



Influence of $\text{Sm}^{3+}:\text{Ag}$ codoping on structural and spectroscopic properties of lead tellurite glass ceramics

Liviu Bolundut^a, Eugen Culea^a, Gheorghe Borodi^b, Razvan Stefan^c, Constantin Munteanu^a,
Petru Pascuta^{a,*}

^aTechnical University of Cluj-Napoca, 103-10 Muncii Avenue, 400641 Cluj-Napoca, Romania

^bNational Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath, 400293 Cluj-Napoca, Romania

^cAgricultural Science and Veterinary Medicine University, 3-5 Calea Manastur, 400372 Cluj-Napoca, Romania

Received 29 August 2014; received in revised form 18 October 2014; accepted 21 October 2014

Available online 28 October 2014

Abstract

Lead tellurite glass ceramics doped with Sm_2O_3 and codoped with fixed amounts of silver (Ag_2O or Ag metallic nanoparticles, AgNPs) have been studied by X-ray diffraction (XRD), density measurements, Fourier transform infrared (FTIR), diffuse reflectance ultraviolet–visible (DR–UV–vis) and photoluminescence (PL) spectroscopies. The crystallite size and the quantitative ratio of the crystallographic phases in the samples were evaluated from the XRD data. FTIR spectroscopy data show that the glass ceramics network mainly consists of TeO_3 and TeO_4 structural units and the conversion between these units depends on the Sm_2O_3 content and the nature of the codopant (Ag_2O or AgNPs) present in the samples. The DR–UV–vis spectra of studied samples were recorded in the 350–1000 nm spectral range at room temperature. The optical band gap (E_g^{opt}) for the studied glass ceramics were calculated from the DR–UV–vis spectra. The important peaks evidenced by PL spectroscopy measurements are due to the Pb^{2+} ions and Sm^{3+} ions present in the studied samples. The $\text{Sm}^{3+}:\text{Ag}$ codoping was found to produce quenching of the luminescence emission of Sm^{3+} ions in the studied samples.

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Keywords: Lead tellurite glass ceramics; Samarium ions; Silver oxide; Silver nanoparticles; Luminescence properties

1. Introduction

The glasses and glass ceramics containing rare earth (RE) ions have attracted a great interest in the last years due to their multiple applications such as temperature sensors, CO_2 gas sensors, solid state laser sources, optical detectors, optical data storage devices, optical fibers, biosensors, solar cells, infrared to visible converters, etc. [1–7].

Tellurite glasses are promising materials for linear and non-linear application in optics. These glasses have low phonon maxima, high refractive index, low melting temperature [8], a large chemical resistance and thermochromic properties [9], good mechanical strength, high dielectric constant and excellent transparency in visible and IR regions [10]. The tellurium dioxide

is a conditional glass former and requires fast quenching in order to form glass. It is also known as a good host in the formation of rare earth doped glasses, because the Te–O bonds are weak and can be easily broken and the heavy metal and the rare earth atoms can enter in the glass networks [11].

In the literature there are relatively few reports on structural and spectroscopic properties of glasses doped with Sm^{3+} ions [12–19]. On the other hand, recently were reported studies concerning the interesting structural and spectroscopic effects produced by the codoping with silver ions or silver nanoparticles of glasses doped with different RE ions [19–23] that confer important potential applications for these materials. Due to these reasons, we prepared some new lead tellurite glass ceramics doped with samarium ions and codoped with silver ions or silver nanoparticles. The samples have a fixed TeO_2 and silver ions contents and the $\text{Sm}_2\text{O}_3:\text{PbO}$ ratio was varied. These materials were investigated using XRD, density measurements and FTIR, UV–vis and luminescent

*Corresponding author. Tel.: +40 264 401 262; fax: +40 264 595 355.

E-mail address: petru.pascuta@phys.utcluj.ro (P. Pascuta).

spectroscopies. The aim of this work was to investigate the influence of the Sm^{3+} doping level and of the codopant nature (Ag ions or AgNPs) on the structural, optical and luminescent properties of the investigated materials.

2. Experimental

Were prepared samples from the $80\text{TeO}_2 \cdot (19.7-x)\text{PbO} \cdot x\text{Sm}_2\text{O}_3 \cdot 0.3\text{AgNPs}$ and $80\text{TeO}_2 \cdot (19.85-x)\text{PbO} \cdot x\text{Sm}_2\text{O}_3 \cdot 0.15\text{Ag}_2\text{O}$ systems (with $x=1, 3, 5, 10$ mol%), by the conventional melt quenching technique. All the reagents used were of high purity (Alfa Aesar, Germany). The TeO_2 , PbO , Sm_2O_3 , and metallic Ag nanoparticles (AgNPs) (particles size of 20–40 nm) or Ag_2O were mixed in stoichiometric amounts to obtain samples with the chemical compositions listed in Table 1.

The reagents were mixed and grounded in an agate mortar to obtain homogeneous mixture. After that, the mixture was placed in a porcelain crucible and heated at 900°C in an electric furnace for 15 min. The melts were quickly cooled to room temperature by pouring onto stainless-steel plates.

