JOURNAL OF MATERIALS SCIENCE 18 (1983) 1353–1358

IR spectra and structures of tellurite glasses

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It is shown with IR spectral investigations that the short range order of certain tellurite glasses, obtained from monomineral crystalline phases, is similar to that of the crystals. They may contain the following polyhedra: TeO_4-trigonal bipyramids (C_{2v} symmetry), deformed TeO_4 groups, TeO_3 trigonal pyramids (C_{3v} point symmetry), or combinations of these polyhedra. The introduction of V_2O_5 and MoO_3 in the binary glasses leads to a $TeO_4 \rightarrow TeO_3$ transition. MoO_3 delays the decay of TeO_4 groups in a wider concentration range.

1. Introduction

Infrared (IR) spectra of vitreous tellurites and a series of glasses of the TeO_2–V_2O_5 and TeO_2–MoO_3 binary systems are the subjects of the present paper which is a continuation of the previous investigations on the crystals [1]. The purpose is to interpret glass structure by IR spectroscopy. The vibrational spectra may be used to identify variation of the bond distances and the effect of environment on the structural units. Some new results are recently reported in this field [2–6], especially for tellurite glasses.

2. Experimental details

The monomineral phases TeO_2, $NaVTeO_5$, Te_2MoO_7, $TiTe_3O_8$, $ZrTe_3O_8$, $BaTeO_3$, $LiVTeO_5$, $TeVO_4$, $Te_2V_2O_9$, $Te_3Nb_2O_{11}$, $ZnTe_3O_8$ were obtained by the manner described in [1]. They were vitrified by melting and the melts were rapidly quenched with the aid of a roller technique. The IR spectra were taken on samples in nujol with a UR-10 Carl Zeiss Jena spectrophotometer in the 1200 to 400 cm^{-1} range (1200 to 700 cm^{-1}, NaCl prism, 700 to 400 cm^{-1}, KBr prism).

3. Results and discussion

The IR spectra of the tellurite phases in crystalline and vitreous states are given in Figs. 1 to 4. The main absorption frequencies in the 800 to 400 cm^{-1} range are assigned to stretching vibrations of the Te–O bonds. The typical broadening of the bands is observed in the spectra of the glasses. In most cases they are similar to the spectra of the crystalline phases, which is direct proof for the similarities of the structural units and of the short range order. For this reason, interpretations of tellurite glass spectra are based on conclusions, drawn for their crystalline phases. As mentioned earlier [1], according to an assumption in vibrational spectroscopy of the solid-state [7–10], the vibrations of a specific group of atoms in a lattice may be regarded as relatively independent from motions of the rest of the atoms. The concept of separate vibrations for glasses is discussed in detail for the first time in the work of Tarte [8]. A similar approximation is used in the present investigation. This empirical analysis can give some useful information concerning the arrangement of atoms in glasses.

The Te–O vibrations of crystalline tellurites, built up by TeO_3-groups, may be examined on the basis of C_{3v} point symmetry. The vibrations of tellurites and of α-TeO_2, built up by TeO_4 groups, may be examined from a viewpoint of C_{2v} point symmetry [1]. In the first case, the Te–O bonds are characterized by two bands for $\nu^{S}_{TeO_3}$ and $\nu^{d}_{TeO_3}$ vibrations. The appearance of a new band in the 700 to 580 cm^{-1} range is due to the decrease in polyhedra symmetry to C_s or C_1 which is the result of the break down of the

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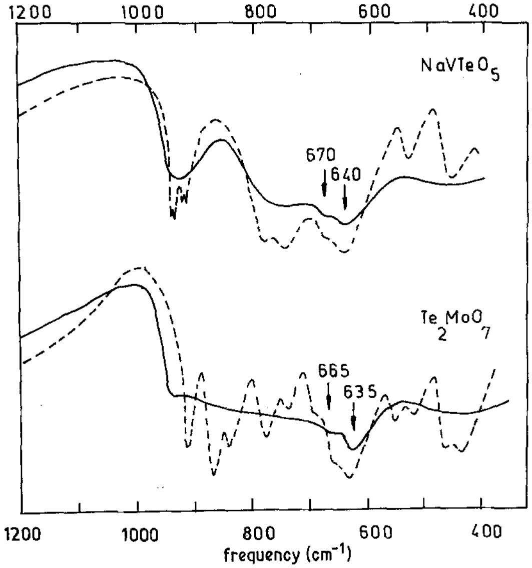

