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IR-Spectral Study of the Effect of WO_3 on the Structure of Tellurite Glasses

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The comparison of IR-spectra of tellurite glasses and their crystal products containing from 5 up to 45 mol% WO_3 indicates that the modifier does not change the coordination of tellurium. The IR-spectra of glasses containing small WO_3 amounts show a band at 925 cm^{-1}, which shifts up to 950 cm^{-1} with the increase in the tungsten concentration. The effect is specific of the vitreous state and may be explained by the change in the coordination of tungsten.

(Keywords: IR-spectra; TeO_2-WO_3 *system; Tellurite glasses; glass structure)*

IR-Spektroskopische Untersuchung des Einflusses von WO_3 *auf die Struktur von Tellurit-Gläsern*

Der Vergleich der IR-Spektren von Tellurit-Gläsern mit denen ihrer kristallinen Phasen, die 5 bis 45 Molprozente WO_3 enthalten, zeigt, daß der Modifikator die Tellurkoordination nicht ändert. Die IR-Spektren der Gläser mit kleinen Mengen an WO_3 zeigen eine Bande bei 925 cm^{-1}, die sich mit der Erhöhung der Wolframkonzentration auf 950 cm^{-1} verschiebt. Diese Wirkung ist für den glasartigen Zustand spezifisch und wird mit dem Koordinationswechsel des Wolframs erklärt.

Introduction

In earlier communications of this series[1—3] an IR-spectroscopy study was carried out on the structure of tellurite glasses of the TeO_2—V_2O_5 and TeO_2—MoO_3 systems with an increase in the content of the second component. The purpose of the present paper was to continue the investigation of the structures of the glasses in the TeO_2—WO_3 system.

Method

The glasses were obtained by the methods described in [1—3]. They were thermally treated and the crystalline phases obtained were identified by X-ray. The IR-spectra were taken on samples in Nujol with a UR-10 (Karl Zeiss, Jena) spectrometer in the 1200–400 cm^{-1} range (1200–700 cm^{-1} NaCl prism, 700–400 cm^{-1} KBr prism). The wavenumber accuracy was ± 1.5 cm^{-1} for the crystals, and ± 3 cm^{-1} for the glasses.

Results and Discussion

The IR-spectra of the glasses and the crystalline products are presented in Fig. 1. They are interpreted through a comparison with the spectra of certain crystalline tungstates whose structures are formed by WO_4 and WO_6 groups[4—6].

The following four normal vibrations are possible when the WO_4^{2-} groups of a T_d-symmetry are isolated[7]: $\nu_1 = 928$ cm^{-1}, $\nu_2 = 320$ cm^{-1}, $\nu_3 = 833$ cm^{-1} and $\nu_4 = 405$ cm^{-1}. The ν_3 and ν_4 alone are active in the IR-spectra. Six normal vibrations are possible for the WO_6 group of an O_h-symmetry where likewise only two vibrations are IR-active[7]. When the crystalline tungstates are built up of deformed WO_4 and WO_6 groups[4—6], the number of bands in the spectra increases as a result of the breakdown in the degeneration.

The spectra of some tungstate glasses are also studied[8—10]. From these investigations it is concluded that glasses of the BaO—P_2O_5—WO_3 system, containing up to 30 *m*% of WO_3 [8] and likewise the vitreous alkaline tungstates[9] are formed by WO_4 groups. With the increase in the WO_3 content, the formation of WO_6-polyhedra is also possible[8, 10]. This has been shown by X-ray structural analyses for glasses having a $K_2W_2O_7$ composition[11]. The structure of the amorphous WO_3 may be examined as a limiting case. Its structural elements, however, are still subject to discussion[12].

In the case of the system studied, the spectra of the crystalline products are the sum of the spectral curves of the initial oxides and this fact is in good agreement with the phase diagram which is of a simple eutectic type[13]. The typical bands are at 940 cm^{-1} (shoulder), 870 cm^{-1}, 825 cm^{-1} and 750 cm^{-1}, of WO_3 [5, 14] and at 780 cm^{-1}, 714 cm^{-1}, 675 cm^{-1} and a shoulder at 635 cm^{-1} corresponding to α-TeO_2 [15].

In the spectra of glasses there is an intense band at 635 cm^{-1} compared with crystals (Fig. 1). It characterizes the presence of non-symmetrical TeO_4 groups[3] which give an indication that Te does not change its coordination number in this range of compositions.

