Monatshefte für Chemie 114, 669—674 (1983)

Monatshefte für Chemie
Chemical Monthly

IR-Spectral Investigation of the Structure of Glasses in the Fe_2O_3—V_2O_5 System

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(Received 20 November 1982. Accepted 14 December 1982)

The structure of glasses in the Fe_2O_3—V_2O_5 system in the 0-50 mol% Fe_2O_3 range is studied by IR-spectroscopy. It is found that the introduction of Fe_2O_3 favours the transformation of the VO_5-groups into VO_4 ones. This effect may be shown with the aid of IR-spectra, owing to the fact that these glasses are characterized by two high-frequency bands at 1 020 and 930 cm^{-1}. The first is determined by the vibrations of the short V = O nonbridging bonds in the VO_5-groups, while the second is assigned to the vibrations of the V—O-bonds in deformed VO_4-tetrahedra.

(Keywords: IR-Spectra; Fe_2O_3—V_2O_5 *System; Vanadate glasses, glass structure)*

IR-spektroskopische Strukturuntersuchung von Gläsern des Systems Fe_2O_3—V_2O_5

Die Struktur von Gläsern des Systems Fe_2O_3—V_2O_5 in dem Bereich von 0—50 Molprozent Fe_2O_3 wurde mit Hilfe der IR-Spektroskopie untersucht. Zusatz von Fe_2O_3 begünstigt die Umwandlung der VO_5- in VO_4-Gruppen. Das kann in den IR-Spektren durch zwei Banden bei 1 020 und 930 cm^{-1} festgestellt werden. Die erste wird durch Schwingungen der kurzen V = O-Nichtbrückenbindungen in den VO_5-Gruppen verursacht, die zweite wird auf Schwingungen der V—O-Bindungen in dem deformierten VO_4-Tetraeder zurückgeführt.

Introduction

Vanadate glasses are a relatively new class of vitreous materials belonging to the amorphous oxide semiconductors. Since electron transport depends on the structure we started a study of the short-range order and the distribution of the V—O—V-bonds. In the present paper the effect of F_2O_3 on the structure of vanadate glasses is discussed in continuation of a series of investigations on binary and ternary vitreous systems containing V_2O_5 [1–6].

0026-9247/83/0114/0669/$ 01.20

Methods

Previously homogenized batches of Fe_2O_3 (Reachim) and V_2O_5 (Reanal—99.5%) were melted in porcelain crucibles in the 800-1 200 °C range and were vitrified by quick quenching with the aid of roller techniques as in [7]. The amorphity of the samples was established by X-ray studies with an URS-50 IM (with Cu K α-radiation and Ni-filter). The glasses were crystallized after a 24 h exposure at a temperature whose exact value for each composition was determined by DTA with a Paulik Paulik, Erday derivatograph. The IR-spectra of the glasses and the crystallization products were taken on a UR-10 Karl Zeiss Jena spectrophotometer in the 1 200-400 cm^{-1} range (1 200-700 cm^{-1} prism NaCl, 700-400 cm^{-1}, KBr prism). The samples were photometered in Nujol. The wavenumber accuracy of the recording of the absorption maxima was ± 1.5 cm^{-1} for the crystals and ± 3 cm^{-1} for the glasses.

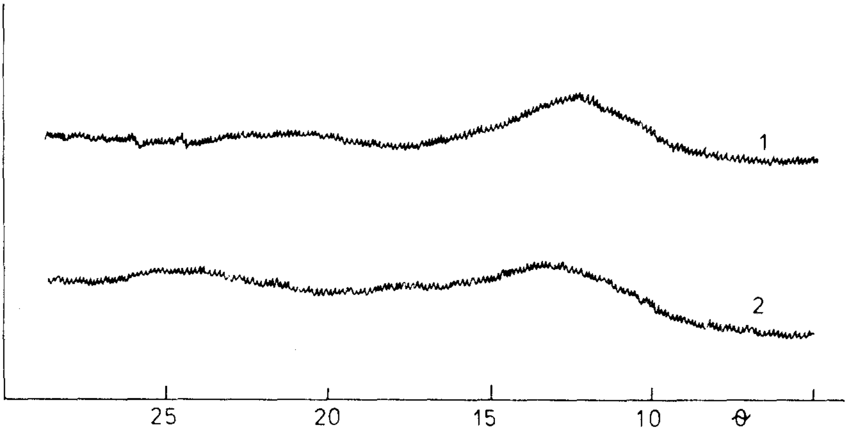

Fig. 1. X-ray diffraction data of two glasses of the Fe_2O_3—V_2O_5 system: *1* 30 mol% Fe_2O_3; *2* 50 mol% Fe_2O_3 ($FeVO_4$)

Results

Glasses in the 0-50 mol% range for Fe_2O_3 were obtained.

