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Full Length Article

Raman, photoluminescence and EPR spectroscopic characterization of europium(III) oxide–lead dioxide–tellurite glassy network

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ABSTRACT

Raman, photoluminescence and EPR spectroscopies were used to characterize some $xEu_2O_3 \cdot (100-x)[4TeO_2 \cdot PbO_2]$ glasses with $x=0$–50 mol% obtained by melt quenching technique. Raman spectra of these glasses were interpreted in terms of vibration modes of deformed Te–O–Te linkages due to the intercalation of $[PbO_n]$ and $[EuO_n]$ entities produced by addition of Eu_2O_3 to the host lead–tellurite glass. Photoluminescence spectra of $xEu_2O_3 \cdot (100-x)[4TeO_2 \cdot PbO_2]$ glasses reveal the presence of Pb^{2+}, Eu^{2+} and Eu^{3+} ions. EPR data confirm the presence of Eu^{2+} ions in the europium–lead–tellurite glassy network and offer information about the compositional evolution of the Eu^{2+} ions local environment and $Eu^{3+} \leftrightarrow Eu^{2+}$ redox process. PL and EPR data show that the decrease of the Eu^{2+} ions luminescence intensity for the $x \geq 40$ mol% Eu_2O_3 region is not due to the clusterization of europium ions but is due the decrease of the amount of Eu^{2+} ions as result of changes in the $Eu^{3+} \rightarrow Eu^{2+}$ redox equilibrium.

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1. Introduction

Tellurite glasses have attracted a great attention in the last years because of their interesting properties such as a wide transmission in the 0.4–5.0 μm range, high refractive index, good corrosion resistance, thermal and chemical stability, and the capacity of incorporating large amounts of rare earth ions (RE) [1]. RE ions play important role in modern technology as optically active elements in solid state luminescence materials due to the energy levels possessed by these ions when incorporated into a solid state matrix [2]. In this view, the trivalent europium ion (Eu^{3+}) is an excellent candidate as red-emitting phosphor for field-emission applications due to its narrow and almost monochromatic nature of the $^5D_2 \rightarrow {}^7F_0$ transition at around 610 nm. On the other hand, persistent spectral hole burning can be performed using the $^5D_0 \rightarrow {}^7F_0$ transition at room temperature, which has potential applications in high-density optical storage [3]. The luminescence properties and potential applications of Eu^{3+} ions have been reported in many types of host materials [4–9]. Note also that the chemistry of the divalent europium ion (Eu^{2+}) is of great interest because of its characteristic photo-stimulated luminescence properties with many potential applications (e.g., lamp phosphors or persistent phosphors). In this view, note that luminescence, Raman and electron paramagnetic resonance spectroscopic data can provide important information on the oxidation state of europium ion in glasses.

The objective of this work was to obtain europium–lead–tellurite glasses by melt quenching technique and to characterize their structural and behavioral properties by means of Raman, photoluminescence (PL) and electron paramagnetic resonance (EPR) spectroscopies. The performed investigation offered interesting information concerning the effects of the gradual increase of Eu_2O_3 content of the studied europium–lead–tellurite glasses including the $Eu^{3+} \leftrightarrow Eu^{2+}$ redox process.

2. Experimental procedure

The $xEu_2O_3 \cdot (100-x)[4TeO_2 \cdot PbO_2]$ glasses with $0 \leq x \leq 50$ mol% were prepared by mixing and melting appropriate amounts of lead (IV) oxide, tellurium(IV) and europium(III) oxide of high purity (99.99%, Aldrich Chemical Co.). Reagents were melted at 875 °C for 10 min. The melts were quenched by pouring onto a stainless steel block.

