

STRUCTURAL AND MAGNETIC BEHAVIOUR OF SOME OXIDE GLASSES CONTAINING CERIUM IONS*

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Abstract

Glasses with the $x\text{CeO}_2(1-x)(3\text{Bi}_2\text{O}_3\cdot\text{PbO})$ composition ($0 \leq x \leq 0.15$) were obtained and studied by IR spectroscopy, magnetic susceptibility and XPS measurements. IR data show that addition of cerium ions generates structural changes of the host glass matrix and the cerium ions play a network modifier role. XPS data show that the cerium ions play also the intermediate ion role in the studied glasses. Magnetic susceptibility data show that the majority of the cerium ions are reduced from the 4+ to the 3+ valence state.

Keywords: glasses, cerium, spectroscopy, magnetic behavior.

1. Introduction

Glasses with rare-earth ions attract a great interest due to their important applications for optical telecommunication, laser technology and immobilization of radioactive materials [1-3]. In addition, bismuthate glasses are very important candidates for low loss optical fibres, IR transmitting windows, etc. [4-6]. In order to extend the available information concerning bismuthate glasses containing cerium ions, in the present work we performed the investigation of the $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ system with $0 \leq x \leq 0.09$ using IR and XPS spectroscopy and magnetic susceptibility measurements.

2. Experimental

Samples of the the $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ vitreous system with $x = 0, 0.005, 0.01, 0.03, 0.05$ and 0.09 were obtained using reagent grade Bi_2O_3 , PbO and CeO_2 . The mixtures

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were milled melted at 1250°C for 20 minutes and poured on stainless steel. IR spectra were recorded in the 400-2000 cm^{-1} range with an Bruker IFS 66-1 spectrophotometer using the KBr pellet technique. XPS spectra were recorded in the 0-1400 eV range using a PHI 5600 Multi-Technique spectrometer with the Al Ka monochromatic radiation. Magnetic susceptibility measurements were performed on a Faraday type balance in the temperature range 80 to 300 K.

3. Results and discussion

Fig.1 shows the IR absorption spectra recorded for the $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ glasses. These spectra are those characteristic of the base glass matrix, $\text{Bi}_2\text{O}_3 \text{ PbO}$. Increasing the CeO_2 content, x , of the samples produce some modifications of their IR spectra.

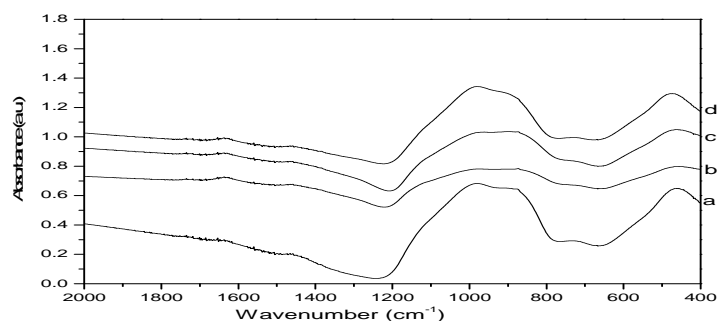


Fig.1 IR spectra of the $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ glasses (a.x=0, b.x=0.01, c.x=0.05 and d.x=0.09).

High resolution XPS spectra of the O 1s photoelectrons are presented in Fig.2.

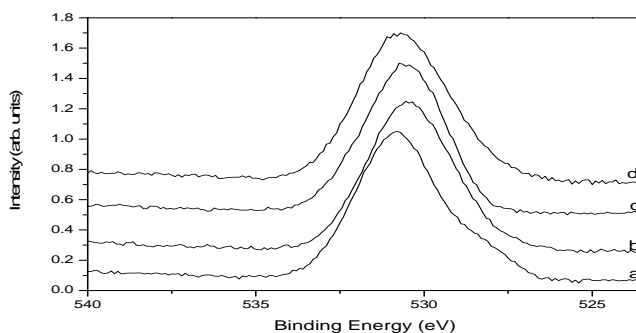


Fig.2 High resolution XPS spectra of the O 1s photoelectrons of $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ glasses (a.x=0, b.x=0.03, c.x=0.05 and d.x=0.09).

