



Effects of Eu:Ag codoping on structural, magnetic and mechanical properties of lead tellurite glass ceramics



Eugen Nicolae Culea^{a,b}, Petru Pascuta^{b,*}, Marius Pustan^b, Daniela Roxana Tamas-Gavrea^b, Lidia Pop^b, Ioan Vida-Simiti^b

^a SC Emerson, 4 Emerson street, 400641 Cluj-Napoca, Romania

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

ARTICLE INFO

Article history:

Received 5 June 2014

Received in revised form 26 September 2014

Accepted 7 October 2014

Available online xxx

Keywords:

Lead tellurite glass ceramics;

Europium ions;

Silver oxide;

Silver nanoparticles;

XRD;

EPR spectroscopy;

Magnetic susceptibility;

Density;

Elastic modulus;

Hardness

ABSTRACT

Structural, magnetic and mechanical properties of lead tellurite glass ceramics doped with variable amounts of Eu_2O_3 (0–10 mol%) and codoped with fixed amounts of Ag_2O (0.50 mol%) or Ag metallic nanoparticles, AgNPs, (0.33 mol%) have been studied. The investigation of the samples was performed by X-ray diffraction (XRD), EPR spectroscopy, magnetic susceptibility and elastic modulus measurements. XRD investigation shows that the studied samples were glass ceramics. XRD data were used to determine the nature and the quantitative ratio of the crystalline phases present in the samples. EPR spectroscopy was used to obtain information on the presence of europium and silver paramagnetic centers (Eu^{2+} , Ag^0 , and Ag^{2+}). No EPR signals assignable to these paramagnetic centers were registered. Magnetic susceptibility data show that the magnetic behavior of the studied glass ceramics is due to the europium ions present in the host matrix as Eu^{3+} and Eu^{2+} ions that show a very important clustering tendency. The fact that the paramagnetic Eu^{2+} ions are involved in aggregates explains why these ions were not detected by EPR in spite of the fact that Eu^{2+} ions are present in appreciable amounts. The level of the europium doping and the nature of the silver codopants (Ag_2O or AgNPs) influence the structural, magnetic and mechanical behavior of the samples. In general, the structural effect of the codoping with Ag_2O (that provides Ag^+ ions capable to enter the host matrix) is more important than that of the AgNPs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Glasses and glass ceramics doped with rare earth (RE) ions show interesting properties being desirable for important applications in the field of solid-state lasers, fiber amplifiers, infrared to visible converters, phosphors, field emission displays, biosensors, solar cells, etc. [1,2]. Between the RE ions, europium is considered extremely interesting since it may confer important spectroscopic properties such as a fluorescence very sensitive to the local environment of the Eu^{3+} ions [3], a persistent spectral hole burning that can be performed at room temperature (potential applications in high density optical data storage) [4], etc.

The properties of glasses doped with noble metal ions or nanoparticles have been extensively studied in the last decade because of their unique optical properties (large third-order nonlinear susceptibility, ultrafast response, etc.) [5] that make them appropriate for important applications in optics, electronics and telecommunications [6,7]. In such cases, the controllable valence state of noble metal ions and the controllable size of noble metal nanoparticles are essential.

The noble metal-RE codoping of glasses and glass ceramics may produce important structural and behavioral changes to the host material

(i.e., up-conversion or important enhancement of light emission), important for different applications [8,9]. A very interesting but yet controverted effect observed in the case of such materials was the enhancement of the RE ion emission, assigned to surface plasmonic resonance effects or to an energy transfer from non-plasmonic noble metal ion aggregates to the RE ions [10].

Obviously, an appropriate host glass or glass ceramic of the codopants is very important in determining the potential applications. In this view, TeO_2 -based glasses are very promising host matrices for optical switching and broadband amplification [11]. For practical applications of optical functional glasses and glass ceramics, it is of importance to improve their elastic and mechanical properties. Although numerous papers on optical properties of TeO_2 based glasses have been reported so far, elastic and mechanical properties of such glasses have been seldom studied [12–14].

