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FTIR Spectra of Molybdenum Tellurite Glasses

A series of binary tellurite glasses in the form $TeO_{2(100-x)} - MoO_{3(x)}$ when $[x=10, 20, 30, 40, 50, 55wt\%]$ were prepared. FTIR spectra were measured in the range $(4000-200) cm^{-1}$ and $(2000-200) cm^{-1}$ respectively. The peak positions were measured and correlated to the composition and structure of the glasses. Results were compared with the crystalline states of TeO_2 . The FTIR spectra of these glass systems indicate that the modified oxides are connected to the chains of TeO_4 units.

Keywords: Te glasses, $TeO_{2(100-x)}-MoO_{3(x)}$, FTIR spectra, crystalline TeO_2

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1. Introduction

Tellurite glasses are relatively new class of vitreous material, having gained popularity as a result of pioneer work by Stenworth [1]. It is well known that pure TeO_2 is vitrified with difficulty [2-3] and there was considerable doubt about the existence of TeO_2 in a true glassy state. TeO_2 glass was, however, prepared and its optical absorption and infrared in tungsten tellurite glasses was studied [4].

Tellurite glasses with TeO_2 as the main former are considered as potential candidate materials for all optical switching materials and laser host. They are of technical interest on account of their low melting points, high refractive indices, dielectric constants, good infrared transmissions, and high thermal expansion coefficients [5].

The structure of amorphous TeO_2 and other tellurite glasses has been the subject of several investigation [2,6]. TeO_2 glasses have been reported to consist of a network of individual interconnected deformed TeO_4 trigonal bipyramids with two equatorial and two axial bonds leaving alone pair of electrons in the equatorial position. This building unit of TeO_4 is then connected to the neighboring units via bridging oxygen to form three dimensional crystalline structure. In tellurite glasses, however, the modifier atoms play one more important role that is causing the variation of the structural unit itself. Structural units of tellurite glasses are reported to be TeO_x ($x=3-6$) polyhedra [7-8]. It is in contrast with the structural unit of silicate glasses (SiO_4 tetrahedron) which is not affected by modifier atoms. Dimitriev *et. al* [6] have studied the short range order of $TeO_2-V_2O_5$ and TeO_2-MoO_3 glasses using infrared spectroscopy by comparing the infrared spectra recorded from both amorphous and crystalline materials, they suggest that transition of TeO_4-TeO_3 took place within basic structural units with the introduction V_2O_5 and MoO_3 in the glass.

Nevo *et. al* [9] have also proposed a structural model of tellurite glasses in the $TeO_2-Fe_2O_3$ systems with high concentrations of TeO_2 based on neutron diffraction analysis. According to their model, the basic coordination polyhedron is the tribonal bipyramid TeO_4 connected through bridging oxygen atoms while Fe atoms assume octahedral arrangement to the oxygen atoms. They do not exclude the possibility of the TeO_3 polyhedra formation, even though its contribution to the radial distribution function (RDF) is considered to be small.

The purpose of the present work is to establish what structural changes may be registered by FTIR spectra in short range order as a consequence of adding MoO_3 as a modifier with different concentrations of the glasses system ($TeO_{2(100-x)}-MoO_{3(x)}$).

The results of Fourier transform infrared (FTIR) spectrophotometer are believed to help interpreting our results.

2. Experiment

The glasses under study have been prepared by mixing high purity TeO_2 and MoO_3 in specified contains. By using alumina crucibles, the oxides melted in an electrical furnace held at $800-850^\circ C$ depending on the contained of MoO_3 for 1 hour and quenched rapidly at $300^\circ C$ for 1 hour. The prepared samples were examined by x-ray diffraction (XRD) for distinguishing the glassy states. The FTIR absorption spectra of the prepared glasses in KBr matrix were recorded on a SHIMADZU-8300 FTIR spectrophotometer at room temperature. The produced glasses were thoroughly grounded and mixed with equal ratio of KBr. The pellets were clean and uniform. The FTIR absorption spectra of the prepared glasses as a bulk were recorded as shown in figure (1).