The density of the $80\text{TeO}_2 \cdot (19.7-x)\text{PbO} \cdot x\text{Sm}_2\text{O}_3 \cdot 0.3\text{AgNPs}$ and $80\text{TeO}_2 \cdot (19.85-x)\text{PbO} \cdot x\text{Sm}_2\text{O}_3 \cdot 0.15\text{Ag}_2\text{O}$ samples was measured based on the Archimedes method using water as immersion liquid (the water density at 20°C is $\rho=0.998\text{ g/cm}^3$). The density of each sample was calculated using the relation

$$\rho = \frac{m_a}{m_a - m_w} \times \rho_w \quad (1)$$

where m_a is the weight of glass ceramic sample in air, m_w is the weight in water and ρ_w is the water density at 20°C . All the measurements were performed using a KERN analytical balance with five digits. The density values were obtained with an estimated error of $\pm 0.2\text{ g/cm}^3$.

The XRD investigation of the samples was made with a Shimadzu 6000 XRD diffractometer, with a monochromator of graphite for $\text{Cu-K}\alpha$ radiation ($\lambda=1.54\text{ \AA}$) having the source power of 40 kV and 30 mA, at the room temperature. X ray diffractograms permitted to identify the type and amount of

Table 1
Chemical composition, the average crystallite size (D), the degree of crystallinity (X_c) and the optical band gap (E_g^{opt}) for the $80\text{TeO}_2 \cdot (19.7-x)\text{PbO} \cdot x\text{Sm}_2\text{O}_3 \cdot 0.3\text{AgNPs}$ and $80\text{TeO}_2 \cdot (19.85-x)\text{PbO} \cdot x\text{Sm}_2\text{O}_3 \cdot 0.15\text{Ag}_2\text{O}$ glass ceramics.

| Sample no. | Composition (mol%) | | | | | D (nm) | X_c (%) | E_g (eV) |
|------------|--------------------|--------------|-----------------------|-------|-------------------------|----------|-----------|------------|
| | TeO_2 | PbO | Ag_2O | AgNPs | Sm_2O_3 | | | |
| S0 | 80 | 20 | 0 | – | 0 | – | 10.3 | 3.348 |
| S1 | 80 | 19.70 | – | 0.3 | 0 | – | 10.6 | 3.332 |
| S1' | 80 | 19.85 | 0.15 | – | 0 | – | 13.5 | 3.322 |
| S2 | 80 | 18.70 | – | 0.3 | 1 | – | 11.3 | 3.319 |
| S2' | 80 | 18.85 | 0.15 | – | 1 | – | 12.4 | 3.335 |
| S3 | 80 | 16.70 | – | 0.3 | 3 | 47.3 | 21.4 | 3.302 |
| S3' | 80 | 16.85 | 0.15 | – | 3 | 35.2 | 19.4 | 3.324 |
| S4 | 80 | 14.70 | – | 0.3 | 5 | 91.0 | 41.4 | 3.296 |
| S4' | 80 | 14.85 | 0.15 | – | 5 | 94.1 | 39.9 | 3.329 |
| S5 | 80 | 9.70 | – | 0.3 | 10 | 97.5 | 70.6 | 3.286 |
| S5' | 80 | 9.85 | 0.15 | – | 10 | 106.0 | 71.2 | 3.435 |

crystalline phases present in the samples. The average crystallite size, D , was calculated using Debye–Scherer formula [24–26]. The degree of crystallinity, X_c , was evaluated as the ratio of the area due to the diffraction peaks and the total diffraction area (which includes diffraction peaks and amorphous halos) using the Reflex computer program, part of Material Studio software [27].

The FTIR absorption spectra were recorded using a JASCO FTIR 6200 equipment in the $360\text{--}1800\text{ cm}^{-1}$ spectral range. All the samples were measured in KBr pellets. The FTIR spectra were carried out with a standard resolution of 2 cm^{-1} . Since the IR features broad, the deconvolution of the spectra was necessary. This procedure was realized using the Spectra Manager software [28] with a Gaussian type function and permitted to separate and identify the IR features characteristic of the main structural units that built up the structural network of the studied samples. Thus, it was possible to locate with a higher precision the center of the band related to some type of vibration for a specific bond, C, and the relative area of the band, A, that is proportional to the concentration (number) of this type of bonds.

Diffuse reflectance UV–vis spectra were registered with a PerkinElmer Lambda 45 UV–vis spectrometer equipped with an integrating sphere, at room temperature. The obtained samples were measured in MgO pellets. The validity of the band position is $\pm 2\text{ nm}$.

Luminescence spectra were recorded using a JASCO FP 6200 spectrofluorimeter at room temperature with a Xe lamp as excitation source. The excitation wavelength was 378 nm. Validity of the band position in the luminescence spectra was estimated to be $\pm 2\text{ nm}$.

3. Results and discussion

3.1. Density measurements

Fig. 1 shows the compositional dependence of density for the studied samples. Compositional evolution of density may offer interesting information related to the structural changes that occur in glasses and glass ceramics. Thus, the increase of the doping level with a heavier ion (samarium in our case) to a non-sensitive host matrix is expected to lead to a linear increase of the density. In our case, as shown in Fig. 1, in spite of the increase of the Sm_2O_3 content of the samples the density remains relatively constant up to $x=5$ mol% and decreases for $x=10$ mol%. This non-linear compositional evolution of density suggests a more complex mechanism where the host matrix is sensitive to the doping level, as was previously reported for other lead-tellurate glasses and vitro-ceramics doped with rare earth ions, too [29]. In such cases the compositional evolution of density can be explained in terms of a competition between the size and compactness of the various structural groups present in the sample. Accordingly, density is related to how tightly the ions and ionic groups are packed together in the structure. Thus, the density compositional evolution revealed by Fig. 1 suggests that samarium ions play a network modifier role in the sense that the increase

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