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# Infra-red spectra of crystalline phases and related glasses in the $TeO_2$–$V_2O_5$–$Me_2O$ system

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The crystal line phases $Me_2O \cdot V_2O_5 \cdot 2TeO_2$ (Me = Li, Na, K, Cs, Ag) and their glasses are studied with the aid of infra-red spectroscopy. The radial distribution function (RDF) curves of two glasses, $Na_2O \cdot V_2O_5 \cdot 2TeO_2$ and $Cs_2O \cdot V_2O_5 \cdot 2TeO_2$, are obtained by an X-ray diffraction study. An attempt is made to identify the main bands in the infra-red spectra of the crystalline compounds and the glasses. The absorption bands in the 970 to 880 $cm^{-1}$ range are assigned to the stretching modes of the $VO_2$ isolated groups. A trend is observed towards a shift of the high-frequency band by the replacement of an alkaline ion with another in the order $Ag^+$, $Cu^+$, $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, which is explained by their different polarizing ability. With the aid of X-ray diffraction studies it is shown that the basic structure units in the glasses studied are the $VO_4$ and $TeO_4$ groups.

## 1. Introduction

Using infra-red spectra and X-ray diffraction analysis certain new structural characteristics have previously been determined [1, 2], and a hypothesis has been suggested about the basic structural elements of the glasses from the $TeO_2$–$V_2O_5$ system. In this paper three-component compositions are studied with the purpose of discussing the effect of the modifying alkaline oxides on the changes in the glass structure.

## 2. Method of investigation

Crystalline phases and glasses are obtained, containing 25 mol% $Me_2O$ (Me = Li, Na, K, Rb, Cs, Ag, Cu), 25 mol% $V_2O_5$ and 50 mol% $TeO_2$. The following compounds were used as raw material in the synthesis: $TeO_2$ (Merck 99.9%), $V_2O_5$ (Reanal 99.5%), $Li_2CO_3$, $K_2CO_3$, $RbNO_3$, $CsCO_3$, $Ag_2O$, $Cu_2O$, CuO (labelled for analysis).

Compounds of Li, Na, K and Ag were synthesized according to the procedure given by Darriet *et al.* [3]. We were unable to obtain the isostructural Rb α-polymorphic form, but a new phase was detected with the participation of $Cs_2O$. The $CuO \cdot V_2O_5 \cdot 2TeO_2$ did not form a ternary compound [4]. After crystallization from the melt and glass, only the $2TeO_2 \cdot V_2O_5$ phase was released.

The crystalline products obtained were identified by X-ray diffraction with a URS-50 IM diffractometer (Cu*Kα* radiation, Ni filter). Glasses were obtained from all compositions quoted, by melting in porcelain crucibles at 700° C for $\frac{1}{2}$ h. The melts were cooled on a copper plate. A stable glass was obtained from the $Cu_2O \cdot V_2O_5 \cdot 2TeO_2$ composition which we were unable to crystallize.

The infra-red spectra of the glasses and the crystalline samples were studied as nujol mulls and some of the checks were made as KBr discs. The spectra were recorded, using a double-beam UR-10 (Karl Zeiss, Jena) spectrophotometer in the range 1400 to 400 $cm^{-1}$ (1400 to 700 $cm^{-1}$ range, NaCl prism, and 700 to 400 $cm^{-1}$ KBr prism).

The diffractograms of the glasses with the compositions $Na_2O \cdot V_2O_5 \cdot 2TeO_2$ and $Cs_2O \cdot V_2O_5 \cdot 2TeO_2$ were taken on a Philips diffractometer (Cu*Kα* radiation, Ni filter, pulse height analyser). Using Fourier analysis [5], the radial distribution

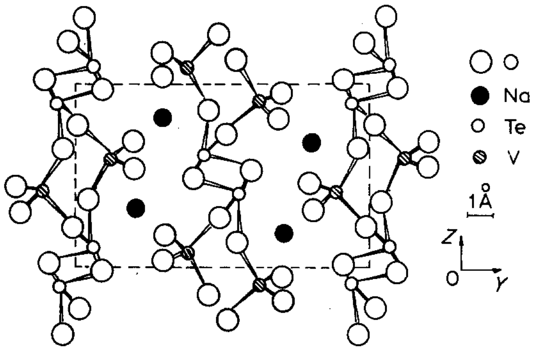

*Figure 1* Crystalline structure of $Na_2O{\cdot}V_2O_5{\cdot}2TeO_2$ according to Darriet *et al.* [3].

function (RDF) of the electrons was calculated. Corrections for background, polarization and Compton scattering were previously introduced in the experimental curve. Normalization was effected according to Norman [6]. The integral was solved with the aid of a strip technique [7] and a correction in the co-ordination number was made after Hoseman *et al.* [8].