Fig. 1 shows the X-ray diffraction data of two representative glasses of the Fe_2O_3—V_2O_5 system, containing 30 and 50 mol% Fe_2O_3. A well-expressed halo about 12.5° is observed.

The IR-spectra of glasses and crystalline products show (Fig. 2) that the introduction of Fe_2O_3 leads to the appearance of a new band at 930 cm^{-1}, in addition to that at 1 020 cm^{-1}. It remains the only high-frequency band in the spectrum of the vitreous $FeVO_4$ (50 mol% Fe_2O_3 : 50 mol% V_2O_5).

Discussion

Vanadate systems are particularly suitable as an object for IR-spectra investigations, owing to the presence of characteristic bands related to vibrations of isolated V—O-bonds. Their frequencies are found in the 1 020–850 cm^{-1} range. Their exact position is the result of the place of the composition in the phase diagram, i.e. of the kind of VO-polyhedra as well as their manner of bonding with the rest of the structural groups. V_2O_5 and the orthovanadates may be viewed as two final cases in the present investigation, since according to the phase diagram[8, 9] no other compounds are formed.

The IR-spectrum of the pure crystalline V_2O_5 (Fig. 2.1) is characterized by a particularly strong band at 1 020 cm^{-1} and an intense band at 830 cm^{-1} [1, 10, 11]. It is built up by deformed VO_5 trigonal bipyramids, bonded in zigzag-like chains[12]. Each VO_5-group contains a short non-bridging $V=O$ bond (vanadyl group). The band at 1 020 cm^{-1} is assigned to its vibrations while that at 830 cm^{-1} is related to the vibrations along the V—O—V chains.

In the case of transitions toward meta-, pyro- and orthovanadates, the frequency of the V—O-vibrations decreases and this is related to the increase in the symmetry of VO-polyhedra, equalization of the lengths of chemical bonds and a decrease in the coordination number of vanadium[6, 13, 14].

The VO_4-tetrahedron is the main vanadium polyhedron in the orthovanadates[13, 14]. The free VO_4^{3-}-tetrahedron, possessing a T_d-symmetry, has two active vibrations at 825 cm^{-1} (ν_3) and at 480 cm^{-1} (ν_4) in the IR-spectrum[15]. Due to the complicated nature of interaction in the crystal the symmetry of VO_4-groups decreases resulting in additional bands because of the breaking down of the degeneracy[16–18].

The orthovanadate of iron ($FeVO_4$) was studied by means of IR-spectra in the crystalline state by a number of researchers[9, 19, 20]. Its IR-spectrum is characterized by absorption bands at 985, 950, 920, 885, 840, 770, 750, 675, 515, 460, and 420 cm^{-1} (Fig. 2.7). The group of bands in the 950–885 cm^{-1} range may be related to the stretching vibrations of the tetrahedral VO_4-groups[19, 20]. It is interesting to note that they are markedly displaced towards higher wavenumbers in comparison with the positions of comparable bands in the spectra of other orthovanadates. According to *Baran*[20] this is the result of strong interactions between Fe—O and V—O vibrations, caused by vanadium and iron coordination polyhedra forming a strongly linked condensed structure; then one deals not anymore with isolated VO_4^{3-}-groups as found in other orthovanadates. So it was shown for the crystalline structure of

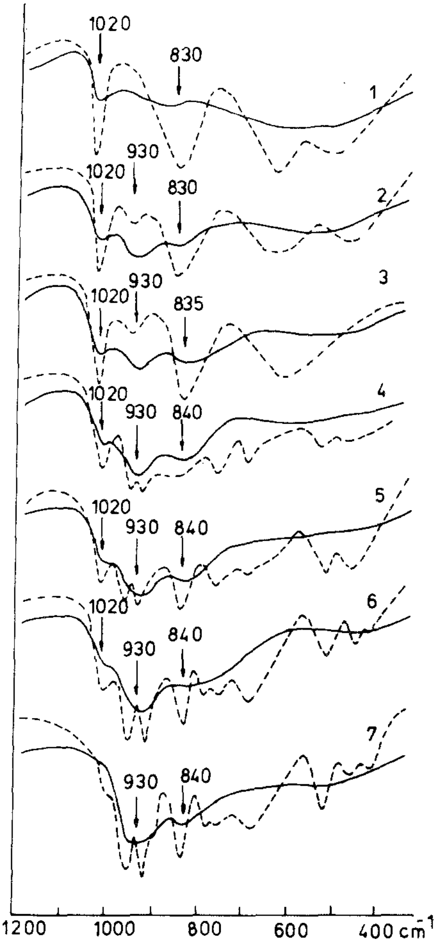

Fig. 2. IR-Spectra of Glasses (———) and their crystal products (– – – –) of the Fe_2O_3—V_2O_5 system: *1* V_2O_5; *2* 10 mol% Fe_2O_3; *3* 15 mol% Fe_2O_3; *4* 20 mol% Fe_2O_3; *5* 30 mol% Fe_2O_3; *6* 40 mol% Fe_2O_3; *7* 50 mol% Fe_2O_3 ($FeVO_4$)