The Raman spectra have been recorded at room temperature with a JASCO NRS 3300 spectrophotometer in a backscattering arrangement and equipped with a CCD detector (−69 °C). The incident laser beam (1 μm² diameter at the sample surface) was focused through an Olympus microscope, and the Raman calibration was achieved by using the Si 521 cm^{-1} peak. Excitation was performed with 736 nm laser at a power of 1.4 mW on the

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sample, with a spectral resolution of 0.48 cm^{-1} network using 1200 L/mm.

Photoluminescence measurements were carried out using an Able & Jasco FP 6500 spectrofluorometer with a xenon lamp of 150 W as excitation source and a photomultiplier tube (PMT) as detector. For comparison, all emission spectra were recorded at room temperature on 0.005 g powder samples using an excitation at 285 nm, with identical incidence intensity, excitation slit (3 mm) and emission slit (5 mm).

EPR measurements were carried out in the X-band (9.52 GHz) using a Bruker E-500 ELEXSYS spectrometer at room temperature. All measurements were done using using equal quantities of samples and the same experimental parameters: microwave power, 2 mW; receiver gain, 30; modulation frequency of 100 kHz and a magnetic field modulation amplitude of 10 G. The processing of the EPR spectra was performed using the Bruker Xepr software.

3. Results and discussion

3.1. Raman spectroscopy

The Raman spectra of $xEu_2O_3 \cdot (100-x)[4TeO_2 \cdot PbO_2]$ glasses with x=0–50 mol% Eu_2O_3 are displayed in Fig. 1. These spectra are characterized by bands located at around 150, 270, 450, 650 and 710 cm^{-1}.

The shape of the Raman spectra is influenced by the europium oxide content of the studied samples.

The Raman band located at ~710 cm^{-1} is due to the Te–O stretching vibrations from $[TeO_{3+1}]$ and $[TeO_3]$ pyramidal units associated with non-bridging oxygen (NBO) units in glassy samples [10–12]. The increase of the Eu_2O_3 content of samples produces an increase of intensity and a shift towards higher wavenumbers, namely to ~735 cm^{-1} for x=50 mol%. This shift is associated with a gradual increase of the maximum phonon energy of the doped glasses from 710 to 735 cm^{-1}. The observed compositional evolution suggests the increase in the number of non-bridging oxygen atoms and a transformation of $[TeO_4]$ into $[TeO_{3+1}]$ and $[TeO_3]$ structural units in the vitreous network. An increase of the amount of structural units with lower coordination numbers is indicative of the depolymerization of lead–tellurite glassy system.

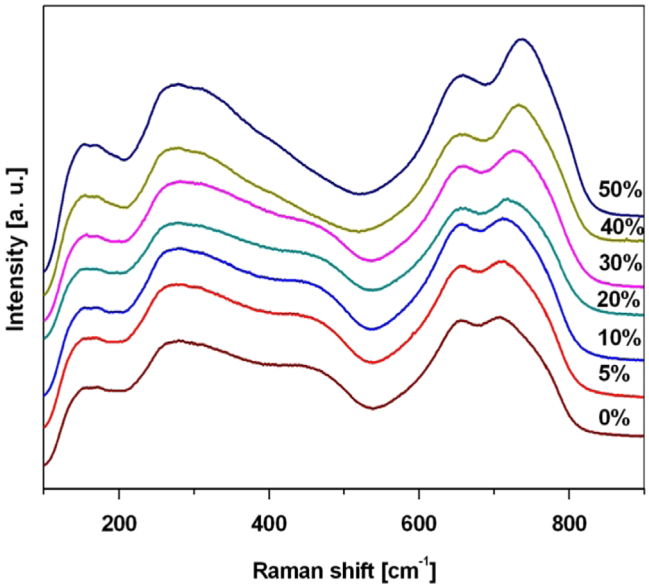

Fig. 1. Raman spectra of $xEu_2O_3 \cdot (100-x)[4TeO_2 \cdot PbO_2]$ glasses with x=0–50 mol% Eu_2O_3.