## 3. Results and discussion

Among the crystalline products obtained, only the structure of $Na_2O{\cdot}V_2O_5{\cdot}2TeO_2$ has been studied [3]. In accordance with the crystallographic results obtained (Fig. 1), the main structural units in the compound are $TeO_4$ and $VO_4$ groups. The $TeO_4$ units are connected by a common edge in the $Te_2O_6$ groups. The link between $Te_2O_6$ and the $VO_4$ polyhedra is achieved by common oxygen atoms and two isolated (non-bridging) V–O bonds remaining in each $VO_4$ group. Later, when performing the spectral analysis, they are considered as an independent $VO_2$ group. The sodium ions are distributed among the individual chains, each ion being co-ordinated with 8 oxygen atoms. Four of them correspond to the non-bridging V–O bonds of two $VO_4$ groups.

A similar manner of co-ordination of the vanadium is typical of the alkaline metavanadates [9]. The infra-red spectra are discussed by Fotiev and Ivakin [10] and Fredericson [11] and in greater detail by Botto *et al.* [12]. According to Botto *et al.*, several absorptions are typical of the metavanadates in the 1000 to 400 $cm^{-1}$ range: two bands between 960 to 910 $cm^{-1}$ and 920 to 875 $cm^{-1}$, corresponding to the symmetric ($\nu^s$) and the antisymmetric ($\nu^{as}$) stretching modes of the isolated $VO_2$ groups. The strong band between 860 to 835 $cm^{-1}$ is due to the antisymmetric stretching motion of the V–O–V bonds, forming the chain of the metavanadates. The low frequency peaks in the 700 to 470 $cm^{-1}$ region are due to bending frequencies and to the symmetric stretching modes of the V–O–V bonds.

The infra-red spectra of the crystalline products obtained are shown in Fig. 2, while the corresponding absorption frequencies are given in Table I. Similarly to [12], we assign the two high-frequency bands to the symmetric and antisymmetric stretching modes of the non-bridging V–O bonds. With the exception of the Cs derivative, the corresponding absorption peak is split into doublets. A similar effect is also observed in the spectra of most of the metavanadates [10, 12]. The phenomenon is explained by the interaction between the vibration frequencies and the decrease in the symmetry of the tetrahedra in the crystal lattice [13].

The intensive band between 860 and 835 $cm^{-1}$, typical of the V–O–V bond in the metavanadates, is lacking in the spectra shown in Fig. 2. This should be expected, since in the compounds studied by us, the similarity with the metavanadates is restricted to the configuration of the $VO_4$ polyhedra, while the formation of the chain is realized through bridges of the V–O–Te bonds. The bands between 810 and 730 $cm^{-1}$ correspond probably to the

TABLE I Infra-red absorption bands of $M_2O{\cdot}V_2O_5{\cdot}2TeO_2$ crystals and glasses

| $M_2O$ | Crystal | | | | | | | Glass |
|---|---|---|---|---|---|---|---|---|
| | Modes of the lattice | | $\nu_{Te-O-Te}$ | $\nu_{V-O-Te}$ | | $\nu^{as}_{VO_2}$ | $\nu^{s}_{VO_2}$ | $\nu_{VO_2}$ |
| $Ag_2O$ | 435 | 515 | 620 | 730 | 785 | 895–900 | 915–920 | 880 |
| $Cu_2O$ | | | | | | | | 910 |
| $Li_2O$ | 460 | 480 | 665 | 750 | 810 | 880 | 920–935 | 920 |
| $Na_2O$ | 450 | 520 | 645 | 730 | 785 | 905–915 | 930–945 | 920 |
| $K_2O$ | 430 | 508 | 665 | 735 | 800 | 920–925 | 945–950 | 930 |
| $Rb_2O$ | | | | | | | | 932 |
| $Cs_2O$ | | 485 | 640 | 755 | 800 | 890 | 950 | 935 |
| CuO | | | | | | | | 970 |

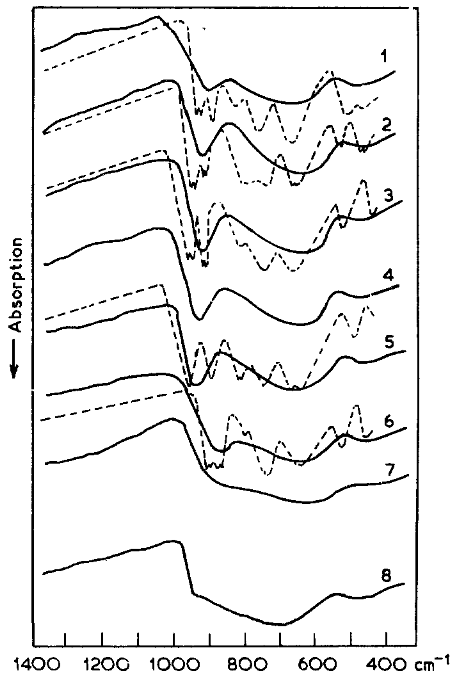

*Figure 2* Infra-red spectra of crystalline phases (– – – –) and glasses (———) $M_2O{\cdot}V_2O_5{\cdot}2TeO_2$ ($M_2O$ = 1, $Li_2O$; 2, $Na_2O$; 3, $K_2O$; 4, $Rb_2O$; 5, $Cs_2O$; 6, $Ag_2O$; 7, $Cu_2O$; 8, CuO).