Due to the mentioned reasons, as part of an ongoing research, recently we reported aspects on the structure and luminescence enhancement of some Eu:Ag codoped lead-tellurite glasses and glass ceramics where silver was added in the form of ions (Ag^+) or of nanoparticles (AgNPs) [15]. Herein, we report on structural, magnetic and mechanical behavior of these glasses. The investigation was performed by using X-ray diffraction (XRD), electron paramagnetic resonance (EPR) spectroscopy, magnetic susceptibility, density, elastic modulus and hardness

* Corresponding author.

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

measurements. The aim of this study was to observe the effect of Eu:Ag codoping on the structural and behavioral properties of the TeO₂–PbO glasses. EPR investigation may provide important information concerning the presence of paramagnetic silver and europium ion species and agglomerates in the host matrix. Magnetic susceptibility measurements may provide important information concerning the clustering process of magnetic europium and silver species that are extremely important for potential applications. Data concerning magnetic, density and mechanical properties (elastic modulus, hardness) of the studied samples are discussed in relation with structural data.

2. Experimental

Samples from the TeO₂–PbO–Ag₂O–Eu₂O₃ and TeO₂–PbO–AgNPs–Eu₂O₃ systems were prepared by the melt quenching technique using reagent grade compounds (Alfa Aesar, Germany). Thus, TeO₂, PbO, Eu₂O₃ and Ag₂O or metallic Ag nanoparticles (20–40 nm particle size) were mixed in suitable quantities according to the chemical compositions listed in Table 1. Note that the amount of Eu₂O₃ increases in the samples up to 10 mol%, while silver is added in constant amounts, 0.5 mol% Ag₂O or 0.33 mol% AgNPs.

The mixtures were milled in an agate ball mil for 30 min and after that were melted in air, in corundum crucibles, at 1000 °C for 15–25 min in an electric furnace. The melts were cooled to room temperature by pouring onto stainless-steel plates.

In general, as resulting from the literature, the method used to produce AgNPs in glasses or glass ceramics consists in the addition of Ag₂O followed by a thermal coprecipitation [16]. Alternatively, the direct codoping with AgNPs is also possible. This method permits a better control of the distribution and size of AgNPs and the removal of some undesirable effects of thermal treatment (i.e., crystallization of host material) but shows also an important disadvantage, namely the fact that the tuning of the AgNPs size is not possible.

In this work, we performed a comparative study of some effects produced by the codoping with Ag₂O or AgNPs on structural, magnetic and mechanical properties of TeO₂–PbO–Ag₂O–Eu₂O₃ and TeO₂–PbO–AgNPs–Eu₂O₃ compounds. In this view, we realized, one hand, a codoping with Ag₂O that ensures the presence of Ag⁺ ions in the host matrix (samples S in Table 1) and, on the other hand, a direct codoping with AgNPs (samples S' in Table 1). The comparison between the two series of samples offers the possibility to make a clear separation of the potential structural and behavioral effects due to the nature of the codopant (Ag⁺ ions or AgNPs).

The X-ray diffraction measurements of the studied samples were made by a XRD-6000 Shimadzu diffractometer, with a monochromator of graphite for Cu–K α radiation ($\lambda = 1.54 \text{ \AA}$) at room temperature.

The EPR measurements of powder samples were carried out in the X-band (9.4 GHz) at room temperature using an ADANI EPR spectrometer using equal quantities of samples.

Table 1
Chemical composition and elastic properties of TeO₂–PbO–Ag₂O–Eu₂O₃ and TeO₂–PbO–AgNPs–Eu₂O₃ glass ceramics.

Sample no.	Composition (mol%)					ν_{calc}	E_{calc} (GPa)	E_{IT} (GPa)	H_{IT} (GPa)
	TeO ₂	PbO	Ag ₂ O	AgNPs	Eu ₂ O ₃				
S1	80	20	0	–	0	0.221	48.09	42.23	18.73
S2	80	19	0	–	1	0.228	49.55	–	–
S3	80	19.50	0.50	–	0	0.225	48.83	37.51	2.58
S3'	80	19.67	–	0.33	0	0.228	49.15	41.85	8.31
S4	80	18.50	0.50	–	1	0.229	49.89	35.82	3.68
S4'	80	18.67	–	0.33	1	0.226	49.66	30.12	7.48
S5	80	16.50	0.50	–	3	0.218	48.64	–	–
S6	80	14.50	0.50	–	5	0.226	59.70	37.59	4.16
S6'	80	19.67	–	0.33	5	0.225	50.48	46.35	0.54
S7	80	9.50	0.50	–	10	0.232	53.51	–	–
S7'	80	9.67	–	0.33	10	0.228	52.67	–	–

Magnetic susceptibility measurements were performed on a Faraday type balance in the 80–300 K temperature range. The sensitivity of the equipment was 10^{-8} emu/g and measurements were performed on samples having a mass of 0.200–0.300 g.

