DSC and FTIR Spectra of Tellurite-Vanadate Glasses Containing Molybdenum

Dariush Souri

Department of Physics, Faculty of Science, Malayer University, Malayer, Iran

Abstract: The ternary TeO_2-V_2O_5-MoO_3 amorphous samples of compositions in the range (0-60) mol% MoO_3 with constant amount of TeO_2 equal to 40 mol% have been prepared by melt quenching technique. FTIR spectra of pure TeO_2, V_2O_5, MoO_3 powders and TeO_2-V_2O_5-MoO_3 glass system were taken. The absorption bands in the FTIR spectra of theses glasses are not characteristics of the mere oxide mixture, thus a chemical interaction between the three oxide materials. The similarity between the FTIR spectra of all glasses indicates a similarity in the network of these glasses and it is suggested that the glass structure is continuous tellurite network with vanadate and molybdate discontinuous. Also, the experimental DSC curves of mentioned glass systems have been investigated. The composition dependence of glass transition temperature implies a decrease in the rigidity of the network with increasing of V_2O_5 content.
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Key words: Differential scanning calorimetry · Fourier transform infra-red spectroscopy · Amorphous semiconductor · Glasses

INTRODUCTION

Oxide and chalcogenide glasses have been investigated by a number of authors for their optical and/or electrical [1-16] properties. Tellurite glasses posses interesting glass-forming ability, glass structure, no hygroscopic properties and low melting point [17-18]. Previous studies on vanadate tellurite glasses such as TeO_2-V_2O_5 [14, 19], TeO_2-V_2O_5-MoO_3[20, 21] showed that they are semiconducting glasses and they switch when a high electric field is applied; also some optical properties such as optical band gap energy and width of the tail of localized states of TeO_2-V_2O_5-MoO_3 glasses have been evaluated using UV-Visible absorption spectra in the range 190-1100 nm [16]. On the other hand, chemical and electrochemical lithium intercalations have been performed on TeO_2-V_2O_5 and TeO_2-V_2O_5-MoO_3, showing that V_2O_5-based glasses are suitable positive electrode materials for lithium batteries [22, 23]. Due to technological advantages in the fields of thermoelectric power applications [24], micro-electronics and display systems, the transition metal oxide semiconductors have attracted the attention of researchers during the last few years. MoO_3 is one of those oxide semiconductors with vast potential in developing passive alphanumeric displays, micro-batteries [13], gas sensors, memory

devices and optical smart windows, because MoO_3 in orthorhombic phase has a unique two-dimensional layered structure [25]. Change in glass composition affect the induced optical absorption due to several reasons namely, the polarization power of network formers, modifiers, their coordination numbers, the concentration of non-bridging oxygen, the presence of multivalent network forming and modifying ions. These effects have been extensively described in the literature [14, 26-28]. As mentioned before, TeO_2 is a glass network former and can form glasses containing non-transition metal oxides [29] and transition metal oxides [13, 14, 16, 18,30]. Several authors have reported the structural information of oxide glasses such as TeO_2-glass [31], TeO_2-MoO_3 [13], TeO_2-V_2O_5[13, 29, 31, 32], TeO_2-V_2O_5-Sm_2O3 [14] and V_2O_5-B_2O_3 [30], therefore not TeO_2-V_2O_5-MoO_3.

It was reported earlier [31] that pure tellurite glasses have an IR absorption band at 640 cm^{-1} which attributed to TeO_4 tetragonal pyramids. This band shifted from 640 to 650-680 cm^{-1} on adding variable amount of MoO_3 to pure TeO_2 from 0 to 70 mol% [13]. On the other hand, it shifted from 640 to 665-680 cm^{-1} on adding variable amount of V_2O_5 from 0 to 50 mol% [31] and it has been demonstrated that 665-680 cm^{-1} IR absorption band is a associated to TeO_3 trigonal pyramids with non-bridging oxygen [14, 31]. Thus, the first purpose of this paper is to

Corresponding Author: Dariush Souri, Department of Physics, Faculty of Science, Malayer University, Malayer, Iran

obtain the FTIR spectra of the ternary TeO_2-V_2O_5-MoO_3 glass system and to determine the absorption band shifts and structural units of these glasses in the presence of two transition metal oxides V_2O_5 and MoO_3. Second purpose of this paper is to determine the glass transition temperature from DSC curves and to study the variation of glass transition.