modes of these bonds. The intensive absorption maximum between 665 and 620 cm$^{-1}$ is assigned to the vibrations of the Te–O–Te bonds of the $Te_2O_6$ polyhedra. A similar band is typical of $TeO_2$ [14], of the alkaline tellurites [15], and of some compositions in the $TeO–V_2O_5$ system [1].

Comparison of the data given in Table I shows that an analogy exists in the spectral characteristics of all the crystalline phases investigated. This is an indication of certain similarities in their structures. What is typical is that a definite shift of the band ($\nu^s_{VO_2}$) towards higher frequency exists in the order Ag, Li, Na, K, Cs (Table I). This effect could be explained by the decreasing polarization capacity of the cations in relation to the V–O bond, i.e. the weaker degree of interaction Me...O leads to a decrease in the distances of the non-bridging V–O bonds. The results for the polarizing effect of the alkaline cations which are obtained by calculating the energy of the bond in the silicate glasses may serve as evidence for this [16].

The regularity, discussed above, is not observed in $\nu^{as}_{VO_2}$. Such an anomaly is typical of the cases when the equivalence between the bonds is impaired, which determine the symmetric and antisymmetric modes [13], and when the angle between the inter-acting bonds [17] is changed. In such a case the difference $\Delta\nu = \nu^s - \nu^{as}$ is also changed.

The irregularity of $\nu^{as}$ in the compounds studied may be explained by the different action of the cation $M^+$ on the geometry of the $VO_4$ polyhedra. For example, the length of the V–O bonds isolated from an Na compound [3] differs by 0.04 (1.64 and 1.68 Å). This is related to the fact that each $VO_2$ group is simultaneously affected by two Na cations (Fig. 1), one of which is symmetrically located towards the two oxygen atoms (Na...O = 2.53 Å), while the other is asymmetrical (Na...O = 2.53 and 2.57 Å).

The infra-red spectra of the glasses in the system studied are presented in Fig. 2. It is seen that the course of the individual spectral curves does not differ significantly from that of the corresponding crystalline phases. This means that no significant changes in the short-range order occur in the glasses. The structural units, close to those which form the crystal lattice are preserved. The random arrangement of the network and the lack of a long order in the glasses is the cause of the broadening of the bands observed [14, 18, 19]. For this reason, only one broad band is observed characterizing the vibrational frequencies of the $VO_2$ groups ($\nu_{VO_2}$). It is noteworthy that the frequency of the band increases in the same order as $\nu^s_{VO_2}$ in the crystalline phases (Table I), depending on the polarizing action of the modifying cation.

No ternary compound [4] is formed in the system $TeO_2–V_2O_5–CuO$ and, therefore, the composition $CuO{\cdot}V_2O_5{\cdot}2TeO_2$ falls within the field of primary crystallization of the compound $2TeO_2{\cdot}V_2O_5$. Owing to this, a band at 970 cm$^{-1}$, which corresponds to the stretching modes of the V–O band isolated [1] is observed in the corresponding glass (Fig. 2). This denotes that the vanadium in the glass $CuO{\cdot}V_2O_5{\cdot}2TeO_2$ is co-ordinated as $VO_5$ polyhedra. It is of interest that the infra-red spectra of a glass with a composition of $Cu_2O{\cdot}V_2O_5{\cdot}2TeO_2$ (Fig. 2) do not differ from those of the rest of the alkaline compounds, which indicates that in this case the vanadium forms $VO_4$ groups.