Figure 1 Infrared spectra of glasses (——) and crystalline phases (– – –) of $NaVTeO_5$ and Te_2MoO_7.

degeneracy of the ν^d modes. Tellurites, containing TeO_4 groups have four bands for ν^s_{eq}, ν^{as}_{eq}, ν^{as}_{ax} and ν^S_{ax} modes. The stretching frequencies in the IR spectrum of crystalline TeO_2 are assigned in the following manner [1]:

$$\nu_1(A_1) \equiv \nu^S_{TeO_2eq} = 780\,\mathrm{cm}^{-1}$$

$$\nu_8(B_1) \equiv \nu^{as}_{TeO_2eq} = 714\,\mathrm{cm}^{-1}$$

$$\nu_6(B_2) \equiv \nu^{as}_{TeO_2ax} = 675\,\mathrm{cm}^{-1}$$

$$\nu_2(A_1) \equiv \nu^S_{TeO_2ax} = 635\,\mathrm{cm}^{-1}$$

In the pure TeO_2 glass the bond at $635\,\mathrm{cm}^{-1}$ increases markedly and becomes a determining one (Fig. 5). The rise in the $\nu^S_{TeO_2ax}$ intensity is the result of a decrease in symmetry.

It is assumed that this is the result of the particular structure of the trigonal bipyramids of the TeO_4 groups and the presence of a free electron pair in one of the bonding positions [11–13]. As stated earlier [6], the appearance of repulsive forces in this zone is the cause for the difficult vitrification of pure TeO_2. It is clear that beyond the existence of an average deformation of the network and long range disorder [14–16] in the glass, an additional deformation and change in some of the Te–O distances is established in separate TeO_4 polyhedra during the glass formation. This is fixed as an inversion of the intensity of the bands in the IR spectra (Fig. 5).

By analogy with the crystalline tellurites [11] it may be accepted that with the introduction of other oxides in the tellurite glass, the new structural arrangement on the back side of the four coordinated tellurium ions favours the stronger polarizability of the free electron pair in certain directions. As a result, part of the TeO_4 groups are transformed into TeO_3.

The comparison of the IR spectra (Figs. 1 to 5) indicates that vitreous tellurites may be divided into several groups.

Tellurite glasses which are characterized by an intensive maximum at 640 to $635\,\mathrm{cm}^{-1}$ and a shoulder at about 670 to $660\,\mathrm{cm}^{-1}$ possess deformed TeO_4 groups. These are the glasses

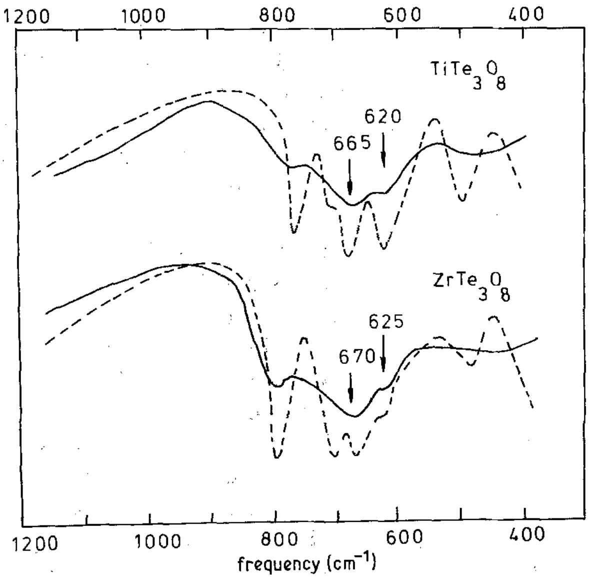

Figure 2 Infrared spectra of glasses (——) and crystalline phases (– – –) of $TiTe_3O_8$ and $ZrTe_3O_8$.