The high resolution XPS spectra obtained for the O 1s photoelectrons were used to determine the fraction of bridging oxygen atoms in the studied glasses: 85.7 ($x=0$), 89.7

($x=0.01$), 93.3 ($x=0.05$) and 92.4 ($x=0.09$). Fig.3 presents the thermal variation of the inverse magnetic susceptibility for the the $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ glasses with $x=0.05$ and $x=0.09$. The data collapse to straight lines indicating a Curie-Weiss behaviour ($\chi^{-1} = (T-\theta_p)/C$, where C is the Curie constant, θ_p is the paramagnetic Curie temperature and T is the temperature).

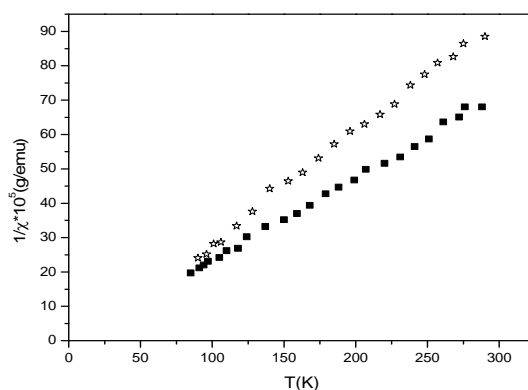


Fig.3 Thermal dependence of the inverse magnetic susceptibility of the $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ glasses (★=0.05, ■=0.09).

The IR spectral features shown in Fig.1 are associated to the structural units involving the Bi^{3+} cation. In this paper we will focus our attention only on the IR absorption feature located at 857 cm^{-1} . This absorption band represents the convolution of the absorption bands reported for different bismuthate glasses at 847 and 860 cm^{-1} , assigned to the total symmetric stretching vibrations of the $[\text{BiO}_3]$ and $[\text{BiO}_6]$ polyhedra, respectively [7]. The increase of the CeO_2 content, x , of the $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ samples determines first the increase of the absorption band at 855 cm^{-1} and its slow shift to 850 cm^{-1} for $x=0.09$, than its decrease and slow shift to the initial position suggesting the increase followed by the decrease of the number of $[\text{BiO}_3]$ structural units. This is due to the reciprocal conversion of the $[\text{BiO}_6]$ and $[\text{BiO}_3]$ structural units. The observed compositional evolution of the IR absorption feature located at 857 cm^{-1} suggests that increasing the cerium ion content of the xCBP glasses produce the increase of the amount of $[\text{BiO}_3]$ structural units up to $x=0.09$ followed by a decrease of the number of these structural unit for $x=0.15$. The structural changes observed by varying the CeO_2 content of the studied samples and evidenced by the IR investigation suggests that the cerium ions play a network modifier role in these glasses. The analysis of the XPS spectra of the O 1s photoelectrons is informative concerning the structural role played by the cerium ions in the $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ glasses. These data permit to observe if the cerium ions generate non-bridging oxygens behaving as glass modifiers or generate bridging

oxygens behaving like intermediates [9, 10]. The XPS data presented in the Table 1 show that the increase of the cerium oxide content, x , generates a weak increase of the number of bridging oxygen atoms in the glass matrix up to $x=0.05$, followed by a slow decrease of this number for $x=0.09$. This compositional evolution of the XPS data permits to state that the cerium ions enter the glass network of $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ glasses as intermediates but the network modifier role, suggested by the IR data, is not excluded. The paramagnetic Curie temperatures were zero suggesting that the magnetic interactions between the cerium ions having localized magnetic moment are very weak. We mention that the cerium ions may appear in oxide glasses in both their 3+ and 4+ valence state but only the Ce^{3+} are magnetic having a magnetic moment $\mu=2.56\mu_B$ [11]. Taking this fact into account, the Curie constants were used to determine the fraction of the Ce^{3+} ions present in the studied glasses. It was found that the fraction of the Ce^{3+} ions/total number of Ce ions was about 95% for both the samples with $x=0.05$ and $x=0.09$.

4. Conclusions

The data obtained by the investigation of the $x\text{CeO}_2(1-x)(\text{Bi}_2\text{O}_3 \text{ PbO})$ glasses evidenciate that the cerium ions appear in the glass matrix mainly in their 3+ valence state and may play both the modifier and intermediate roles in the host glass.

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