3. Result and Discussion

The FTIR spectra of the glasses have been studied together with the spectra for crystalline TeO_2 , which are presented in figures (1) and (2). By comparing the present spectra of the glasses with their crystalline constituents [10], it has been found that most of the sharp bands characteristic of the crystalline TeO_2 were disappeared in figures (1) and (2). The bands have broadened and shifted slightly ongoing from the crystalline to the amorphous (glassy) state, while new bands have appeared by the addition of MoO_3 oxide.

Figure (1) shows the FTIR spectra of the glasses as a bulk. It shows a broad band corresponding in the OH stretching (ν_{OH}) at 3143 cm^{-1} for pure TeO_2 . This band may be due to presence of the inclusion of water molecules in the pores.

The most diagnostic peaks have been shown in Table (1). Figure (2) shows the FTIR spectra of the glass system with KBr in pellet form. The main infrared band at 625 cm^{-1} which is attributed to symmetrical stretching vibration of Te-O_{ax} bonds in the deformed TeO_4 units. By analogy with the crystalline TeO_2 , it may be concluded that the maximum do belong to deformed TeO_4 groups. Dimitriva *et. al* [6] concluded that glasses containing symmetric TeO_4 groups equivalent to maximum at 670 cm^{-1} and shoulder at 635 cm^{-1} , while glass containing deformed trigonal bipyramid for TeO_4 groups corresponded to a shoulder at 670 cm^{-1} (which we could not find in the present study) and maximum at 635 cm^{-1} .

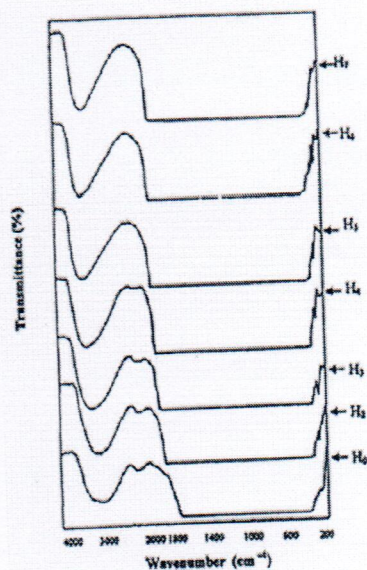


Fig. (1): FTIR spectra of glasses in $\text{TeO}_2\text{-MoO}_3$ system as a bulk

Adding MoO_3 to the tellurite glass, the maximum was shifted slightly to higher wavenumber as we increased the modifier content. This is due to changes of coordination state of tellurium atom from TeO_4 through TeO_{3+1} to TeO_3 with bond breakage between tellurium (Te) and axial oxygen (O_{ax}) as we increased the modifier atoms [8] (the notation TeO_{3+1} means that there are three short Te-O bonds and a comparatively longer Te-O bond in the TeO_{3+1} polyhedra) [9].

Table (1) The absorption bands of FTIR spectra for $\text{TeO}_2\text{-MoO}_3$ systems [16,18]

Sample No. and Glass System	Infrared absorption band position (cm^{-1})										
TeO_2 (crystal)[16][18]	-	270	350 [16]	-	-	580	660	771	-	-	-
TeO_2 (glass) [18]	-	-	340	-	-	-	640	740	-	-	-
H0 TeO_2 glass	-	268	350	-	-	-	625	-	-	-	3143.8
H2 $(\text{TeO}_2)_{90} - \text{MoO}_3(10)$	216	262.3	345	365	-	-	625	-	-	-	3200
H3 $(\text{TeO}_2)_{80} - \text{MoO}_3(20)$	214	264	340.6	370	-	-	630	-	840	930	3260
H4 $(\text{TeO}_2)_{70} - \text{MoO}_3(30)$	214	264	341	369	-	-	635	-	855	935	3300
H5 $(\text{TeO}_2)_{60} - \text{MoO}_3(40)$	214	268.1	339	372	-	-	635	-	864	940	3300
H6 $(\text{TeO}_2)_{50} - \text{MoO}_3(50)$	214	264	329	372	-	-	640	-	870	950	3300
H7 $(\text{TeO}_2)_{45} - \text{MoO}_3(55)$	214	260	325	372	-	-	648	-	880	960	3300

