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IN V₂O₅-TeO₂ SYSTEM**

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XANES AND EXAFS STUDY OF ELECTRONIC STRUCTURE AND ORDERING
IN V_2O_5 -TeO₂ SYSTEM

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Abstract: X-ray Absorption Near Edge Structure and Extended X-ray Absorption Fine Structure (EXAFS) measurements have been made at the K-edge of vanadium in crystalline and amorphous V_2O_5 -TeO₂ systems and XANES measurements have also been made at the L_{III} edge of Te in these systems as well as crystalline and amorphous Te elements using synchrotron radiation. The spectra shows subtle differences in fine structure and intensities of corresponding peaks. These in turn yield qualitative information on differences in the density of states in different cases and smearing of near-neighbour distances as one goes over from crystalline to disordered state.

1.- Introduction:

The Tellurium based oxide glasses are interesting as they exhibit peculiar electronic properties and are highly conductive compared to the vanadium phosphate glasses or other glasses with same amount of charge carriers. They are characteristic semiconducting systems that exhibit hopping conductivity. Experimental work on tellurite glasses has given inconsistent results with regard to the nature of the structural unit. X-ray diffraction studies by Dimitriev and Dimitrov⁽¹⁾ on V_2O_5 -TeO₂ system including several components concludes that with increasing V_2O_5 content the Te coordination changes from 4 to 3 whereas V preserve its five fold coordination throughout although a considerable distortion takes place as compared to V_2O_5 system. The tellurium atoms are predominantly four-fold coordinated in this system but the basic structural unit in the glass is a trigonal bipyramid⁽²⁾.

The d.c. conductivity decreases with temperature and highly switched when a high electric field has applied and also a good network forming capacity⁽³⁾. In a similar system (V_2O_5 -P₂O₅) studied by Stizza et al⁽⁴⁾

1. Y. Dimitriev and V. Dimitrov, Mat. Res. Bull., 13, 1071, (1978).
2. P.A.V. Johnson, A.C. Wright, A. Yarker and Sinclair, J. Non-Cryst. Solids, 81, 163, (1986).
3. R. Singh and K. Sethupati, Key Engineering Materials, 13-15, 505, Ed. Anil K. Bhatnagar, Trans Tech Publications, (1987).
4. S. Stizza, I. Davoli, M. Tomcellini, A. Marcelli, A. Bianconi, A. Gzowski, L. Murawski, EXAFS and Near Edge Structure, Eds. A. Bianconi and L. Murawski, Springer Verlag, (1984).

and Wong et al⁽⁵⁾ using X-ray absorption technique showed that indeed vanadium is present in mixed valent 4+ and 5+ state. In this paper we present our X-ray absorption measurements at K-edge of vanadium and L of Te in both forms i.e. crystalline as well as amorphous one and discuss the spectral changes observed in terms of near-neighbour environment, hybridization of states etc.

2.-Experimental:

The samples studied were given to us by Prof. Hiroshi Harishma, Kio University, Yokohama, Japan. Method of sample preparation has been described elsewhere⁽⁶⁾. The XANES measurements at K-edge of Vanadium and L edge of tellurium and EXAFS measurements at K-edge of vanadium were performed at Frascati Synchrotron Radiation Facility using ADONE ring operated at 1.5 GeV and 200 mA. The spectra were recorded at 300 K with statistics of better than 0.2% at the peak position.

3.-Results and Discussion:

Figure 1 shows the vanadium K-absorption edge spectra in crystalline and amorphous V_2O_5 - TeO_2 compounds. Fig.2 shows Te L_{III} edge spectra of the two glasses alongwith the spectra of Te in crystalline and amorphous states. Fig. 3 shows vanadium EXAFS measured at K-edge in the crystalline and the amorphous V_2O_5 - TeO_2 system. Confining attention first to the fig.1 we see that the spectra look similar in most respects. The strong first peak P is observed in both crystalline as well as amorphous compounds

