

Structural analysis of lead-borate composites containing PbMoO_4 nanocrystals

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Glass-crystalline composite materials based on a lead-borate glassy matrix and PbMoO_4 nanocrystals were obtained by the incorporation technique. The samples were prepared by conventional melting. The content of the PbMoO_4 was varied in the range from 5 to 40 wt.%. The appearance of the crystalline phase was identified by powder X-ray diffraction (XRD) analysis. The change in the network structure of the obtained materials was investigated by infrared spectroscopy (IR). The existence of BO_3 , BO_4 , PbO_n (where $n=3$ and/or 4), as well as of MoO_4 units was proven. The dependence of the density as a function of the composition was also clarified.

Keywords: composites, density, structural investigations

INTRODUCTION

The methods for fabrication of various glass-ceramic nanostructured materials and nanodevices determine the special properties of the obtained products. The investigations are directed towards the selection of appropriate precursors and a combination of non-traditional methods for the synthesis of nanopowders, nanoparticle suspensions and coatings, bulk nanocomposite materials, nanophase alloys, ultrathin wires, etc. [1]. The structural investigations of the materials are performed concerning the possibility to control and to guide their specific properties.

The obtaining of new nanostructured glass-ceramic composites imposes several requirements towards the matrix: it should be a kinetically stable amorphous compound with a slightly pronounced tendency towards crystallization in the case of an appropriate heat treatment, as well with low melting temperature and limited reaction ability. Thus, lead-borate glasses are suitable materials for this purpose due to their unique properties such as low melting temperatures, wide glass formation regions, as well as good radiation shielding properties [2, 3].

Lead molybdate crystals have recently received even greater attention as possible acousto-optic materials, modulators, ion conductors, scintillators in nuclear instruments, etc. [4, 5].

The present work aims to analyze the influence of the composition on the microstructural transformation and density of the obtained composite materials. In particular, the aim of the

structural investigation (using XRD analysis and IR spectroscopy) is to explain the relationship between the structure and properties of these materials.

EXPERIMENTAL

Synthesis of samples

Composite materials based on previously obtained lead-borate glass with composition $2\text{PbO} \cdot \text{B}_2\text{O}_3$ and PbMoO_4 nanocrystals were prepared by the incorporation method [6]. The choice of the matrix composition was made according to the phase diagram of the system $\text{PbO} \cdot \text{B}_2\text{O}_3$ [7]. The preparation of composite materials consisted of:

i) synthesis of melted glass (g-PbB) using chemically pure materials (B_2O_3 and Pb_3O_4 as the main source of PbO [8]) in a platinum crucible at 900°C for 30 min;

ii) synthesis of powdered polycrystalline PbMoO_4 by solid-state sintering of a stoichiometric mixture of 50 mol% PbO and 50 mol% MoO_3 (Alfa Aesar) or 1:1.55 weight ratios. PbO was heated for 2 hours at 450°C and MoO_3 – for 3 hours at 650°C . The homogenized mixture was sintered in a porcelain crucible at 800°C for 2.5 hours;

iii) preparation of thoroughly mixed batches of both components in the compositional range from 95 to 60 wt.% g-PbB and, respectively, from 5 to 40 wt.% PbMoO_4 , melting of the batches under normal atmospheric condition at 850°C for 2 hours and fast cooling by pouring the melts between two copper plates (Table 1).

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Table 1. Composition of the investigated samples

Sample abbreviation	Composition	
	g-PbB, (wt.%)	PbMoO ₄ , (wt.%)
P1	95	5
P2	90	10
P3	80	20
P4	70	30
P5	60	40

Methods of characterization

The phase composition of the obtained materials was determined by powder X-ray diffraction analysis using diffractometer Philips with Bragg-Brentano geometry and graphite monochromated CuK α radiation ($\lambda=1.54$ Å, 40 kV, 50 mA). The performed reflectance angle was in the range 10°-70° (0.5° of each step). All investigations were performed at ambient temperature.

The infrared absorption spectra were measured with a Varian 680-IR spectrometer in transmission mode in the MIR 400-4000 cm⁻¹ spectral range with a 2 cm⁻¹ spectral resolution. The samples were prepared as standard KBr pellets.

The density of the samples (ρ) was measured by the pycnometric method at a constant temperature. The immersion liquid used as a medium for density measurement was toluene with density at 25 °C - 0.8623 g/cm³. The measurement accuracy was about $\pm 2\%$.

