



Effects on the characteristics of bonding and local structure in molybdenum-lead-lead dioxide glasses and vitroceraamics



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ABSTRACT

Molybdenum ions doped lead-lead dioxide glasses and vitroceraamics of the $x\text{MoO}_3 \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ system where $x = 0, 5, 10, 20, 30, 40$ and 50mol% MoO₃ were obtained by melt quenching method.

The FTIR spectra show that the main structural units of lead atoms form chains with Mo–O–Mo bridge bonds in [MoO₆] structural units between which there are isolated [MoO₄] irregular tetrahedral units. The number of the [MoO₄] structural units increases with increasing the MoO₃ concentration of samples up to 50mol%.

UV–Vis spectra show noticeable changes of the intensity of absorption bands located in the 280–400 nm region after adding of MoO₃ to the host matrix. These changes can be correlated with the contributions of Pb⁺², Mo⁺³ and Mo⁺⁵ ions.

The EPR spectra show resonance lines situated at $g=5.2$ and 2 due to the presence of Mo⁺³ and Mo⁺⁵ ions.

The presence of both lead and molybdenum ions in the vitreous matrix generates a competition regarding their coordination with oxygen ions which leads to modifications of the gap energy values. Accordingly, these modifications cause the depolymerization of the host network, the increase of the structural disorder and formation of Pb₂MoO₅ and PbO crystalline phases, in agreement with XRD data.

Our quantum chemical calculations on the local structure of the studied vitroceraamic network show that the doping of the host matrix with molybdenum ions changes the bond length and bond angles of the vibrating structural units. The accommodation of the host network with progressively higher MoO₃ contents is possible by the increase of the amount of [MoO_n] polyhedrons in the vicinity of the [PbO₃] structural units. It can be pointed out that the favourable environment of the host matrix offers the possibility to the molybdenum ions to choose some preferred sites of coordination.

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1. Introduction

The MoO₃ and PbO₂ are known as non-conventional network formers and in addition to their fundamental importance, molybdenum and lead containing glasses possess a variety of specific features and interesting properties [1,2]. They are potential candidates for practical applications as amorphous semiconductors, for waste storage, as infrared transmission components, thermal and mechanical sensors, reflecting windows [2–7].

Such properties depend mainly on the relative amounts of the different valence states of the transition metal ions added to the glass network. When glasses are doped with two different transition metal ions, their technological applications become of high interest but the study of structural and behavioral properties becomes more complicated [8,9].

On the other hand, due to their unique properties, lead oxides (including four basic types, namely PbO, PbO₂, Pb₂O₃ and Pb₃O₄) have wide applications such as network-modifiers in luminescent glassy materials, pigments, storage batteries and nanoscale electronic devices [10].

The present study is a continuation of our investigations of glass formation and structure of glasses in the MoO₃ - PbO₂ - Pb complex system. The purpose is to characterize the structures of the obtained glasses/vitroceraamics and to clarify the role of the

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molybdenum (VI) oxide in the formation of these structures. XRD and FTIR, UV–Vis and EPR spectroscopies, together with molecular modeling calculations were employed in order to correlate the structural transformations with the behavioral changes of the studied MoO_3 – PbO_2 – Pb system.

2. Experimental procedure

Glasses were prepared using reagent grade purity molybdenum (VI) oxide, lead (IV) oxide and metallic lead of high purity in suitable proportion. The mechanically homogenized mixtures were melted in sintered corundum crucibles at 900 °C in an electric furnace. The samples were put into the electric furnace direct at this temperature. After 10 min, the molten material was quenched at room temperature by pouring onto a stainless-steel plate.

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

The FT-IR spectra of the glasses were obtained in the 350–1550 cm^{-1} spectral range with a JASCO FTIR 6200 spectrometer using the standard KBr pellet disc technique. The spectra were carried out with a standard resolution of 2 cm^{-1} .

UV–Visible absorption spectra of the powdered glass samples were recorded at room temperature in the 250–1000 nm range using a Perkin-Elmer Lambda 45 UV/VIS spectrometer equipped with an integrating sphere. These measurements were made on glass powder dispersed in KBr pellets. The validity of the band position is $\pm 2 \text{ nm}$.

EPR measurements were performed at room temperature using an ADANI portable EPR PS 8400-type spectrometer, in the X frequency band (9.1 GHz) and a field modulation of 100 kHz. The microwave power was 5 mW.

The starting modeling structures were built using the graphical interface of Spartan'04 [11] and preoptimized by molecular mechanics. Optimizations were continued at DFT level (B3LYP/CEP-4G/ECP) using the Gaussian'03 package of programs [12].

It should be noticed that only the broken bonds at the model boundary were terminated by hydrogen atoms. The positions of boundary atoms were frozen during a calculation and the coordinates of internal atoms were optimized in order to model the active fragment flexibility and its incorporation into the bulk.