Experimental Procedure: The ternary $40TeO_2$-$(60-x)V_2O_5$-$xMoO_3$ glass systems (x=0,10,20,30,40,50 and 60 mol%; hereafter, termed as TVM00, TVM10, TVM20, TVM30, TVM40, TVM50, TVM60, respectively) were prepared by well dry mixing of 25gr batches of the high purity oxide powders V_2O_5 (MERCK, 99.99% pure), MoO_3 (MERCK, 99.99% pure) and TeO_2 (MERCK, 99.99% pure) as starting raw materials in a mortar for 15 min. Appropriate amounts of oxide powders was weighed using a precise balance having an accuracy of 0.1 mg. Then, the mixture was preheated in atmospheric condition at 400 °C for 30 min in order to dehydration and was melted in porcelain crucible in the temperature range 600-780 °C for 0.5 h, depending on the composition, in an electric furnace (Shimifan F.47) in air; where the melt was mixed up after every 5 min to prevent the separation of the three components. The melt was poured on to a polished steal mould and immediately pressed by another polished steel block (press-melt quenching method), where the blocks were kept at room temperature. All of the produced glass bulk samples were annealed at 150°C for 2 hours to eliminate the mechanical stresses resulting from the quenching [20]. The characterization of the glass samples was performed by x-ray diffraction (XRD) studies using (SEIFERT analyzer Cu K_α radiation, model 3003).

The FTIR absorption spectra of the produced glass samples were recorded at room temperature on a ABB-Bomem single beam MB spectrometer (model MB104, made in Canada) over a spectral range of 500-6500 cm^{-1} with resolution of 4 cm^{-1}. First, discs of KBr, 1 cm in diameter, were prepared by pressing and their infrared absorption spectra measured, showed transparency to light. Then, potassium bromide (KBr)-glass pressed powder pellets were used at 1:30 volume ratio of glass to KBr (preparation of pellets with high IR transmission) to collect the IR spectra and using these results, we able to determine structural units.

The glass transition temperature T_g, was determined from the change of the base line in the DSC charts obtained for each sample on DSC (PL-England). All measurements were carried out in N_2 medium with about 28 mg sample placed in a platinum crucible. The temperature range was from 20 to 400 °C with heating rate of 20 °C /min. the reference sample was Al_2O_3.

RESULTS AND DISCUSSION

X-ray Characterization: X-ray diffraction characterizations were carried out on the different obtained samples which showed the characteristic diffraction patterns of amorphous materials evidencing no crystal structure (Figure 1).

Differential Scanning Calorimetry (DSC): Figure 2 shows the DSC charts obtained for the TeO_2-V_2O_5-MoO_3 glass-system; for better clarity of the plots, DSC charts of the glasses has been plotted in two charts.
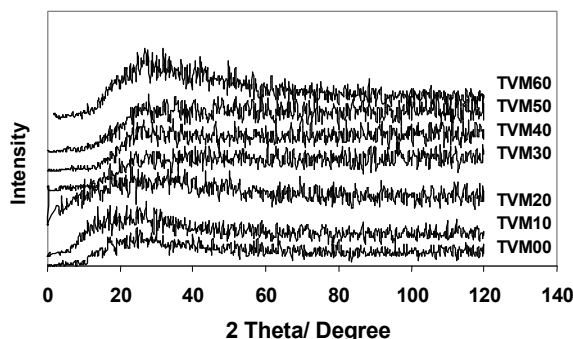

