Structural and physical characteristics of CeO$_2$–GeO$_2$–PbO glasses and glass ceramics

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ABSTRACT

Samples of the xCeO$_2$(100 − x)[GeO$_2$·PbO] system with $0 \leq x \leq 15$ mol% were prepared and characterized by X-ray diffraction, FT-IR spectroscopy and magnetic measurements. The X-ray diffraction (XRD) investigation revealed the presence of a crystalline phase for samples with $x \geq 3$ mol%, namely that of Ce$_{1.88}$Pb$_{2.12}$O$_{6.53}$. The structural role of germanium, lead and cerium ions was discussed. The presence of the CeO$_4$, GeO$_4$, GeO$_6$ and PbO$_4$ structural units was evidenced by FT-IR spectrocopy in the studied glasses and glass ceramics. It was shown that the ratio of the mentioned structural units depends on the CeO$_2$ content of the xCeO$_2$(100 − x)[GeO$_2$·PbO] system. As a part of an on-going investigation of the physical properties of xCeO$_2$(100 − x)[GeO$_2$·PbO] glass ceramics, the magnetic behavior of this system was studied. The fractions of the cerium ions in the 3+ and 4+ valence states were determined.

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1. Introduction

Recently multicomponent glasses have received much attention as materials which offer various applications in optics and opto-electronics. It is known that, in general, the oxide glasses possess a good mechanical strength, chemical durability and thermal stability [1–3]. Among the different vitreous systems studied earlier, the PbO–GeO$_2$ glasses are technologically important because of their potential use as low loss optical glasses in the infrared region [4–6]. Moreover the study of lead–germanate glasses is of particular interest since they can be easily obtained into fiber form for their use in optoelectronics. These glasses are also suitable for waveguide applications. The lead–germanate glasses show important properties such as a good chemical durability and mechanical stability, a higher glass transition temperature and, as a consequence, higher laser damage thresholds at 3 μm [7,8].

On the other hand, glasses and crystals containing rare-earths have attracted great attention because of their extensive applications in fields such as information display, advanced laser materials and fiber optical communication [9–11]. It is worth mentioning that Ce, as well as other rare-earth and transition metal ions in glasses, exists in multivalent states which give rise to the interesting magnetic and semiconducting behavior of the host glasses (i.e. [12–18]).

In order to obtain more information concerning the important class of lead–germanate glasses doped with rare-earth ions, in the present paper we studied some structural and magnetic properties of the xCeO$_2$(100 − x)[GeO$_2$·PbO] system with $0 \leq x \leq 15$ mol%. The effect of the progressive addition of CeO$_2$ on the structural and physical properties of the GeO$_2$·PbO host matrix was followed by means of X-ray diffraction, FT-IR spectroscopy and magnetic susceptibility measurements.

2. Experimental

Samples of the cerium–lead–germanate system having the general formula xCeO$_2$(100 − x)[GeO$_2$·PbO] where $x = 0$, 1, 3, 5, 7, 10, 15 mol% were prepared by the melt quenching method. Required quantities of analar grade GeO$_2$, PbO and CeO$_2$ were mixed and miled together with the aim to obtain a fine powder. The mixture was melted in sintered corundum crucibles in an electric furnance at a temperature of 1100 °C for 15 min. The samples were obtained by pressing the melts between two steal plates.

The samples were studied by X-ray diffraction using a XRD-6000 SHIMADZU diffractometer. The Cu Kα radiation (λ = 1.54056 Å), a working voltage of 40 kV, a working current of 30 mA and the scanning speed of 2°/min were used.

The FT-IR investigation was performed using a JASCO FT-IR 6200 spectrometer. The FT-IR spectra were recorded at room temperature, using the KBr pellet technique in the 400–1700 cm^{-1} range. In order to obtain good quality spectra the samples were crushed in an agate mortar to obtain a fine powder.

The magnetic susceptibility measurements were performed using a Faraday-type balance in the 80–300 K temperature range. The diamagnetic susceptibility of the GeO$_2$·PbO base glass was measured, too, and the magnetic susceptibility data for all the samples were corrected taking into account the diamagnetic contribution of the host matrix.

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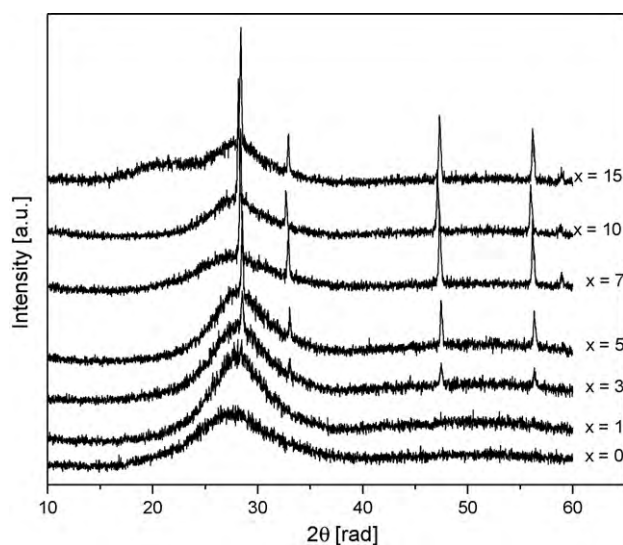*E-mail address:* Lidia.Pop@phys.utcluj.ro (L. Pop).

Fig. 1. X-ray diffraction patterns for the xCeO$_2$(100 − x)[GeO$_2$·PbO] system.

Fig. 3. The result of the deconvolution of the FT-IR spectrum for the 1CeO$_2$·99[GeO$_2$·PbO] sample.

