

GLASSES IN THE B_2O_3 - V_2O_5 SYSTEM OBTAINED BY FAST QUENCHING

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Glass formation tendency in the B_2O_3 - V_2O_5 system was investigated with different cooling rates (10^2 - 10^5 K/s) of the melts. Prepared glasses were characterized by X-ray phase analysis, differential thermal analysis (DTA), infrared spectroscopy (IR), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The existence of BO_3 and VO_5 structural units forming the glass network was proved. The microheterogeneous structure of the samples was observed in the central region of the system by means of TEM and found to consist of V_2O_5 crystals, droplet - like formations and hydrate products.

Keywords: Glass formation, IR spectroscopy, Microstructure, Metastable phase separation

INTRODUCTION

The B_2O_3 - V_2O_5 system is a simple eutectic system and, at slow cooling, V_2O_5 only crystallizes from the melt. There is a region of metastable phase separation [1, 2] transformed in the stable liquid phase separation for the three-component TeO_2 - B_2O_3 - V_2O_5 system [3, 4]. That is why the preparation of homogeneous glasses is possible only after fast cooling of the melts in order to prevent the nucleation of crystals and metastable phase separation. According to Dimitriev et al. [2] single phase glasses can be formed in the region 0 - 29 mol.% V_2O_5 by pouring onto a Cu plate. From the data of IR spectroscopy [5, 6] of definite glass compositions it has been concluded that the main structural units in the network are the BO_4 , BO_3 and VO_5 groups, while Hogarth et al. [7] have reported only BO_3 and VO_4 units. The peculiarity of this model system is the absence of the typical modifying ions, and that both network-forming oxides (V_2O_5 , B_2O_3) exhibit a competitive action in network formation.

The purpose of the present investigation is to obtain glasses over a wide concentration range and to study the change in their structure depending on the composition and thermal history of the samples.

EXPERIMENTAL

All batches were prepared using V_2O_5 and H_3BO_3 (reagent grade) as starting materials. The homogenized batches were melted for 30 min in air at 900°C in

platinum crucibles for compositions with a high B_2O_3 concentration and in silica crucibles for other compositions. The amorphous state of the samples was established by X-ray phase analysis (Dron-3, diffractometer Co K α radiation) and electron diffraction (EM-400, Philips). The obtained glasses were investigated by differential thermal analysis (Paulik Erdey derivatograph), infrared spectroscopy using KBr pellet technique (Nicolet - 320, FTIR spectrometer), transmission electron microscopy (EM-400, Philips) and X-ray photoelectron spectroscopy (Escalab Mk II). The samples are presented according their nominal compositions. The preliminary chemical analysis shows displacement with 5 - 10 mol.% in direction of increase of V_2O_5 content.

RESULTS

Using low cooling rates (10^2 K/s) the transparent samples were obtained from compositions containing less than 20 mol.% V_2O_5 . By the roller - quenching technique (10^4 - 10^5 K/s) the vitrification over the whole concentration region of the V_2O_5 - B_2O_3 system has been achieved. The phase transition parameters during the heating were determined by DTA analysis. The

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maximum of exothermic effects corresponding to the crystallization temperature, T_x , for the different glass compositions, is in the range 245-255 °C. In addition, DTA curves exhibited endothermic effects at 640-660 °C associated with the melting of the crystals at liquidus temperature. The DTA curves of the glasses with high crystallization ability are shown in figure 1.

The increase in V_2O_5 content leads to the formation of heterogeneous samples due to the metastable phase separation and the crystallization. Complications can also appear due to the hygroscopicity of the glasses and the separation of H_3BO_3 on the glass surface. X-ray phase analysis and electron diffraction (ED) studies showed that in all concentration range only V_2O_5 crystallizes from slowly cooled melts. This result confirmed the literature data [1] reporting no chemical interaction between the initial components (B_2O_3 and V_2O_5) in this system. By TEM observation (figures 2 - 5) several types of structures are established: *i*) one-phase amorphous regions; *ii*) droplet - like formations or more complicated aggregates dispersed in glassy matrix; *iii*) microcrystals of V_2O_5 (ranging in size from 1 nm to 5 nm); *iv*) microheterogeneous structure containing hydrated matrix and aggregates from the second phase.

The IR spectra of the V_2O_5 -rich glasses are shown in figure 6. The spectra of glasses with a high (95, 90 mol.%) V_2O_5 content are characterized by a broad absorption band at 1265 cm^{-1} , an intense band at 1020 cm^{-1} , a broad band with a maximum centered at about 800 cm^{-1} and a band at 620 cm^{-1} . With increasing B_2O_3 concentration, the band at 1020 cm^{-1} is shifted to lower (1000 cm^{-1} , 980 cm^{-1}) frequencies, the band at 1265 cm^{-1} is preserved, but with glass composition 60 V_2O_5 .40 B_2O_3 it is transformed into a shoulder. The spectra of this glass and others with higher B_2O_3 content exhibits pronounced bands at 1460 cm^{-1} and 1200 cm^{-1} , a broad absorption band with a maximum at about 790 cm^{-1} and lower-intensity bands at 650 and 550 cm^{-1} .