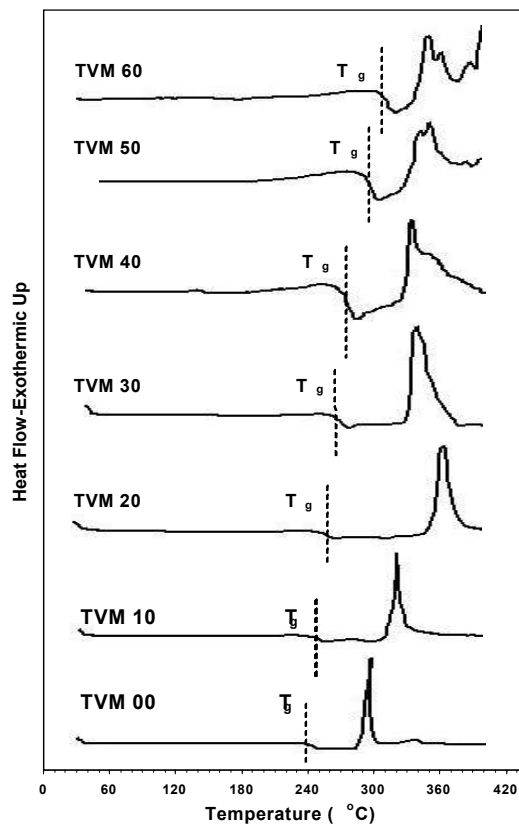Fig. 1: XRD patterns of TVMx glasses for different molar composition ratios

Fig. 2: DSC curves of the ternary TVMx glasses

Table 1: The density and DSC data for TeO$_2$-V$_2$O$_5$-MoO$_3$ glass system

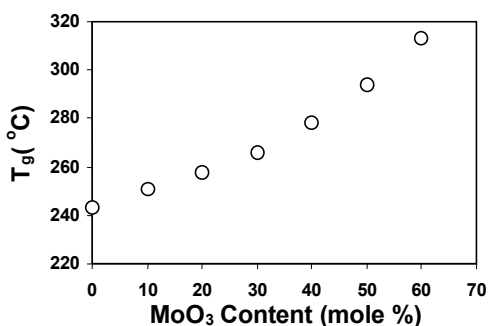| *Glass*	T_g *(°C)*	T_{cr} *(°C)*	$ñ (gr\ cm^{-3})$ *[16]*
TeO$_2$-glass	222 [30]	-	-
TVM00	243	293	3.857
TVM10	251	322	3.880
TVM20	258	364	4.053
TVM30	266	337	4.209
TVM40	278	335	4.394
TVM50	294	343	4.596
TVM60	313	350	4.895

Fig. 3: Variation of glass transition temperature with composition for TVMx glasses

The DSC curves for the glasses show a glass transition correspond to temperature T_g that we usually just take the middle of the incline to be the T_g. This transition is followed by one exothermic peak corresponding to crystallization temperature T_{cr}; in other word DSC measurements show a pronounced crystallization exotherm after the glass transition temperature indicating the glassy nature of the materials at temperature below the glass transition. The data of T_g, T_{cr} and the glass density ñ are presented in Table 1.

Figure 3 shows the Variation of the glass transition temperature with MoO$_3$ Content in the TeO$_2$-V$_2$O$_5$-MoO$_3$ glass system. From the Figure, one sees that the glass transition temperature is very sensitive to the MoO$_3$ concentrations. The addition of MoO$_3$ to vitreous TeO$_2$-V$_2$O$_5$ from 0 to 60 mol% results in a regular increase of T_g from 243 to 313 °C. This result suggests that the glass structure remains almost constant as could be seen from FTIR spectra in the next subsection; such a result was reported also for vanadium tellurite blown film glasses [31].