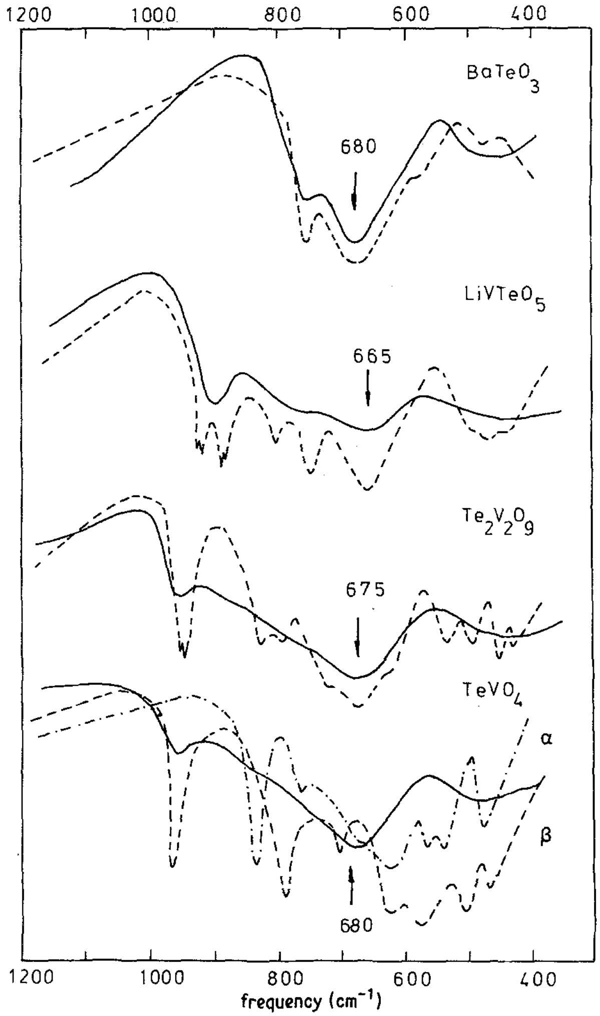

Figure 3 Infrared spectra of glasses (——) and crystalline phases (– – –) of $BaTeO_3$, $Te_2V_2O_9$, $LiVTeO_5$ and $TeVO_4$.

obtained from TeO_2, $NaVTeO_5$ and Te_2MoO_7 (Fig. 1).

The second group of tellurite glasses is characterized by the presence of an intense maximum at 670 to 665 cm^{-1} and a shoulder at 625 to 620 cm^{-1} (Fig. 2). The elementary structural polyhedron is the TeO_4 group which should be more symmetrical and should correspond to a C_{2v} point symmetry. Typical examples are $TiTe_3O_8$ and $ZrTe_3O_8$.

The spectra of the third group of glasses (Fig. 3) to which $BaTeO_3$, TeV_2O_9, $LiVTeO_3$ and $TeVO_4$ are referred, are characterized by an intense band in the 680 to 665 cm^{-1} range. It follows from the similarity between the spectra of vitreous and crystalline $BaTeO_3$ and $LiVTeO_5$ that their glasses are built up by symmetrical TeO_3 groups.

The vitreous $TeVO_4$ have a spectrum different from the spectra of both crystalline modifications. As far as the tellurium coordination is concerned. it is closer to that of α-$TeVO_4$. The almost symmetrical band at 690 cm^{-1} indicates that the structure of the TeO_3 polyhedra in the glass is more symmetrical than in α-$TeVO_4$. The existence of the threefold coordinated tellurium in this glass is established also by X-ray structural analysis [17].

According to a model [15, 16] developed on the basis of X-ray investigations, the bridge Te–O–Te bonds are broken in the $Te_2V_2O_9$ glass and two TeO_3 groups are formed. They are linked independently by separate vanadate chains. The presence of a weak shoulder at about 635 cm^{-1} in the spectra of $Te_2V_2O_9$ glass means that its TeO_3 groups have some deformation.

The $Te_3Nb_2O_{12}$ and $CuTeO_3$ glasses are placed in a separate group because their spectra are similar to those of their crystalline phases (Fig. 4). It may be assumed that different tellurite polyhedra are