Actual tellurite glasses are made up of not only one structural unit but the mixture of TeO_4 , TeO_{3+1} and or TeO_3 [7,9]. This is due to the local inhomogeneity. The electrons do not transfer from the modifier atom to all the structural units, and consequently two or more states of the structural unit exist in the actual tellurite glasses. Mochida *et. al* [11] found with the aid of IR spectra and according to Yakhkind [12] that the number of TeO_{3+1} group is stimulates modified oxides. New appearance of the maximum at 840 cm^{-1} as the MoO_3 content increases above 20%wt. is an indication of the growing role of complexes in the

formation of the network. This maximum shifts to higher wavenumber as the content of modified oxide (MoO_3) increases. The new shoulder appearing at 930 cm^{-1} can be related to the presence of short, isolated Mo=O bond [13].

In tellurite glasses, however, the modifier atoms play one important role, causing the variation of the structural unit itself. It is in contrast with the structural unit of silicate glasses (a SiO_4 tetrahedron which is not affected by modifier atoms) [8]. So, as the MoO_3 content increases all the Te-O-Te bonds will be attacked and the number of Te-O-Mo bridging bonds will increase without a direct attack

on the isolated Mo=O bonds [8]. A similar mechanism has been suggested for glasses of the TeO₂-V₂O₅ system in which a bond corresponding to V=O vibrations is found at 975 cm⁻¹ [14]. The maximum at 840 cm⁻¹ could be attributed to the stretching vibration modes of equatorial bonds of Mo-O [13].

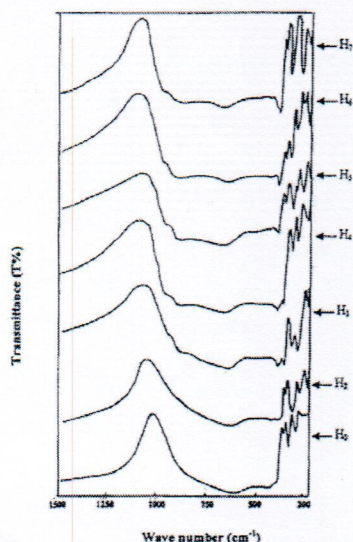


Fig. (2): FTIR spectra of glasses in TeO₂-MoO₃ system with KBr in pellet form

4. Conclusion

New peaks at (389-372) cm⁻¹ have been observed by FTIR spectra, their sources have not clearly been identified but Cheremisinov and Zlomanov [15], from their analysis by Raman spectrum of TeO₂ [both crystalline and amorphous], suggested that these peaks are related to various modes of TeO₄ units and are not connected to the formation of TeO₃ pyramids.

We suggest that they may be due to the various modes of TeO₃₊₁ units. The increase in the intensity of these peaks with the addition of MoO₃ gives a supports to the above suggestion. Two other peaks of 350 cm⁻¹ and 268 cm⁻¹ have been noticed in all studied TeO₂ glass systems and the maxima at 350 cm⁻¹ and 268 cm⁻¹ were noticed as well in the crystalline TeO₂ [16]. This means that they all belong to Te-O modes of vibration.

A maximum at about 216-214 cm⁻¹, which appeared by adding MoO₃, may be due to non-bridging oxygen atoms, which is confirmed to be exist in the structure by Nevo et al. [9] for TeO₂-

Fe₂O₃ glasses. Jong Heo et al. [17] suggest the presence of non-bridging oxygen atoms in Li₂O-TeO₂ and Na₂O-TeO₃ systems and this is confirmed by Sekiya et al. [7] on alkali tellurite glasses.

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