RESULTS AND DISCUSSION

XRD characterization

The XRD pattern of the polycrystalline PbMoO₄ powder is shown in Fig. 1. The observed diffraction peaks are very sharp and distinct, indicating good crystallinity of the prepared material. The formation of PbMoO₄ (JCPDS 74-1075) was proven. It is well-known that lead molybdate has a scheelite-type tetragonal structure and space group symmetry of I4₁/a [9]. In the crystal lattice, lead (Pb) atoms are connected by eight oxygen (O) atoms to form [PbO₈] clusters whereas molybdenum (Mo) atom is coordinated by four O atoms which result in [MoO₄] tetrahedral units [10]. The previous results of TEM analysis [11] showed that the PbMoO₄ particles exhibited sizes up to 50 nm.

Fig. 2 presents the X-ray diffraction patterns of the composites. The results show that the samples containing 5 wt.%, 10 wt.% and 20 wt.% PbMoO₄ are X-ray amorphous. Only a broad amorphous halo is observed in the diffractograms at an angle of 2 θ between 20 and 35°. In the samples with 30 wt.% and 40 wt.% PbMoO₄, distinct diffraction maxima on the halo are observed, i.e. the samples

are glass-crystalline. Crystalline phase identification of PbMoO₄ is made by PDF 77-0431. The diffractograms also show that the intensity of the peaks increases with increasing PbMoO₄, which is an indication of the increase in the crystalline phase content.

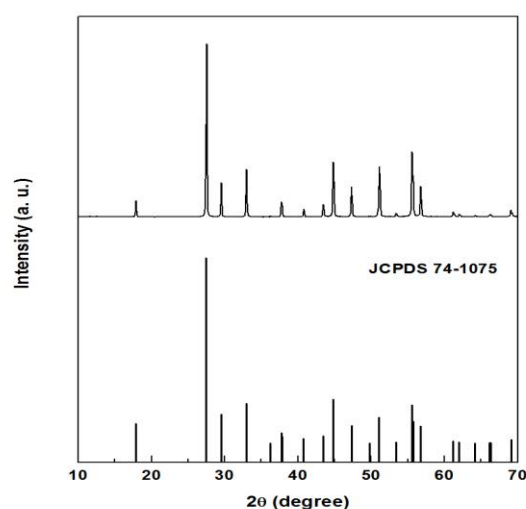


Fig. 1. XRD pattern of polycrystalline PbMoO₄ powder. The theoretical pattern is presented below for comparison.

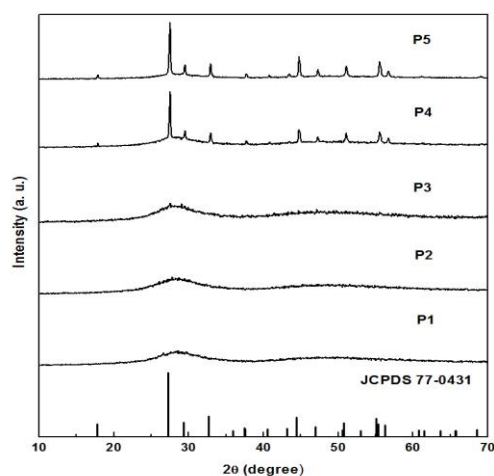


Fig. 2. X-ray diffraction patterns of the composite materials.

IR analysis

The vibrational assignments of the bands for the composite materials spectra were done by comparing the experimental data with those of the related crystalline compounds [12]. To interpret the structure of the investigated samples as accurately as possible, the results obtained were compared to the currently known data on the $PbO-B_2O_3$ system IR spectra, some other binary borate systems, as well as various systems with the participation of B_2O_3 and $PbMoO_4$.

Two spectral ranges are typical of the investigated samples: from 400 to 2000 cm^{-1} and from 2000 to 4000 cm^{-1} . The large absorption region centered at about 3440 cm^{-1} is assigned to the vibrations of OH-groups and water molecules. In the second spectral region, there are bands related to the vibrations of the different structural units (Fig. 3). The obtained absorption bands and their assignments are summarized in Table 2.

For easier interpretation of the obtained spectra, they were compared to the spectrum of the matrix of $2PbO.B_2O_3$. The spectra in the range of 1500-1700 cm^{-1} are similar. The bands are due to the

inevitable moisture in the applied KBr-pellet method [13].