Decreasing of T_g can be interpreted as decreasing of the thermal stability of the glass. The thermal stability of the glass is a result of the glass structure; in other word, in this work, the change in T_g indicates a change related to the manner in which V$_2$O$_5$ and MoO$_3$ get arranged in
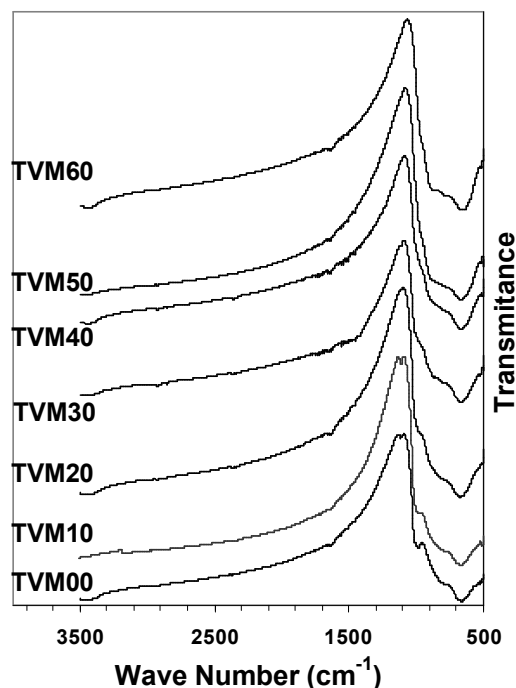

Fig. 4: FTIR spectra for TVMx glasses; see Table2

the glass. The thermally stable glasses will have close packed structure, while the unstable glasses will have loose packed structure [33]. Thus the addition of MoO$_3$ increases the stability of the glass and the rigidity of the network, which is in agreement with the data of the glass density (criteria of packing).

FTIR Analysis: The structure of the glasses was also studied using FTIR analysis in the wave number range 500-3500 cm^{-1}. There are no characteristic absorption bands in the range 1100-3500 cm^{-1}, only shallow oscillations due to interference effects in the glass. Figure 4 shows FTIR spectra of 40TeO$_2$-(60-x) V$_2$O$_5$-x MoO$_3$ glasses in the range 500-3500 cm^{-1}. For comparison, the spectra of KBr pellets individual pure powders are also shown in Figure 5.

Table 2: Observed FTIR absorption bands in the ternary TVNx glass systems besides the E_{opt} and E_e.

Glass	FTIR absorption bands (cm^{-1})	E_{opt} (eV) [16]	E_e(eV) [16]
TeO$_2$-glass	-640---	-	-
TVM00	524 677 100 1122 1643	1.7	0.892
TVM10	507 678 993 1116 1635	1.9	0.303
TVM20	536 682 975-1649	2	0313
TVM30	524 675 879 1122 1650	2.17	0.292
TVM40	522 675 852-1652	2.25	0.374
TVM50	524 675 885-1656	2.55	0.463
TVM60	524 665 881-1647	2.85	0.356
Pure V$_2$O$_5$ powder	588-831 1024-	-	-
Pure TeO$_2$ powder	-677 775--	-	-
Pure MoO$_3$ powder	--823 1001-	-	-
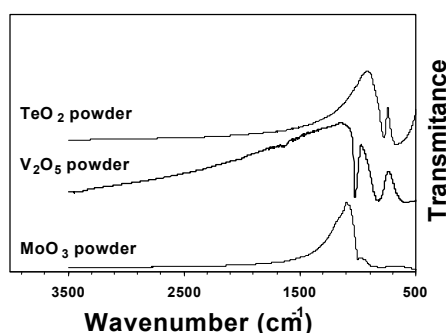
Fig. 5: FTIR spectra of pure TeO$_2$, V$_2$O$_5$ and MoO$_3$ powders.

Comparison of the absorption bands of all the ternary glass systems and individual oxide powders reveal that, the FTIR spectra of the glass systems are not characteristics of a mixture of the three oxides. We suggest that, this property of the spectra indicates a chemical interaction between the three oxides [13]. The similarity between the FTIR spectra of all glasses indicates a similarity in their networks. In compare with the results obtained previously [13, 18, 31], we suggest that the glass structure is continuous tellurite network with vanadate and molybdate discontinuous. The absorption band in pure tellurium oxide powder is at 677 cm^{-1}. During the addition of other oxides and making glasses, this band changes to a shoulder (655-682 cm^{-1}). Also pure tellurite glasses have an IR absorption band at 640 cm^{-1} which is attributed to TeO$_4$ tetragonal pyramids [14, 31, 33]. The major observed absorption bands in the ternary TeO$_2$-V$_2$O$_5$-MoO$_3$ glass system are summarized in Table 2 as well as some optical properties such as optical band gap energy E_{opt} and width of the tail of localized states from our previous work [16].