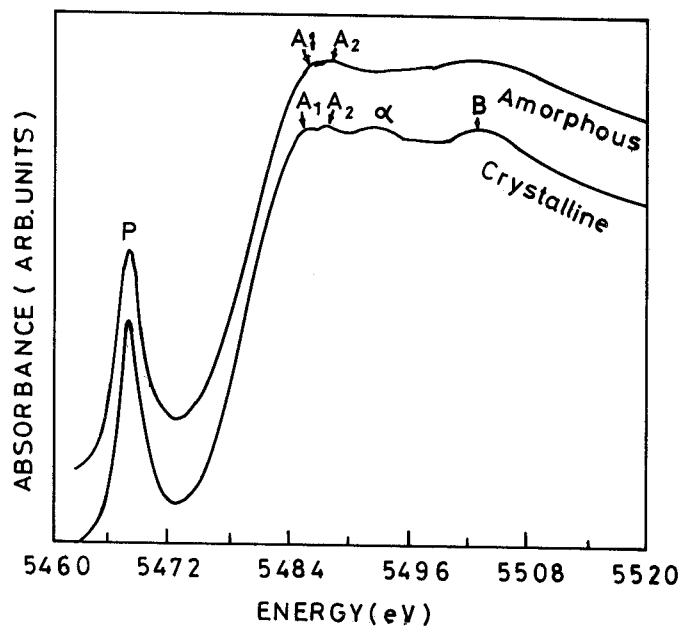


Fig.1 Vanadium K-edge and XANES in V_2O_5 - TeO_2 system

5. J. Wong, R.P. Messmer, D.H. Maylotte and F.W. Lytle, EXAFS and Near Edge Structure, 130, Eds. A. Bianconi, L. Incoccia and S. Stipich, Springer Verlag, (1983).
6. H. Harishma, M. Ide and T. Yoshida, J. Non-Cryst. Solids, 86, 32796, (1986).

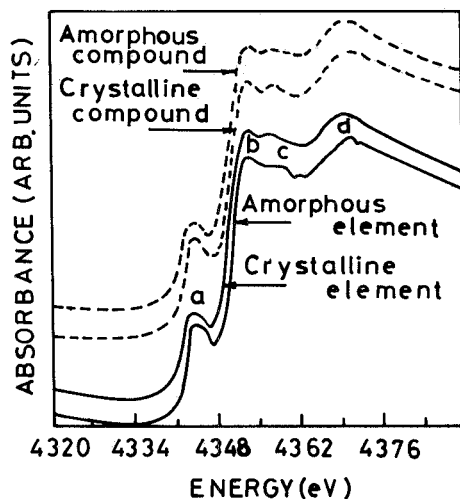


Fig.2 Te L_{III} XANES

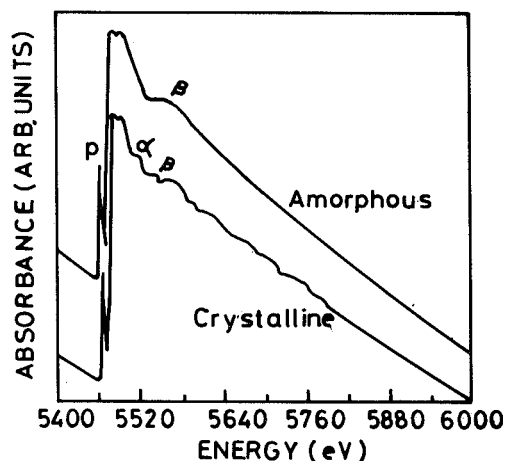


Fig.3 Vanadium K-EXAFS in V₂O₅-TeO₂ system

with good intensity and at identical energy position. This peak is ascribed to 1s-4p dipole transition and appears as a strong white line in both cases similar to that observed in these compounds by Stizza et al.⁽⁴⁾ The high intensity of this white line can be ascribed to very high density of unoccupied final states (4p) in the two cases. The peak P is found to be a little broader and asymmetric in case of the amorphous sample. The well defined narrow states are likely to yield a narrow white line in case of the crystalline system. These may get broadened and asymmetric in case of the disordered system. Also, the slightly higher intensity observed in case of the crystalline system tends to strengthen this conjecture.