In the case of glasses having 5 to 30 *m*% of WO_3 an intense band is observed also at 935–925 cm^{-1}. In the spectra of the crystalline products in this region of the system there is only a weakly expressed shoulder

(Fig. 1 *a*). The difference in the intensities of the two absorption maxima may be explained by the fact that the glasses, having the WO_3 content mentioned above, are built up of deformed WO_4 polyhedra. In such a case, the band at 935–925 cm^{-1} may be referred to a vibration of the $\nu_1(A_1)$ type which becomes active when the symmetry of the tetrahedron decreases. The shoulder at 870–860 cm^{-1} moreover corresponds to vibration $\nu_3(B_1)$. A similar effect is observed in [8,16]. We assume that the WO_4-tetrahedra substitute a part of the TeO_4-groups (Fig. 2), which is possible because of the close ion radii of Te^{4+} (0.70 Å) and W^{6+} (0.62 Å) and the similar nature of the *Me*—O bonds. This leads to alternation of TeO_4 and WO_4 groups and the formation of Te—O—W bonds in the structure. That makes possible a decrease of the repulsive forces in the zone of the free electron pairs in the TeO-polyhedra, in opposite to pure tellurite glass[2,3]. This kind of interaction is seen as a main cause for the easy vitrification of the compositions mentioned above. With the rise in the WO_3 concentration (between 30 and 45 *m*%), the position and the outline of the high-frequency band are altered (Fig. 1 *b*). Similar spectra possess the alkaline pyrotungstates[5,10].

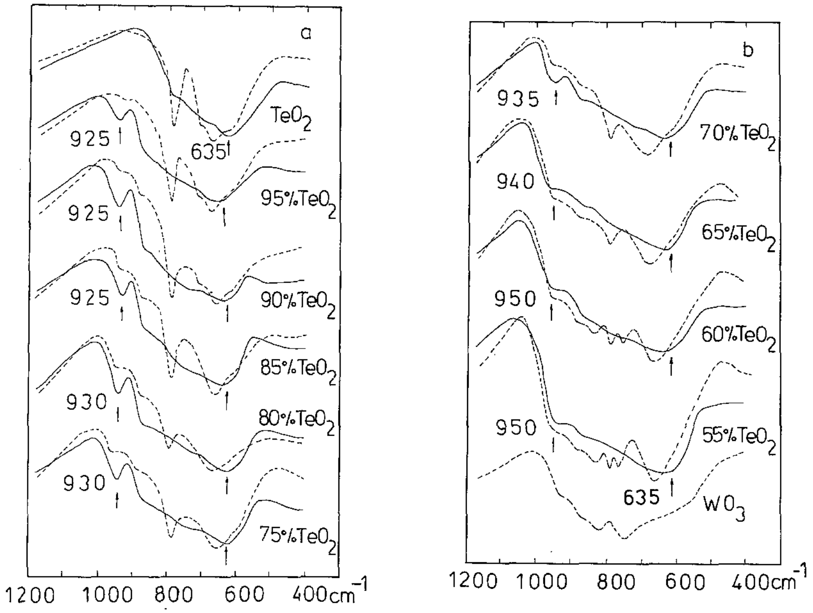

Fig. 1 *a* and *b*. IR-Spectra of glasses (———) and their crystal products (— — —) of the TeO_2—WO_3 system

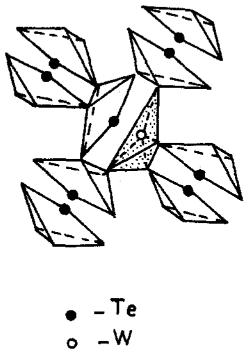

Fig. 2. Scheme of arrangement of WO_4-polyhedra in the network of the tellurite glass

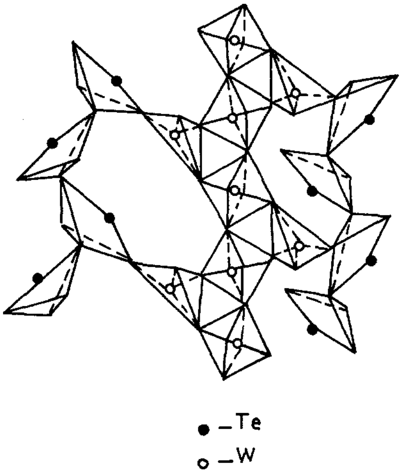

Fig. 3. Interconnection of the WO_4, WO_6 and TeO_4 polyhedra in the network of the tellurite glass with high WO_3 content

Taking into account their structure[17] this effect may be explained by the simultaneous presence of both WO_4 and WO_6 groups, thus the band between 950 and 935 cm^{-1} is a superposition of ν_1 (WO_4) and ν_3 (WO_6).

In accordance with the analysis made, a structural model for glasses with an increased WO_3 content is suggested (Fig. 3). The WO_6 groups in the glasses are associated by corners in chains linked to the TeO_4 groups by WO_4-tetrahedra. The rise in the WO_3 content leads to a decrease in the number of WO_4 and TeO_4 polyhedra and the structure becomes more flexible. This is the reason for the deterioration of the glass-forming ability. It is likewise in agreement with the general principles for glass-formation, according to which XO_4 complexes should be prevalent in the stable glass[18].

Conclusion

It has been found with IR-spectra that in glasses of the TeO_2—WO_3 system in the region of 0–45 mol% of WO_3, the tellurium is present in deformed TeO_4 groups (a band at $635\,cm^{-1}$). When the WO_3 concentration is small, the tungsten participates in the glasses as WO_4 groups (a band at $925\,cm^{-1}$). With the increase in the WO_3 content, also WO_6 groups are formed (a band at $950\,cm^{-1}$).

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