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Structural investigation of MnO-P_2O_5-TeO_2 glasses by FTIR spectroscopy

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Glasses of the xMnO·(100-x)[$2P_2O_5$·TeO_2] system, with $0 \le x \le 50$ mol %, were prepared in the same conditions and investigated by FTIR spectroscopy. IR spectra of these glasses were analyzed in order to identify the contribution of each component to the local structure that determined the physical properties of these glasses. The $2P_2O_5$·TeO_2 glass matrix is formed from two glass formers: P_2O_5 as a classical one and TeO_2 as a non-conventional one, which determined the basic structure of the studied glasses. The results have shown that phosphorous and tellurium ions take part in the network of studied glasses as PO_4, TeO_4 trigonal bipyramid and TeO_3 trigonal pyramid units. At higher manganese ion content, the P=O bonds break, the P–O–P bonds can probably be replaced by P–O–Mn bonds. The bands corresponding to the IR absorption of MnO are not directly evidenced. The phosphate chain length decreases in the glasses with high MnO content due to the depolymerization of the phosphate structure, leading to the increase of the number of short phosphate chain units or rings.

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1. Introduction

Phosphate based glasses are technologically important and are widely used in applications like solid-state electrolytes, glass-to-metal seals, laser hosts and biomaterials. Many of the phosphate glasses have low glass transition temperatures and glass formation takes place over a wide compositional range [1-3].

The structure of binary and ternary phosphate glasses has been studied by neutron and X-ray diffraction [4], Raman scattering [5-7], infrared [8] and nuclear magnetic resonance [9-11] spectroscopies. The phosphate network is based on corner-sharing PO_4 units which form chains, rings or isolated PO_4 groups [12]. The addition of oxides such as TeO_2 results in the conversion of three-dimensional network to linear phosphate chains. The introduction of transition metal ions such as manganese in glasses leads to a change in glass structure, electrical, optical and magnetic properties.

In the present work, the xMnO·(100-x)[$2P_2O_5$·TeO_2] glass system, with $0 \le x \le 50$ mol%, was prepared under the same conditions and characterized by IR spectroscopy, in order to understand the role of MnO on the local structure.

2. Experimental

The starting materials used in the present investigation were $(NH_4)_2HPO_4$, TeO_2 and $MnCO_3$ of reagent grade purity. The samples were prepared by weighing suitable proportions of the components, powder mixing and mixture melting in sintered corundum crucibles at 1250 °C for 5 minutes. The mixtures were put into the furnace directly at this temperature. The melts were poured onto stainless steel plates.

The FTIR absorption spectra of the glasses in the 400 – 1500 cm^{-1} wavenumber were obtained with an Equinox 55 Bruker spectrometer. The measurements were done using the KBr pellet technique. The samples were crushed in an agate mortar to obtain particles of micrometer size to avoid structural modifications due to ambient moisture.

3. Results and discussion

The experimental FT-IR spectra of xMnO·(100-x)[$2P_2O_5$·TeO_2] glass system with various content of manganese oxide ($0 \le x \le 50$ mol%) were presented in Fig. 1. The bands obtained and their assignments are summarized in Table 1.

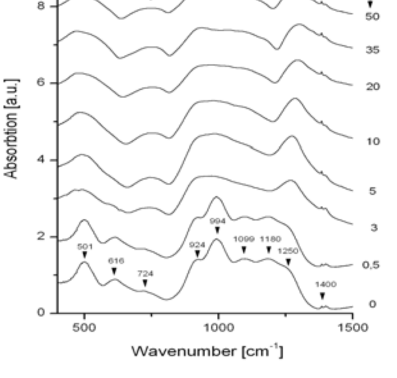

Fig. 1. Infrared absorption spectra of xMnO·(100-x)[P_2O_5·TeO_2] glasses.