Knowledge of the crystalline structure of $Na_2O{\cdot}V_2O_5{\cdot}2TeO_2$ made it possible to use the Fourier analysis to interpret the structure of the corresponding glass. In addition to it, for the sake of comparison, the glass with the composition

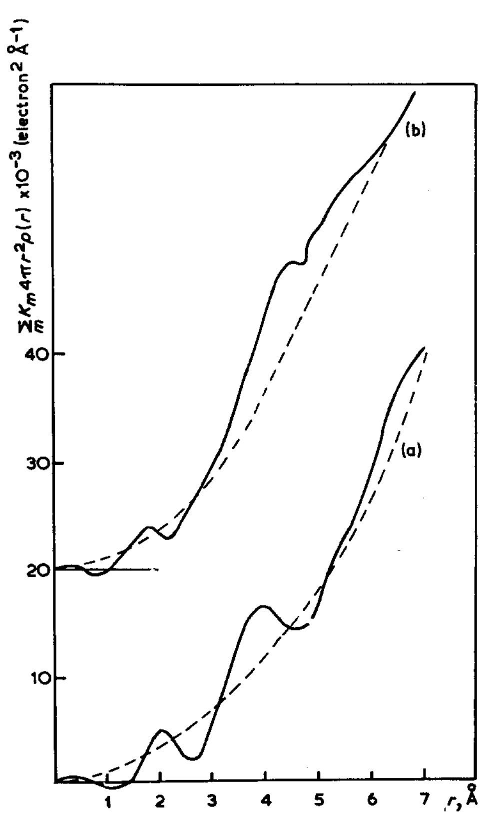

*Figure 3* Radial distribution curves of the glasses $Na_2O \cdot V_2O_5 \cdot 2TeO_2$ (a) and $Cs_2O \cdot V_2O_5 \cdot 2TeO_2$ (b).

$Cs_2O \cdot V_2O_5 \cdot 2TeO_2$ is discussed, which is the terminal member of the series studied.

The radial distribution curves (Fig. 3) yield direct information on the short-range order in the glasses investigated. Two maxima are observed in them. The first one in a glass, containing $Na_2O$ (a) is at 2 Å, and in glass (b) with $Cs_2O$ at 1.8 Å. In both cases it is determined by the distances Te–O and V–O in the structure of the glasses. The average distances V–O and Te–O are 1.74 and 2.02 Å, respectively, in the crystalline phase $Na_2O \cdot V_2O_5 \cdot 2TeO_2$. Since these distances do not exceed the boundaries of the first maximum, the area below it may be viewed as the sum of the areas, referring for the Te–O and V–O bonds. To calculate the co-ordination number (*CN*) of V and Te in relation to oxygen, the procedure used in [20–22] has been employed. In the case of both glasses the co-ordination of V and Te is satisfactorily interpreted as $TeO_4$ and $VO_4$ groups. The values calculated in glass (a) are $CN_V = 4.4$, $CN_{Te} = 3.8$, and in glass (b) $CN_V = 4.3$ and $CN_{Te} = 4.3$. The basic structural units obtained in glass (a) agree well with the crystalline structure for $Na_2O \cdot V_2O_5 \cdot 2TeO_2$, already mentioned. The shift in the first maximum in glass (b) to 1.8 Å is an indication of the existence of certain differences in their structures, i.e. few of the distances Te–O and V–O are shorter in comparison with those in glass (a). This result is also in agreement with the infra-red spectra data obtained on the weaker polarizing action of the $Cs^+$ on the V–O bonds.

The second maximum on the RDF curve, 4.0 Å for glass (a) and 4.4 Å for glass (b), is not well resolved. Since the samples are multicomponent glasses, the radial curve is a superposition of numerous elementary partial curves and the interpretation at high values of $r$, in particular, is not adequate. In glass (a) this value probably refers to the distance V–V, which is 3.8 Å in the crystalline compound. If we accept that in the glass with $Cs_2O$ the maximum is determined by the distance of the same bonds, one is impressed by the fact that these distances are longer than those in the glass with $Na_2O$.

## 4. Conclusions

On the basis of the similarity between the infra-red spectra of the glasses $M_2O \cdot V_2O_5 \cdot 2TeO_2$ (M = Li, Na, K, Rb, Cs, Ag, Cu) and the corresponding crystal phases, the conclusion may be drawn that the short-range order is preserved after glass formation. The infra-red spectra of the compounds $M_2O \cdot V_2O_5 \cdot 2TeO_2$ (M = Li, Na, K, Cs, Ag) exhibit two absorption bands at 950 to 880 cm$^{-1}$ which are assigned to the stretching vibrations of the $VO_2$ group, consisting of non-bridging V–O bonds.

A gradual shift of the $\nu_{VO_2}$ band towards higher frequency is observed in the spectra of the ternary glasses, when a monovalent ion is substituted with another in the order $Ag^+$. $Cu^+$, $Li^+$, $Na^+$, $K^+$, $Rb^+$ and $Cs^+$. This effect is the result of the shortening of the V–O isolated bond.

It is found by X-ray diffraction studies that in the vitreous $Na_2O \cdot V_2O_5 \cdot 2TeO_2$ and $Cs_2O \cdot V_2O_5 \cdot 2TeO_2$, the basic structure polyhedra are $VO_4$ and $TeO_4$ groups. The similarity of the infra-red spectra of the glasses gives support to other investigated glasses being built up by the same units.

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