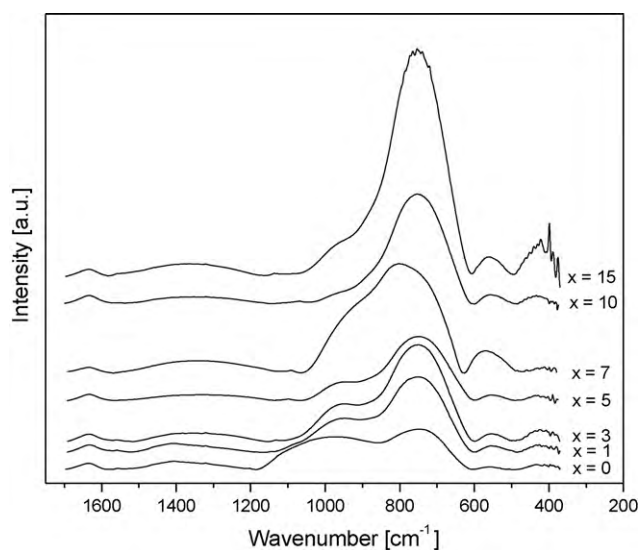**Fig. 2.** FT-IR spectra of the xCeO$_2$(100 − x)[GeO$_2$·PbO] system.

3. Results and discussion

The X-ray diffraction patterns of the samples from the xCeO$_2$(100 − x)[GeO$_2$·PbO] system are shown in Fig. 1. The diffractograms for the samples with $x \leq 1$ mol% show the broad diffuse scattering characteristic of amorphous structure. For the samples with $x \geq 3$ m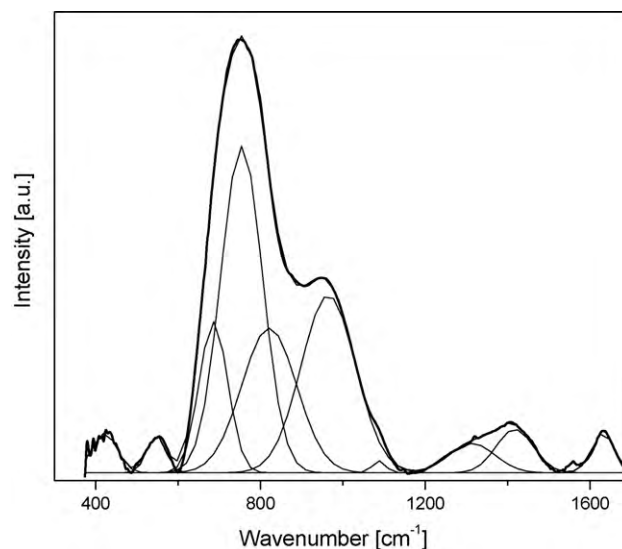ol% the diffractograms present a superposition of the broad diffuse scattering characteristic of amorphous structure with some peaks characteristic of crystalline phases. In order to identify the crystalline phases that appear in the diffraction patterns we followed a standard procedure, namely the computer analysis based on the powder diffraction file (PDF). This analysis permitted the identification of the crystalline phase present in the samples which was determined to be the Ce$_{1.88}$Pb$_{2.12}$O$_{6.53}$ one (PDF nr. 48-0059, face centered cubic lattice with the $\alpha = 5.417$ cell parameter). The assignments and relative intensities (I) of the four most important crystalline peaks are: $2\theta = 28.583$ rad with $I = 100$ ($h = 1$, $k = 1$, $l = 1$), $2\theta = 33.049$ rad with $I = 39$ ($h = 2$, $k = 0$, $l = 0$), $2\theta = 47.433$ rad with $I = 57$ ($h = 2$, $k = 2$, $l = 0$) and $2\theta = 56.270$ rad with $I = 50$ ($h = 3$, $k = 1$, $l = 1$).

Vibrational FT-IR spectra of the xCeO$_2$(100 − x)[GeO$_2$·PbO] samples with $x = 0$, 1, 3, 5, 7, 10, 15 mol% are shown in Fig. 2. Since most of the IR bands present in these spectra are very broad and asymmetric due to the amorphous (or partly amorphous) nature of the samples, a deconvolution procedure of the experimental spectra was necessary. This procedure was performed with the Spectra Manager program using a Gaussian type function. Fig. 3 shows the deconvolution, in Gaussian bands, of the spectrum for the 1CeO$_2$·99[GeO$_2$·PbO] sample. The deconvolution procedure allowed us a better identification of the IR bands that appear in the experimental spectra, offered the possibility to calculate their relative area and thus to follow more precisely their compositional evolution. Each component IR absorption band is related to some type of vibration in specific structural groups. The positions of the most important absorption bands evidenced in the FT-IR spectra and their assignments are summarized in Table 1. The assignments

Table 1
FT-IR bands and there assignments for the xCeO$_2$(100 − x)[GeO$_2$·PbO] samples.

Wavenumber [cm^{-1}]	Assignments
425	Symmetric bending vibration mode of Pb–O in PbO$_4$ units [25,26] bending vibration mode of Ce–O in CeO$_4$ units [27]
555	Symmetric stretching mode of Ge–O–Ge bonds [19,22,23] asymmetric bending vibration modes of Pb–O–Pb bonds [25]
690	Stretching mode of Ge–O–Ge bonds in GeO$_6$ units [21,24,27]
760	Asymmetric stretching mode of Ge–O–Ge bridges connecting GeO$_4$ units [22,23]
870	Asymmetric stretching mode of Ge–O–Ge bonds from GeO$_4$ units [19,22,27]
965	Symmetric stretching vibration modes of Pb–O bonds [25,26]
1130	Asymmetric stretching vibration modes of Pb–O bonds [25]
1320	Bending vibration mode of Pb–O–Ge bonds
1430	Asymmetric stretching vibration modes of Ge–O–Ge bonds [19]
1635	OH bending mode of vibration