In the glass matrix spectrum, the following bands are present: ~501 cm^{-1}, ~616 cm^{-1}, ~724 cm^{-1}, ~924 cm^{-1}, ~994 cm^{-1}, ~1099 cm^{-1}, ~1180 cm^{-1}, ~1250 cm^{-1} and 1400 cm^{-1}. Taking into account the IR results reported about some phosphate glasses we may assume that the ~1400 cm^{-1} band can be assigned to P=O stretching vibrations [13]. The band at ~1250 cm^{-1} is characteristic for the stretching vibration of the P=O group in polymeric phosphate chains [14]. The band around 1180 cm^{-1} is assigned to the P–$O^{(-)}$ ionic stretching vibrations [15]. The band around 1099 cm^{-1} is due to the stretching vibrations of the PO_4^{3+} group [16].

Table 1. FT-IR absorption bands and their assignments for xMnO·(100-x)[P_2O_5·TeO_2] glasses.

Wavenumber (cm^{-1})	Assignment
~501	Bending harmonics of O=P–O
~616	Symmetrical stretching vibrations of Te–O
~724	Specific vibrations of Mn–O bonds
~924, ~994	Stretching vibrations of P–O–P
~1099	Asymmetric stretching vibrations of P–O–P
~1180	Stretching vibrations of the PO_4^{3-} group
~1250, ~1400	Stretching vibrations of P–O Stretching vibrations of P=O

The bands centered at ~994 cm^{-1} and ~924 cm^{-1} are due to the P–O–P asymmetric bond stretching vibrations and the band at ~724 cm^{-1} corresponds to the stretching vibration of P–O–P [15]. The band at ~616 cm^{-1} was assigned to the symmetrical stretching vibrations of Te–O bond in TeO_4 tetragonal bipyramid (TBP) group [17]. The band at ~501 cm^{-1} is ascribed to the bending harmonics of O=P–O [16]. Taking into account that the presence of the structural units of P_2O_5 in the IR absorption spectra is relatively dominant compared to that of the structural units of TeO_2 we may conclude that in this case TeO_2 acts as a glass network modifier.

The addition of MnO to the P_2O_5·TeO_2 glass matrix produces some changes in the IR spectrum. The band at ~1240 cm^{-1} shifts toward higher wavenumbers, from 1250 cm^{-1} to 1286 cm^{-1}. The band at ~1180 cm^{-1} disappears for $x > 3\ mol\%$. The band at ~1099 cm^{-1} shows a shift towards lower wavenumbers, from 1099 cm^{-1} to 1070 cm^{-1}. The band at ~994 cm^{-1} gradually shifts to lower wavenumbers from 994 cm^{-1} to 932 cm^{-1}. The band at ~724 cm^{-1} disappears for $x > 3\ mol\%$. Over the absorption band at ~ 616 cm^{-1}, the contribution of the specific vibrations of Mn–O bonds can be superposed. The decreasing of the intensity of this band is due to the changing of the coordination of Te from a TeO_4 TBP group to a TeO_3 trigonal pyramid. The band disappears for $x > 5\ mol\%$. The band at ~501 cm^{-1} gradually shifts to lower wavenumbers with the increasing MnO content, from ~500 cm^{-1} to ~480 cm^{-1} and the band broadens.

The introduction of transition ions, such as manganese into glass matrix gives changes in their structure, electrical, optical and magnetic properties [18, 19]. Xu et al. [19] has been suggested that the excellent chemical durability of iron phosphate glasses is attributed to the replacement of P-O-P bond by more resistant P-O-Fe bond. We can expect that a similar substitution (the P–O–P bonds replaced by P–O–Mn bonds) can appear in the present investigated glasses.

From the shape of FTIR spectra for x > 3 mol% it results that in the studied glasses the disorder of the structure increases for higher values of MnO concentrations.

4. Conclusions

Under the same preparation conditions, homogeneous glasses of the xMnO·(100-x)[$2P_2O_5$·TeO_2] glass system up to x = 50 mol % were obtained. It is notable that the presences in the tellurite-phosphate glasses of manganese ions determine structural modifications, which will certainly influence suitable modification of their properties. With the increase of the manganese ion concentration the bands broaden, some of them disappearing at concentrations higher than 3 mol%. The structure becomes more disordered with the increase of the MnO content.

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