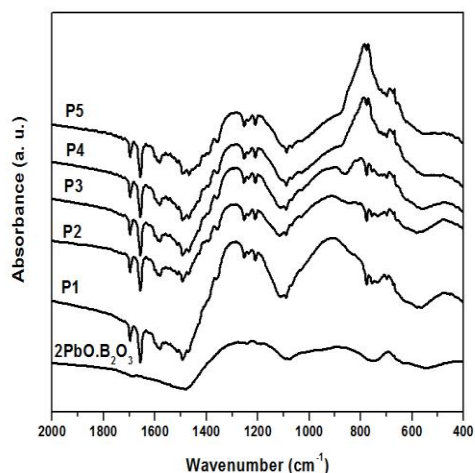


Fig. 3. Infrared absorption spectra of the samples

Table 2. Infrared absorption bands and their assignment

Peak position (cm^{-1})	Assignment	References
690, 706	Bending vibrations of B-O-B linkage in BO_3 triangles	14, 15
1150-1450	Stretching vibrations in borate triangle units	16, 17
1198 1220	Asymmetric stretching vibrations of B-O and/or B-O' bonds in borate triangular units from pyro- and ortho-borate groups	18 19
1240	Stretching vibrations of B-O bonds of borate triangles non bridging oxygens (NBO's)	19
1296	Vibrations of B-O rings, which are formed by the connection of the bridge oxygen ions between $[BO_3]$ triangles and $[BO_4]$ tetrahedra	17
910, 1040	Stretching vibration of B-O bonds in BO_4 units	16, 20, 21
480, 650	Bending vibration of Pb-O-B	23, 24
670	Vibration of Pb-O bonds from PbO_4 pyramidal units	22
1100	Asymmetric stretching vibrations of Pb-O in $[PbO_n]$ units	25
800-830	Characteristic vibrations of distorted isolated MoO_4 tetrahedra	21, 26
770, 790	Mo-O antisymmetric stretching vibration of $[MoO_4]^{2-}$ tetrahedra from $PbMoO_4$	28
418	Symmetric vibration of the Mo-O-Mo linkage	21, 27
1500-1700	Due to the inevitable moisture in the KBr-pellet method	13

The absorption bands may be divided into three regions: 1450-1150 cm⁻¹, 1100-800 cm⁻¹ and 750-600 cm⁻¹. The bands at 690 cm⁻¹ and 706 cm⁻¹ are ascribed to the B-O-B bridges bending vibration of BO₃ triangles [14, 15].

The absorption bands in the region 1450-1150 cm⁻¹ originate from the B-O stretching of various BO₃ units (both bridging and non-bridging types) [16, 17]. The band at 1198 cm⁻¹ [18] is obtained by the asymmetric stretching vibrations of B-O and/or BO bonds in borate triangular units (BØ₃ и BØ₂O) from pyro- and ortho-borate groups (Ø: oxygen atom bridging two boron atoms; O: non-bridging oxygen atom). The band at 1220 cm⁻¹ [19] is also due to asymmetric stretching vibrations of BO bonds in BO₃ units from pyro- and ortho-borate groups and those at 1240 cm⁻¹ - of borate triangles non-bridging oxygens (NBOs). The broad band about 1296 cm⁻¹ is attributed to the vibrations of B-O rings, which are formed by the connection of the bridge oxygen ions between [BO₃] triangles and [BO₄] tetrahedra [17]. There are also several slightly intensive peaks at 1369 cm⁻¹, 1396 cm⁻¹, 1410 cm⁻¹ and 1433 cm⁻¹ due to B-O bonds stretching vibrations of BO₃ units from various borate groups [12]. The shoulder at about 910 cm⁻¹, due to the asymmetric stretching vibrations of boron in tetrahedral oxygen coordination B₄ [16, 20], reduces its intensity with the increase of PbMoO₄ content. This is related to the decrease in the number of superstructure units (BO₃+BO₄), respectively of the BO₄ groups. This may be due to an increase in the PbO/B₂O₃ ratio due to the partial dissolution of PbMoO₄. The same trend is observed for the band at 1040 cm⁻¹ associated to the B-O stretching vibration in BO₄ units from tri-, tetra- and pentaborate groups [16, 21].

