

FTIR spectroscopic investigations of MnO-P₂O₅-TeO₂ glasses

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Glasses of the xMnO (100-x)[P₂O₅ · TeO₂] system, with 0 ≤ x ≤ 50 mol%, were prepared and investigated by infrared spectroscopy in attempt to determine the local structure of glasses. The results shown that PO₄ are the main structural unit of the glass system and the manganese ions are located in the glass matrix network. It is evidenced the presence of TeO₃ and TeO₄ units as possible structural units in our glasses.

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1. Introduction

The analysis of vibrational spectra of glasses can be applied to the solution of both industrial and basic research problems. In an applied study, the vibrational spectra can be used to identify the specific groups that are present in glasses.

Phosphate glasses are technologically important materials, primarily because of their relatively large thermal expansion coefficients, low optical dispersions and low glass transition temperatures (T_g) [1-3]. They have found important applications in e.g. glass-to-metal seals, laser hosts and biocompatible materials.

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 PO₄ units which form chains, rings or isolated PO₄ groups [12]. The addition of oxides such as TeO₂ results in the conversion of three-dimensional network to linear phosphate chains. The introduction of transitional metal ions such as MnO in glasses leads to a change in glass structure and electrical, optical and magnetic properties.

In the present work, the xMnO (100-x)[P₂O₅ · TeO₂] system, with 0 ≤ x ≤ 50 mol%, was prepared under the same condition and characterized by IR spectroscopy, in order to understand the role of MnO on the local structure.

2. Experiment

The starting materials used in the present investigation were (NH₄)₂HPO₄, TeO₂ and MnCO₃ 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 950 °C for 10 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 spectral range 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 IR spectra of xMnO (100-x)[P₂O₅TeO₂] glass system with various content of manganese oxide (0 ≤ x ≤ 50 mol%) were presented in Fig. 1. The bands obtained and their assignments are summarized in Table 1.

In the matrix spectrum, the following bands are present: ~500 cm⁻¹, ~622 cm⁻¹, ~720 cm⁻¹, ~920 cm⁻¹, ~993 cm⁻¹, ~1093 cm⁻¹, ~1190 cm⁻¹ and ~1240 cm⁻¹. The band at ~1240 cm⁻¹ is characteristic for the stretching vibration of the P=O group in polymeric phosphate chains [13]. The band around 1190 cm⁻¹ is assigned to the P–O⁽⁻⁾ ionic stretching vibration [14]. The bands centered at ~993 cm⁻¹ and ~920 cm⁻¹ are due to the P–O–P asymmetric bond stretching vibrations and the band at ~720 cm⁻¹ corresponds to the stretching vibration of P–O–P [15]. The band at ~622 cm⁻¹ was assigned to the symmetrical stretching vibrations of Te–O bond in TeO₄ tetragonal bipyramid (TBP) group [16]. The band at ~500 cm⁻¹ is ascribed to the bending harmonics of O=P–O. The presence of the tellurite structural units in the glass matrix structure indicates that the TeO₂ acts as a glass network former.

The addition of MnO to the P₂O₅ · TeO₂ glass matrix produces some changes in the IR spectrum. The decrease of the IR absorption band at ~1240 cm⁻¹ indicates the decrease of the number of double bonded oxygen atoms.

The band at $\sim 1240\text{ cm}^{-1}$ gradually disappears by merging into the $\sim 1190\text{ cm}^{-1}$ band. The band at $\sim 1093\text{ cm}^{-1}$ gradually shifts to lower wavenumbers at $\sim 1070\text{ cm}^{-1}$ for $x = 50\text{ mol}\%$. These facts are due to the breaking of the P=O bonds, the reduced force constant between P and O and the formation of more non-bridging oxygen ions [17].

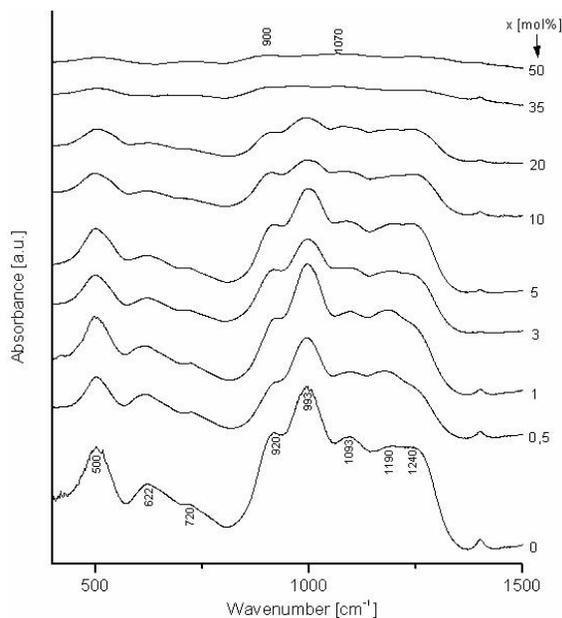


Fig. 1. Infrared absorption spectra of $x\text{MnO} (100-x)[\text{P}_2\text{O}_5 \cdot \text{TeO}_2]$ glasses.

Table 1. Frequencies and their assignments for IR spectra of $x\text{MnO} (100-x)[\text{P}_2\text{O}_5 \cdot \text{TeO}_2]$ glasses.

Wavenumber (cm^{-1})	Assignment
~ 500	Bending harmonics of O=P–O
~ 622	Symmetrical stretching vibrations of Te–O
~ 720	Specific vibrations of Mn–O bonds
~ 920 ~ 993	Stretching vibrations of P–O–P
~ 1093	Asymmetric stretching vibrations of P–O–P
~ 1190	Stretching vibrations of the PO_4^{3-} group
~ 1240	Stretching vibrations of P–O
	Stretching vibrations of P=O

The band at $\sim 920\text{ cm}^{-1}$ shifts to lower wavenumbers at $\sim 900\text{ cm}^{-1}$ for $x = 50\text{ mol}\%$. The intensity of this band decreases with increasing MnO content and disappears for $x > 35\text{ mol}\%$. Over the absorption band from $\sim 622\text{ cm}^{-1}$, 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 $x > 35\text{ mol}\%$. The intensity of the band at $\sim 500\text{ cm}^{-1}$ decreases with the increasing MnO content.

The introduction into glasses of transitional ions, such as MnO, 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. So that, a similar substitution (where the P–O–P bonds are replaced by P–O–Mn bonds) can appear in the present investigated glasses.

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 intensity of the absorption bands decreases. The bands broaden, some of them disappearing at concentrations higher than 35 mol%. The structure becomes more and more disordered with the increase of the MnO content.

4. Conclusions

Under the same preparation conditions, homogeneous glasses up to $x = 50\text{ mol}\%$ were obtained. IR spectra of these glasses have been analyzed in order to identify the contribution of each component to the structure and to point out the role of the manganese ions as a modifier of the glass network.

Phosphate and tellurium take part in the network of these glasses as PO_4 , TeO_3 and TeO_4 units. At higher manganese ion content, the P=O bonds break, the P–O–P bonds can be probable replaced by P–O–Mn bonds. The bands corresponding to the IR absorption of MnO are not directly evident.

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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