It is clear from Figure 4 and Table 2 that the 640 cm^{-1} which is characteristics of pure TeO$_2$ glass, changes to a broad band and shifts from 640 to 665-678 cm^{-1} on addition of V$_2$O$_5$ and MoO$_3$. Dimitriev *et al.* [29, 32] attributed this absorption band, 665-680 cm^{-1}, to TeO$_3$ trigonal pyramids. The weakness of this band may be due to decrease of the amount of 4-coordinate tellurium in the studied glasses. It is suggested that the 3-coordinated Te may become significant with increasing the concentration of V$_2$O$_5$. In the TeO$_2$ glasses containing 60 mol% V$_2$O$_5$, a new band is observed at 1000 cm^{-1}, which shifts to lower wave numbers with decreasing the concentration of V$_2$O$_5$. This band is combined with one of the characteristic bands of pure MoO$_3$. This peak is probably attributed to V=O band of VO$_5$ group [14, 18, 32]. So, in contrast to Dimitriev observation, its intensity does not significant frequency and is due to the presence of V^{5+} ions; these ions have coordinated by five oxygen. The VO$_5$ fragments may be attached to other metal ions via V=O double bonds or V-O single bonds.

Chopra *et al* [14] reported that the intensity of the band decreases with decreasing the V^{5+} ions and increasing V^{4+} ions (increasing of V^{4+}/V$_{tot}$ fraction).

Also, the peak shifts to lower wave number with decreasing the content of V$_2$O$_5$. Such lowering in stretching frequency may be the second reason of the observation of the new band at about 1000 cm^{-1}, which shifts to lower wave numbers.

Addition of other transition metal ions besides V$_2$O$_5$ in TeO$_2$ glass, cause another complex situation in the spectra. Oxygen deficiency and the presence of V^{4+} in the mixed oxides lead to the simultaneous formation of VO$_6$ and VO$_5$ polyhedra with several short V-O bonds. This is probably, the reason for a new shoulder observed at about 1120 cm^{-1} for TVM00 and TVM10.

The absorption band at 879-885 cm^{-1} arises due to MoO$_4$ tetrahedra [13]. For TVM30, TVM40, TVM50 and TVM60 glasses, this band become stronger with increasing of MoO$_3$ content. Therefore, it is suggested that the similarity between the IR spectra of all glasses

indicates a similarity in the network of these samples, namely continuous tellurite network with vanadate and molybdate discontinuous. The mentioned behavior of theses glasses occur due to mixed effect of V_2O_5 and MoO_3 as modifiers.

CONCLUSION

FTIR spectra of pure TeO_2, V_2O_5, MoO_3 powders and TeO_2-V_2O_5-MoO_3 glass system were taken. The absorption bands in the FTIR spectra of theses glasses are not characteristics of the mere oxide mixture, thus a chemical interaction between the three oxide materials. it is suggested that the similarity between the IR spectra of all glasses indicates a similarity in the network of these samples, namely continuous tellurite network with vanadate and molybdate discontinuous. The mentioned behavior of theses glasses occur due to mixed effect of V_2O_5 and MoO_3 as modifiers. Also, the experimental DSC curves of mentioned glass systems have been investigated. The composition dependence of glass transition temperature implies a decrease in the rigidity of the network with increasing of V_2O_5 content.