The high content of lead oxide in lead-borate glasses plays a dual role - a network former and a network modifier in the glass matrix, having essentially B₂O₃ as a glassy former. At sufficiently large amounts of PbO (60 % or higher), its effect as a glass-forming agent for the structural network of the glass is obvious. The lead oxide is incorporated into the structure as [PbO₄] structural units. This is confirmed by an increase in the intensity of the band located at about 670 cm⁻¹. This band can be attributed to Pb-O bonds vibrations from [PbO₄] pyramidal units [22]. The occurrence of a band around a 650 cm⁻¹ and a shoulder around a 480 cm⁻¹ are attributed to a Pb-O-B bending [23, 24]. Therefore, in this case, PbO can be considered as a network participant as Pb²⁺ modified boron-oxygen rings and chains. The absorption band at a higher frequency, located at about 1100 cm⁻¹, is attributed

to Pb-O asymmetric stretching vibrations in [PbO_n] structural units with n = 3 and/or 4 [25]. The dissolution of the lead molybdate is also indicated by the presence of a shoulder in the range 830-800 cm⁻¹ in composites P1-P3. The molybdenum ions, in this case, act as a glass-forming agent and are incorporated in the glass matrix as distorted, isolated MoO₄ tetrahedra [21, 26].

The increase in the PbMoO₄ content leads to an increase in the band intensity at 418 cm⁻¹ assigned to the symmetric vibration of the Mo-O-Mo linkage [21, 27]. Additionally, the spectra of composites P4 and P5 exhibit two well-resolved bands at 790 cm⁻¹ and 770 cm⁻¹, which can be specified as Mo-O antisymmetric stretching vibration of the MoO₄²⁻ tetrahedra [28] from PbMoO₄.

Density

The density responds to variations in composition sensitively in technological practice. Density, in general, is explained in terms of a competition between the masses and sizes of the various structural groups present in the glasses. Accordingly, density is related to how tightly the ions and ionic groups are packed together in the structure. The density values of all composite materials are listed in Table 3.

The density of the composite materials shows a non-linear dependence with the increase of PbMoO₄ content as shown in Fig. 4.

Table 3. Density values of the composite materials

Sample	P1	P2	P3	P4	P5
ρ , (g/cm ³)	6.00	5.89	6.08	6.16	6.21

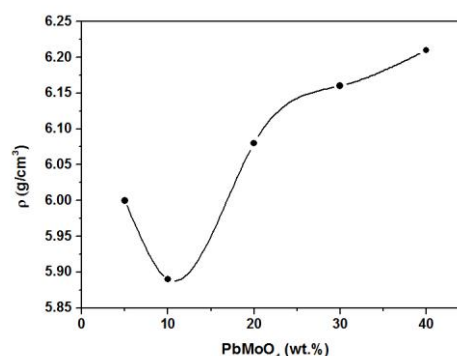


Fig. 4. Density dependence on composition

In fact, there is a sudden drop in density at 10 wt.% PbMoO₄. This is attributed to the conversion of BO₄ tetrahedral units into BO₃ triangular units. Then, with the increase in PbMoO₄ content, density values gradually increase. This result is consistent with the IR spectroscopy results which show that at

the sample P2 a change in matrix structure takes place - the shoulder at about 910 cm⁻¹ reduces its intensity, which is associated with decreasing the amount of the BO₄-groups. This may be due to an increase in the PbO/B₂O₃ ratio due to the partial dissolution of PbMoO₄. Moreover, the intensity of the absorption band at 670 cm⁻¹ which is the characteristic frequency of Pb–O vibrations from PbO₄ units increases. The presence of a shoulder in the range 830-800 cm⁻¹, which is indicative of the participation of molybdenum in the composite glass matrix as distorted, isolated MoO₄ tetrahedra also indicates dissolution of the lead molybdate.

CONCLUSIONS

IR spectroscopic and XRD analyses were employed to study the structural changes in composite materials based on an amorphous lead-borate matrix and PbMoO₄ nanocrystals. IR spectra indicated that the main structural units building the amorphous network are BO₃ triangles and BO₄ tetrahedra in superstructures, in addition to the PbO_n (where n = 3 and/or 4) structural units. It was established that PbMoO₄ was dissolved partially. Molybdenum ions acted as network formers as MoO₄ tetrahedra. It was proved that molybdenum favored the BO₄→BO₃ transformation.

Typical diffraction patterns of glass-crystalline samples were obtained for the composite materials containing more than 20 wt.% PbMoO₄.

The compositional variation of density was discussed. The measurements showed that the densest packing of coordination polyhedra in these materials was obtained for a sample containing 10 wt % PbMoO₄.

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