The density of the samples was measured using Archimedes' method with deionized water as the immersion liquid. Mass was measured using a digital balance with the sensitivity of 0.1 mg.

Nanoindentation experiments were performed using an AFM XE 70 atomic force microscope equipped with a nanoindentation module. A three-sided pyramid diamond indenter (Berkovich type) attached by a cantilever with high stiffness (144 N/m) was used.

3. Results and discussion

3.1. XRD data

Some XRD investigation data of the TeO₂–PbO–Ag₂O–Eu₂O₃ and TeO₂–PbO–AgNPs–Eu₂O₃ systems were reported in our earlier work [15]. The analysis of the XRD data shows that samples S1–S4 and S1'–S4' contain large amounts of amorphous phase where a small quantity of crystalline phase is dispersed. This crystalline phase was identified as the Pb₂Te₃O₇ [15]. In addition, in samples S5–S7 and S5'–S7' a second crystalline phase appears, too. This crystalline phase was identified as the Eu₂Te₄O₁₁. Note that the crystalline Eu₂Te₄O₁₁ appears in appreciable amounts only in the samples codoped with Ag₂O (S6 and S7), while in the corresponding samples containing AgNPs it was not observed (S6') or appears in a very small amount (S7').

The degree of crystallinity of the samples, X_c, was evaluated following the procedure described by authors [17]. To assess X_c, the Reflex computer program (part of Material Studio software suit) was used [18]. The compositional evolution of X_c is presented in Fig. 1.

The analysis of the data from Fig. 1 shows that increasing the europium oxide content of the samples increases the degree of crystallinity for both series of samples (codoped with Ag₂O and respectively with AgNPs). Note the important increase of X_c that occurs for the 1 mol% → 3 mol% Eu₂O₃ content transition for both series of samples (S4 → S5 and S4' → S5'). The addition of the codopant, Ag₂O or AgNPs, enhances the crystallization process, too. X_c values are higher for the samples codoped with Ag₂O (S3–S7) in comparison with those codoped with AgNPs (S3'–S7'). The fact that the addition of Ag₂O produces a more important devitrification than that produced by AgNPs

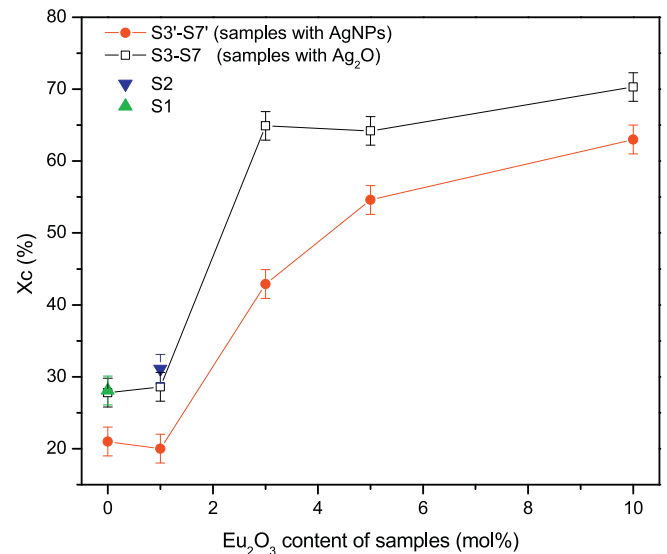


Fig. 1. Compositional dependence of the crystallinity of TeO₂–PbO–Ag₂O–Eu₂O₃ and TeO₂–PbO–AgNPs–Eu₂O₃ glass ceramics (lines are only a guide for the eyes).

Download English Version:

<https://daneshyari.com/en/article/7901239>

Download Persian Version:

<https://daneshyari.com/article/7901239>

[Daneshyari.com](https://daneshyari.com)