g batch 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 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 in the DTA measurements were for each material the same (10 K/min) and were performed in atmospheric air under normal pressure.

Optical absorption spectra were recorded with a Varian 5 Absorption Spectrophotometer employing a spectral bandwidth of 0.2 nm in UV-VIS and of 0.5 nm in near infrared. Emission measurements were carried out in the UV-VIS spectral range. Luminescence spectra were recorded with an Optron Fluorometer System consisting of 150W xenon lamp coupled to excitation monochromator, emission monochromator with 750 mm focal length equipped with a photomultiplier and a signal recovering unit. Moreover, emission spectra were excited by Femtosecond Libra Laser at 395 nm and resulting signal was detected by a streak camera (Hamamatsu Model C5680). 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 were taken from the literature [5].

3. Results and discussion

3.1. Thermal analysis

In Fig. 1 the DTA curves recorded for (65-x)TeO_2-20ZnF_2-12PbO-3Nb_2O_5-xEu_2O_3 samples glasses with 0.5, 2 and 5 mol ratio of Eu_2O_3 are compared with oxyfluorotellurite matrix glass TZPN. The characteristic glass temperatures such as glass transition temperatures (T_g) and onset of crystallization temperatures (T_c) were estimated in accordance with the Keavney and Eberlin method were the value of T_g indicating initiation of the glass softening consistently increases along with concentration of Eu_2O_3 from 369 °C to 371 °C and 374 °C for samples containing 0.5, 2, 5 mol% of Eu_2O_3, respectively. Whereas the value of T_g for 65TeO_2-20ZnF_2-12PbO-3Nb_2O_5 (undoped) glass is the lowest and equals to 365 °C. This situation is different in the case of glass crystallization temperatures which are higher for a less concentrated sample i.e. TZPNEu0.5 in relation to the values determined for the samples containing 2 and 5 mol of Eu_2O_3.

As it can be seen in Fig. 1 for both glasses (65-x)TeO_2-20ZnF_2-12PbO-3Nb_2O_5-xEu_2O_3 with x = 2 and 5 mol% of Eu_2O_3 the crystallization peaks can be relatively found around 530–550 °C. It should be noticed that for the sample TZPNEu5 the crystallization peak is not pronounced and in respect to that only suggested crystallization temperature may be inferred from exothermal band. Similar effect was documented by Junjie Zhang at al [2]. for 70TeO_2–20BaO–5La_2O_3–5LaF_3 (TBL) oxyfluorotellurite glass system too.

Actually, this study provides valuable information about ability of glass formation and thermal stability of the glass. The glass stability can be determined qualitatively by a difference of thermal stability criteria: Dietzel factor ΔT [9] and Saad - Poulain factors H' and S [10] (calculating method of which were presented in our earlier paper on the oxyfluorotellurite glass systems doped by dysprosium ions with chemical composition (65-x)TeO_2-20ZnF_2-12PbO-3Nb_2O_5-xDy_2O_3 where x = 0.5, 2 and 5 mol% [11]). Larger values of these parameters leads to high thermal stability of the glass.

The ΔT, H' and S values for the present glasses are listed in Table 1 together with the values determined for TZPN glass ($\Delta T = 187$ °C, $H' = 0.51$ and $S = 18.44$). The ΔT, H' and S values for TZPNEu0.5 glass sample are significantly higher in relation to the TZPN glass matrix but they are lower for 2 and 5 mol% of Eu_2O_3 -doped glasses. Based on the results reported in Table 1 it can be observed that doping of TZPN glass with rare earths ions improves glass thermal properties but only at low concentration (<2 mol%) europium ions. In the case of higher amounts of rare earths glass stability is slightly decreased. Eventually, the decrease of ΔT, H' and S implies that the thermal stability of the materials under study is affected by the concentrations of Eu_2O_3. As suggested by Y. Benmadani et al. [12] in the case of glasses with a particularly high content of rare earths this glass stability reduction can be due to formation of the microcrystallites within the glass.

Fortunately, the TZPNEu glasses are characterized by higher