REFERENCES

1. Shamim, A., K.M. Khan, A. Ahmad, M. Suleman, A. Mateen and A. Naseem, 1989. Int. J. Electron., 67(2): 235-242.
2. Hosseini, A.A. and C.A. Hogarth, 1999. J. Sci. I.R. Iran, 10(2): 136-142.
3. Hosseini, A.A., C.A. Hogarth and J. Beynon, 1994. J. Materials Sci. Lett., 13: 1144-1145.
4. Hosseini, A.A., J. Beynon and C.A. Hogarth, 1994. Int. J. Electron., 76(5): 907-911.
5. J.Al-Ani, S.K. and C.A. Hogarth, 1985. Int. J. Electron., 58(1): 123-131.
6. J. Al-Ani, S.K., 1993. Int. J. Electronics, 75(6): 1153-1163.
7. Arekat, S.R., 1998. Journal of Non-Crystalline Solids, 224: 201-204.
8. Auran, P. and A.G. Vedeshwar, 1997. Journal of Non-Crystalline Solids, 220: 63-68.
9. El-Naggar, A.M., 2001. Optics and Laser Technol., 33: 237-242.
10. Tanaka, K., N. Toyosawa and H. Hosono, 1999. Journal of Non-Crystalline Solids, 224: 43-49.
11. Othman, A.A., 2001. Radiation Physics and Chemistry 61: 563-565.
12. Mehra, R.M., J. Baveja, L.P. Purohit, R. Kumar, A.V. Singh, P.C. Mathur and P.C. Taylor, 2000. Journal of Non-Crystalline Solids, 266-269: 708-712.
13. Pal, M., Y. Tsujigami, A. Yoshikado and H. Sakata, 2000. Phys. Stat. Sol., (a) 182: 727.
14. Chopra, N., A. Mansingh and G.K. Chadha, 1990. Journal of Non-Crystalline Solids, 126: 194-201.
15. Gonz-alez-Leal, J.M., R. Prieto-Alc-on, J.A. Angel, E. M_arquez, 2003. Journal of Non Crystalline Solids, 315: 134-143.
16. Elahi, M. And D. Souri, 2006. Indian Journal of Pure and Applied Physics, 44.
17. Sidkey, M.A., A. Abd El-Moneim and L. Abd El-Latif, 1999. Materials Chemistry and Physics, 61: 103-109.
18. Turky a, G. And M. Dawy, 2002. Materials Chemistry and Physics, 77: 48-59.
19. Hirashima, H., M. Ide and T. Yoshida, 1986. Journal of Non-Crystalline Solids, 86: 327-335.
20. Souri, D. And M. Elahi, 2007. Phys. Scr., 75: 2-219.
21. Souri, D. And M. Elahi, 2006. Czechoslovak Journal of Physics, 56/4: 419-425.
22. Levy, M., M.J. Duclot and F. Roussea, Journal of Power Sources, 26: 381-388.
23. Hussain, O.M. and K.S. Rao, 2003. Chemistry and Physics, 80: 638-946.
24. Souri, D., 2008. J. Phys. D: Appl. Phys., 41: 105102.
25. Bishay, A., 1960. J. Am. Ceram. Soc., 43: 417.
26. Bishay, A. and M. Maklad, 1966. Phys. Chem. Glasses, 7: 154.
27. Shaju, K.M. and T. Kawaguchi, 1995. J. Mat. Sci., 30: 3457.
28. Dimitriev, Y., V. Dimitrov, E. Gatev, E. Kashchieva and H. Petkov, 1987. Journal of Non-Crystalline Solids, 95(96): 937-944.
29. Sharma, B.K., D.C. Dube and A. Mansingh, 1984. Journal of Non-Crystalline Solids, 65: 39-51.
30. Abd El-Moneim, A., 2002. Materials Chemistry and Physics, 73: 318-322.
31. Dimitriev, Y., V. Dimitrov, M. Arnaudov and D. Tpalov, 1983. Journal of Non-Crystalline Solids, 57: 147-156.
32. Rajendran, V., N. Palanivelu, B.K. Chaudhuri and K. Goswami, 2003. Journal of Non-Crystalline Solids, 320: 195-209.
33. Sinclair, R.N., A.C. Wrigth, B. Bachra, Y.B. Dimitriev, V.V. Dimitrov and M.G. Arnaudov, 1998. Journal of Non-Crystalline Solids, 232-234: 38-43.