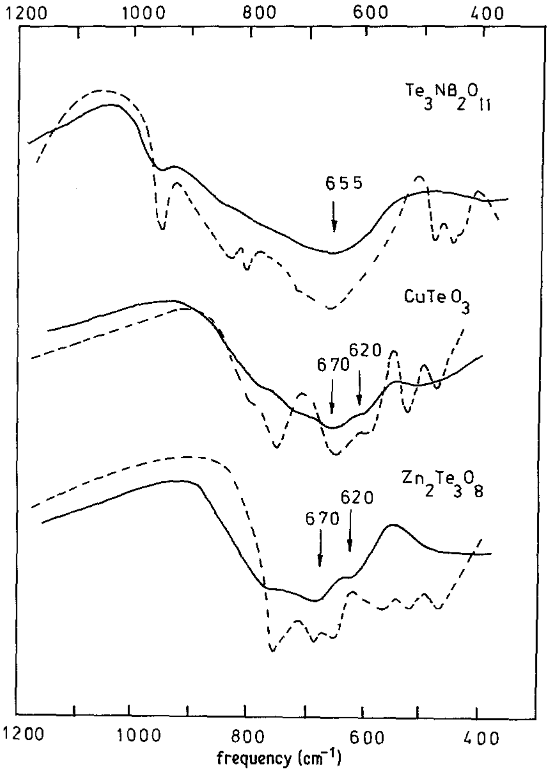

Figure 4 Infrared spectra of glasses (——) and crystalline phases (– – –) of $Te_3Nb_2O_{11}$, $CuTeO_3$ and $Zn_2Te_3O_8$.

simultaneously formed in these glasses as in the crystals [1]. The $Zn_2Te_3O_8$ glass could be added to this group. Its spectrum differs from that of the crystalline phase, yet it is similar to the spectrum of the vitreous $CuTeO_3$. It follows from the comparison made that when the $Zn_2Te_3O_8$ is vitrified, the content of the TeO_3 groups is raised which agrees with the results obtained by [3] for the system TeO_2–ZnO.

In addition, a band at 780 cm^{-1} is recorded in the spectra of all glasses investigated, which is due to the $\nu^{S}_{TeO_{2eq}}$ vibrations of the TeO_4 groups or to $\nu^{S}_{TeO_3}$ vibrations of the TeO_3 groups. The intensity of the band markedly decreases in the spectra of the glasses. It may be used as an additional test to show whether the samples are indeed in the vitreous state.

By the way, it is difficult spectroscopically to determine whether a given glass is built up by symmetrical TeO_4 groups or asymmetrical TeO_3 without any additional information. The tendency for the transition of tellurium (IV) ions from one into another coordination may be detected successfully by the changes in the compositions of a system.

According to Yakhkind [2] with the increase in the content of modified oxides, the formation of TeO_{3+1} groups is stimulated. Moshida *et al.* [3] find with the aid of the IR spectra that the number of TeO_{3+1} groups is stimulated. Mochida *et al.* [3] M_2O and after 20 mol% MO.

A similar tendency is evident in our experiments in spite that atypical modifiers were introduced, but only oxides such as V_2O_5 and MoO_3 favour the glass formation. Earlier the same vitreous systems [4, 6] were investigated mainly in relation to V–O and Mo–O characteristic vibrations. It is seen that the introduction of V_2O_5 (Fig. 6) causes a rise in the bond intensity at 680 cm^{-1}, at the expense of the band at 635 cm^{-1}. As they are not well resolved, they may be viewed formally as one very broad vibration band whose maximum shifts to 685 cm^{-1} with the change in the compositions to 80 mol% V_2O_5. This "movement" may be related to a quantitative effect of TeO_3 group

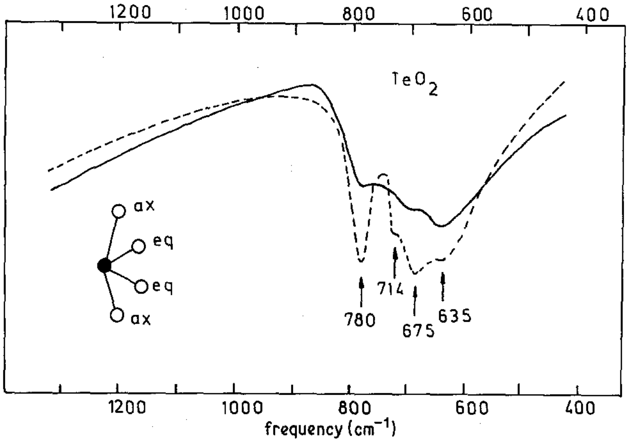

Figure 5 Infrared spectra of glass (——) and crystalline phase (– – –) of TeO_2.