The band around 650–660 cm^{-1} was ascribed to the $(Te_{ax}–O)_s$ axial symmetric stretching vibration modes in $[TeO_4]$ trigonal bipyramids with bridging oxygen (BO) atoms [13]. This Raman band was assigned to coupled symmetric vibrations along Te–O–Te axes in $TeO_{3+\delta}/TeO_4$ units and TeO_4/TeO_3 pairs and was considered to be a relative measure of the connectivity between $TeO_{3+\delta}$, TeO_4, and TeO_3 species [14]. The Raman band centered at ~450 cm^{-1} offers information on the stretching vibrations of Te–O–Te bonds that join the $[TeO_4]$ trigonal bipyramids [15,16].

By increasing the Eu_2O_3 content of the studied glasses up to 50 mol%, the Raman band centered at ~450 cm^{-1} was modified suggesting that the Te–O–Te bonds from the glassy network were affected. At lower Eu_2O_3 contents, the intensity of this band increases with the gradual increase of the europium oxide amount and attains its maximum value for x=10 mol% Eu_2O_3. Then, for a further increase of the Eu_2O_3 content, the intensity of the ~450 cm^{-1} band decreases up to 30 mol% and disappears for higher concentrations. This compositional evolution indicates that the Te–O–Te linkages are broken by increasing the europium ions amount in the host glass up to 10 mol%. As result, the formation of some Te–O–Pb and Te–O–Eu linkages is promoted in the glassy network.

The Raman band located at ~270 cm^{-1} is assigned to Pb–O stretching and O–Pb–O bending vibrations while the band from ~310 cm^{-1} is due to Pb–O vibration in $[PbO_4]$ structural units [11]. The Raman band situated at ~150 cm^{-1} is due to the Pb–O symmetric stretching vibrations [17,18] and its intensity increases with the Eu_2O_3 content up to 50 mol%. This compositional evolution can be explained considering that the surplus of NBOs will be converted into bridging ones by the formation of $[PbO_4]$ structural units.

A sharp decreasing trend toward lower wavenumbers of the Raman bands situated between 100 and 400 cm^{-1} was observed by adding of Eu_2O_3 content to the host matrix. This effect may be due to a gradual formation of Pb–O–Pb and Pb–O–Eu bridging bonds and $[PbO_4]$ structural units leading to a more disordered structure and a decrease of the connectivity of the network.

Raman data suggest that lead and europium ions show a pronounced preference towards the $[TeO_3]$ structural units yielding to the deformation of Te–O–Te linkages and producing NBOs that decrease the average coordination number of the tellurium atoms. Addition of Eu_2O_3 to the host glass results in the intercalation of $[EuO_n]$ structural units in the lead–tellurite chain network.

3.2. Photoluminescence spectroscopy

The photoluminescence (PL) studies provide information regarding the nature of luminescent centers from the samples. Thus, in this study our interest was focused on the europium and lead ion species present in the host lead–tellurite glass matrix.

Fig. 2 shows the PL spectra of the $xEu_2O_3 \cdot (100-x)[4TeO_2 \cdot PbO_2]$ glasses with x=0–50 mol% Eu_2O_3 excited at 285 nm and recorded at room temperature. Note that only the RT spectra are presented and will be discussed. The excitation wavelength was selected according to the information obtained from a previous UV–vis investigation of samples [19].

The photoluminescence of Pb^{2+} ions in host materials may present different features. Usually, at room temperature, emissions assigned to the $^3P_1 \rightarrow {}^1S_0$ transition are observed [20–24], represented by two emission bands located at ~324 nm [22] and at ~438 nm [23,24]. At low temperatures, the highly forbidden $^3P_0 \rightarrow {}^1S_0$ emission may appear, too [20,21]. As shown in Fig. 2, the two emission bands from ~324 nm and ~438 nm appear in the PL spectra of the $xEu_2O_3 \cdot (100-x)[4TeO_2 \cdot PbO_2]$ glasses. The

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