3. Results and discussion

Fig. 1 shows the XRD diffractograms of the samples obtained in the $x\text{MoO}_3 \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ system where $x = 30$ –50 mol% MoO_3 . It can be seen that for the samples with $x \leq 30$ mol% MoO_3 , the amorphous state of samples is checked since there are only two broad diffraction halos characteristic of the glassy structure. The sample with $x = 40$ mol% MoO_3 is vitroceraic. A vitroceraic sample containing Pb_2MoO_5 and PbO crystalline phases was obtained for the composition with $x = 50$ mol% MoO_3 , too.

Lead molybdenum oxide crystal, Pb_2MoO_5 , has the lanarkite-type lattice with the $C2/m$ space group which contains MoO_4^{2-} isolated irregular tetrahedral units with the average Mo–O distance of 1.777 \AA [13]. Another peculiarity of Pb_2MoO_5 structure is the existence of Pb–O infinite zig-zag chains along the z crystallographic direction (Pb–O distances in the chains are 2.298 \AA). Every fifth oxygen atom belongs to Pb–O chains while all other oxygen atoms belong to MoO_4^{2-} structural units.

3.1. FTIR spectroscopy

The structure of molybdenum-lead-lead dioxide glasses and vitroceraics was investigated using FTIR spectroscopy. The FTIR

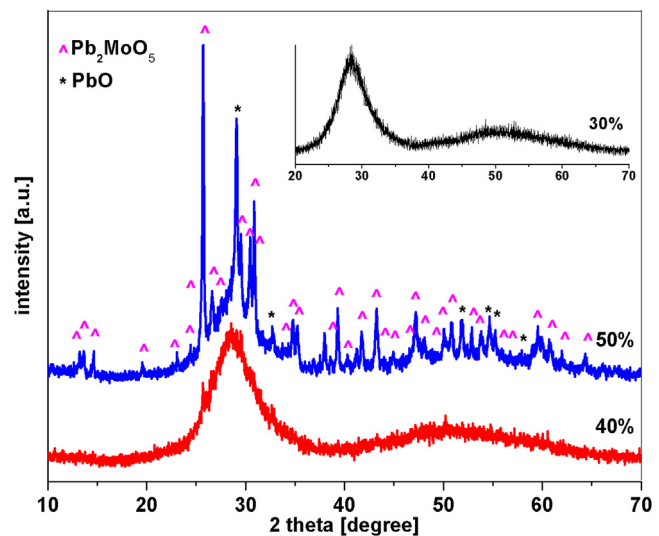


Fig. 1. X-ray diffraction patterns for $x\text{MoO}_3 \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ samples where $x = 30$ –50 mol% MoO_3 .

spectra of $x\text{MoO}_3 \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ glasses and vitroceraics with $x = 0$ –50 mol% MoO_3 are given in Fig. 2. The interpretation of the FTIR spectra is based on previously reported spectral data concerning different structural units namely $[\text{MoO}_6]$, $[\text{MoO}_4]$ and $[\text{PbO}_n]$ where $n = 3, 4$ and 6.

The broad absorption band centered at about 470 cm^{-1} may be assigned to the bending mode of Pb–O–Pb and O–Pb–O linkages in $[\text{PbO}_4]$ structural units. The absorption band centered at about 1030 cm^{-1} can be attributed to the Pb–O stretching vibrations in the $[\text{PbO}_3]$ structural units [14].

The IR absorption band centered at $\sim 800 \text{ cm}^{-1}$ was assigned to the Mo–O stretching vibrations of isolated $[\text{MoO}_4]$ structural units while the absorption band situated at $\sim 870 \text{ cm}^{-1}$ can be attributed to the vibrations of Mo–O–Mo bridge bonds in $[\text{MoO}_6]$ structural units where there are no short Mo=O bonds [15].

The addition of gradually higher MoO_3 contents to the $4\text{PbO}_2 \cdot \text{Pb}$ host matrix produces some changes in the FTIR spectra that can be summarized as follows:

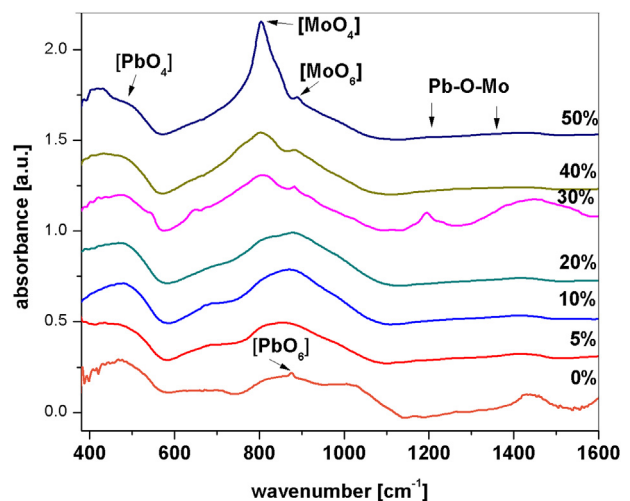


Fig. 2. FTIR spectra of the $x\text{MoO}_3 \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ glasses and vitroceraics where $0 \leq x \leq 50$ mol% MoO_3 .

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