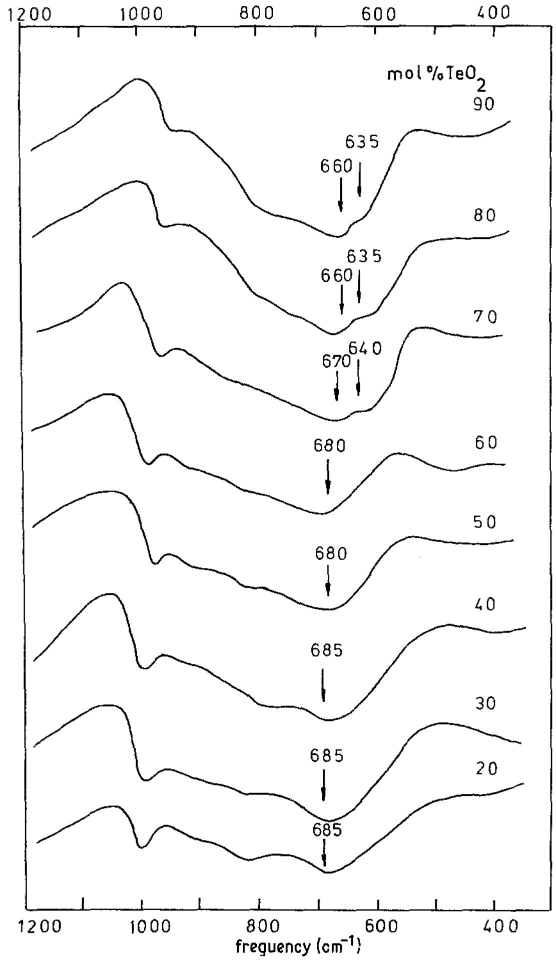

Figure 6 Infrared spectra of glasses in TeO_2–V_2O_5 system.

accumulation and a decrease in the number of TeO_4 groups in the glass. The same results have been obtained by X-ray structural investigations [16].

The spectra of the glasses in the TeO_2–MoO_3 system up to 40 mol% MoO_3 (Fig. 7) does not indicate a significant change in the place and intensity of the band at 640 to 635 cm^{-1}. Therefore, the deformed TeO_4 groups are preserved in a wide concentration range. As is shown in [6], after this composition, these groups begin to decay. It is namely for this reason that a band, reaching 675 cm^{-1} at 80 mol% of MoO_3 is observed in the spectra of the glasses.

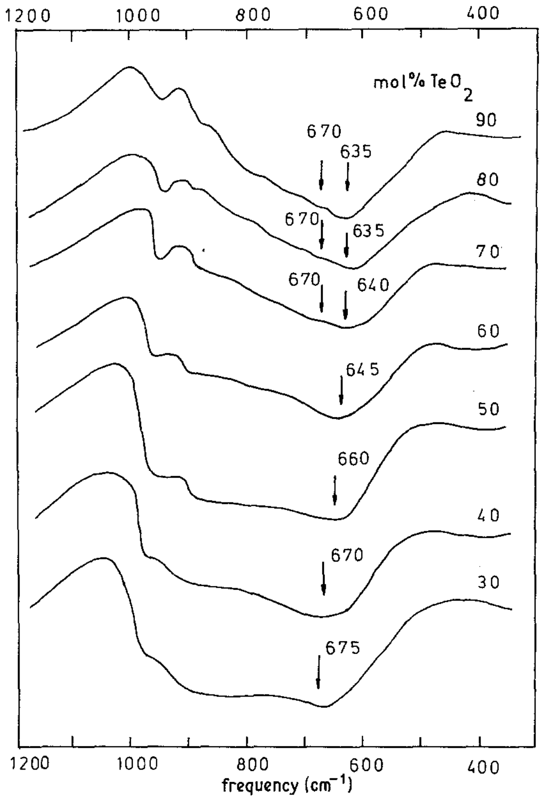

Figure 7 Infrared spectra of glasses in TeO_2–MoO_3 system.

4. Conclusion

1. Symmetrical TeO_3 groups dominate in the case where the bands in the 700 to 670 cm^{-1} range are most intensive in the IR spectra. The detection of a shoulder in the 640 to 630 cm^{-1} range is due to the decrease in the symmetry of the TeO_3 groups.

2. Glasses, containing symmetric TeO_4 groups, are characterized by a maximum at 670 cm^{-1} and a shoulder at 635 cm^{-1}.

3. Glasses, built up by deformed TeO_4 groups have intense bands in the range of about 640 to 635 cm^{-1} and a shoulder at about 670 cm^{-1}.

The introduction of V_2O_5 and MoO_3 in the binary glasses leads to a TeO_4 → TeO_3 transition.

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Received 19 May
and accepted 29 September 1982