On the higher energy side of P, the differences in the two spectra appear to get more pronounced. The principal absorption appears split (A₁ and A₂) in both cases. The higher energy shoulder in case of the crystalline V₂O₅-TeO₂ system, however falls off more rapidly and also has an additional peak α which is conspicuous by its absence in the disordered system. This only serves to strengthen the belief that the origin of peaks A₁, A₂ and α lies in the multiple scattering resonance arising as a result of the backscattering of the ejected photoelectron waves by near-neighbours and their subsequent interference. Bianconi et al.⁽⁷⁾ have ascribed this to MS resonances of the ejected photoelectron from the neighbouring atoms surrounding the absorber atom. This is further borne out, beyond all doubt, by the difference in the appearance of the next peak B which is rather sharp in case of the crystalline samples and flat and broad in the amorphous one. The n-n shells in the latter tend to lose their sharpness and the radial distribution function is characterised by a large spread over the average distance and hence it is no wonder that the peak

7. XANES Spectroscopy, A. Bianconi, Chapter 11 of X-ray absorption: Principles, Application Techniques of EXAFS, SEXAFS and XANES, Eds. R. Prinz and D. Koningsberger, J. Wiley and Sons, (1985).

B appears different as it does in the two cases. Moreover, the number of n-n shells contributing in case of the amorphous materials tend to lose long range order and hence the disordered system is only likely to show much less fine structure as it does, in fact, in this case.

Fig. 2 shows Te L_{III} edge XANES in four samples of Te i.e. crystalline and amorphous tellurium and V_2O_5 - TeO_2 compounds. The four spectra look similar at first glance. The first peak 'a' observed in all the four cases shows a regular decrease in the intensity in going from crystalline Te to amorphous V_2O_5 - TeO_2 compound via the crystalline compound and the amorphous Te. This peak arises due to the $2p \rightarrow 5pd$ final state dipole transition. Also we see that inspite of high density of states in the d-band this peak is neither sharp nor intense, perhaps due to hybridization of the d states with the much broader states resulting in a lower density of states and increased band width. Moreover, this peak is found to shift to a little towards high energy side with respect to the Te crystalline element by 0.3 eV in case of amorphous Te and the V_2O_5 - TeO_2 crystalline and by 0.8 eV in amorphous compound. This is due to change in the n-n environment and increase in oxidation state and hence effective charge on the absorbing atom which generally causes a chemical shift.

Peak 'b' at about 10 eV beyond peak 'a' observed in the four spectra is probably due to MS resonances. It is however, sharper in case of the crystalline samples as compared to the corresponding disordered systems. This is only to be expected in case of the peaks arising due to MS resonances. Proceeding a little further towards higher energy side we observe another peak 'c' about 7 eV beyond the peak 'b' and remarkably strong in intensity in crystalline element and compound but flattens out in case of the two disordered samples. Further on, the peak 'd' appears in all the spectra with nearly equal intensity and sharpness and is probably due to a n-n distance well defined in both the ordered as well as disordered samples which is most likely to be same for the first shell.

Now let us turn our attention to fig. 3 showing vanadium K-edge EXAFS in both amorphous and crystalline compounds. A look at these reveals that the crystalline spectrum has lot more fine structure. The near absence of fine structure beyond the peak ' β ' in case of the disordered system is an indication of a very high density of disorder in the system. The flattening and disappearing of fine structure in such cases is a feature that is characteristic of disordered systems⁽⁸⁾. The peak ' α ' splits and shows enhancement in case of crystalline system even though the EXAFS oscillations in this region in both cases are probably predominantly due to contribution from the first shell. This points to possible presence of two sharp distances in case of the crystalline compound that tend to get smeared out into a single diffuse overlapping shell since one cannot expect any change in the coordination number in the two cases.

Broadening of peaks in amorphous system also points a qualitative enhancement of bond length as compared to crystalline one which is consistent with other systems like Cu-Zr, Ni-Ti systems⁽⁸⁾ and such an increase in bond-length has also reported in literature using other techniques such as XRD and neutron powder diffraction^{(1) (2)}.

Thus we see that XANES and EXAFS features have yielded qualitative results about the local chemistry of glasses in terms of hybridization, edge shift, effective charge and near-neighbour environment and band width. In EXAFS region the broadening of peaks in glass spectrum with respect to crystalline compound are due to inherent structural disorder.

8. K.B. Garg, K.S. Jerath, H.S. Chauhan, U. Chandra, R.K. Singhal and K.V.R. Rao, *Pramana J. Phys.*, 31(3), 233, (1988), 27(6), 821, (1986).