$FeVO_4$[21] that there exist three types of independent Fe-atoms, two of which form deformed octahedra, while the third one forms a trigonal bipyramid with three tetrahedrally coordinated independent V-atoms. The FeO-coordination polyhedra form a double chain possessing six common points.

The crystal-glass transition (Fig. 2) influences the IR-spectra. A certain broadening of the bands and a decrease in their intensities is observed together with a decrease in their number which is the result of the disorder in structure and of the overlapping of the bands. The preservation of the band at 1020 cm^{-1} in the spectrum of a vitreous V_2O_5 (Fig. 2.1) is an indication[1] for the presence of VO_5-groups with a short nonbridging $V=O$ bond in the structure.

The spectrum of the pure vitreous $FeVO_4$ is characterized by a high-frequency band at 930 cm^{-1}. According to the similarity in the IR-spectra between the vitreous and the crystal $FeVO_4$ (Fig. 2.7) this band may be related to stretching vibrations of the VO_4-groups.

Along with the above-mentioned band at 1020 cm^{-1} in the spectra of binary glasses, also the other one at 930 cm^{-1} is observed raising its intensity with the increase in the Fe_2O_3 content in a direction toward $FeVO_4$ (Figs. 2.2-6). The existence of the two bands in the spectra of binary glasses is evidence for the simultaneous presence of two kinds of polyhedra: VO_5- and VO_4-groups.

Two mechanisms for the incorporation of modifying ions in the lattice of the vitreous V_2O_5 have been suggested in an earlier paper[6]. According to the first mechanism, the M^{n+}-ions rest in between the vanadate chains and layers and may affect the isolated $V=O$-bonds. As a result of this, they are markedly elongated and the vibration frequencies shift towards low-wavenumbers. In the second case the ions occupy a position in the chain itself and their influence on the $V=O$-bonds is limited. The preservation of the $V=O$ position at 1020 cm^{-1} in the IR-spectrum of the glass is an indication of the fact that it is not directly influenced and the coordination number and the symmetry of the VO-polyhedra do not change. The strong displacement of the frequency to 930 cm^{-1} is proof for the interaction of the $V=O$-bonds with the Fe^{3+}-ions with the formation of Fe—O—V-bridges and the transformation of VO_5 groups into VO_4 ones. Thus, with the introduction of the first amounts of Fe_2O_3 structural complexes are formed in the glasses similar to those in $FeVO_4$, containing VO_4-groups.

Additionally a shoulder is observed which shifts gradually from 830 cm^{-1} in the case of the pure V_2O_5 to 840 cm^{-1} in that of $FeVO_4$. A strong band is found in the spectra of the corresponding crystal phases in these places (Fig. 2). This 830 cm^{-1} band in the spectrum of crystalline V_2O_5 is assigned to vibrations along the V—O—V chains. There are no V—O—V chains in the structure of $FeVO_4$[21] but there exist FeO-polyhedra and VO-polyhedra bonded along the tops which signifies the formation of Fe—O—V bonds instead of V—O—V ones. The band at 840 cm^{-1} in the spectrum of crystalline $FeVO_4$ and the shoulder in the vitreous material may be assigned to the vibrations of these bonds.

It may be assumed that due to the preservation of a part of the V—O—V- and Fe—O—V-bonds in binary glasses (the shoulder at 840-830 cm^{-1}) there will be favourable conditions for the formation of more complicated chain complexes. Possibly, this is one of the causes for the successful achievement of the vitreous state of a wide concentration range in the Fe_2O_3—V_2O_5 system.

Conclusion

It is established that the short-range order of glasses in the Fe_2O_3—V_2O_5 system is similar to that of the corresponding crystalline phases. The main vanadate polyhedra in the vitreous $FeVO_4$ are the VO_4-groups. A transformation of the VO_5-groups into VO_4 takes place with the change in the composition of binary glasses in a $FeVO_4$ direction. This may be established through the change in the intensity of the bands at 1 020 and 930 cm^{-1} in the IR-spectra.

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