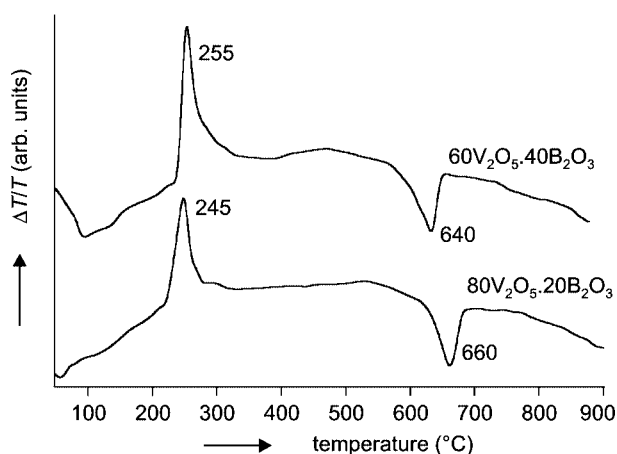


Figure 1. DTA thermograms of glasses.

DISCUSSION

The interpretation of the IR-spectra is based on the literature data of a series of crystalline and amorphous vanadate phases [8 - 12] and borate phases [13 - 15]. The IR spectrum of pure crystalline and amorphous V_2O_5 is characterised by the intense band at 1020 cm^{-1} , related to vibration of isolated V=O vanadyl groups in VO_5 trigonal bipyramids, the absorption band at 830-820 cm^{-1} , due to vibrations of V-O-V chains, and the band at about 600 cm^{-1} which correspond mainly to the bending vibrations. It is known that in the structure of vitreous B_2O_3 about 80% of the boron atoms are present in boroxol rings, B_3O_6 , which are linked by independent BO_3 groups [16]. Their vibrations in the IR spectrum are observed at 1420 cm^{-1} (shoulder), strong band at 1260 cm^{-1} and band at 720 cm^{-1} [17 - 21]. The spectroscopy studies of a series of two- and three-component borate glasses containing modifying oxides show transformation of the BO_3 groups from the boroxol rings into BO_4 groups, which participate in the formation of superstructural units. The B-O stretching vibrations of tetrahedral BO_4 groups are in the range 1050-900 cm^{-1} . The amount of BO_4 fractions in the network of $M_2O - B_2O_3$ and $MO - B_2O_3$ glasses passes through a maximum value affected by the content and the type of the modifying oxides [19 - 21]. It is also known that in the binary borosilicate and borogermanate glassy systems B atoms are 3-fold coordinated by oxygens [22 - 24]. The network of $B_2O_3 - P_2O_5$ glasses is built up of BO_4 units above 35 mol.% P_2O_5 by analogy with the structure of BPO_4 crystalline phase [25].

The bands observed in the glass spectra (95 V_2O_5 .5 B_2O_3 and 90 V_2O_5 .10 B_2O_3) at 1020, 800 and 620 cm^{-1} can be assigned to VO_5 vibrations of trigonal bipyramids (figure 6). The slight shift of the band at 1020 cm^{-1} to 980 cm^{-1} with rising B_2O_3 content is an indication that there is no direct attack to the short V=O bond [26]. B_2O_3 is probably incorporated in the vanadate network by breaking of the V-O-V chains and formation of V-O-B bonds. The bands at 1265 cm^{-1} in the spectra of the samples with a high V_2O_5 content can be attributed to the vibration of isolated BO_3 groups by analogy with the structure and IR spectra of $FeBO_3$ [15]. The changes in the spectra appeared at B_2O_3 content above 20 mol.%. The intense bands at 1460 cm^{-1} and 1200 cm^{-1} in the spectra of these glasses probably result from absorption of moisture from the air and surface crystallization of H_3BO_3 (figure 6). This fact complicated the interpretation of the IR-spectra of B_2O_3 -rich glasses.

An additional information about formation of the amorphous network and the bridging bonds may be obtained from XPS analysis. Our preliminary results [27] indicate that O1s spectra of $B_2O_3 - V_2O_5$ glasses are complex. The curve fitting of O1s spectrum in our case requires a few peaks to appear as expected from the binding energy of O_{V-O-V} (529,8 eV) [28], O_{B-O-B} , (531.1 eV) [29], and O_{B-O-V} bridging bonds. The



Figure 2. TEM micrograph of amorphous sample having composition $60V_2O_5.40B_2O_3$ (mol.%) obtained by fast quenching.

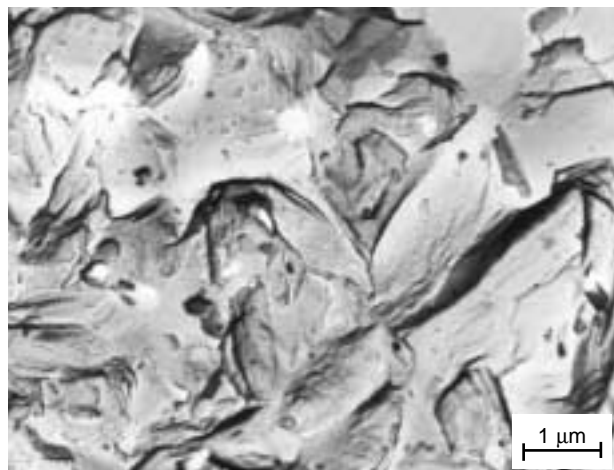


Figure 4. TEM micrograph of V_2O_5 crystals in slowly cooled sample having composition $80V_2O_5.20B_2O_3$ (mol.%).

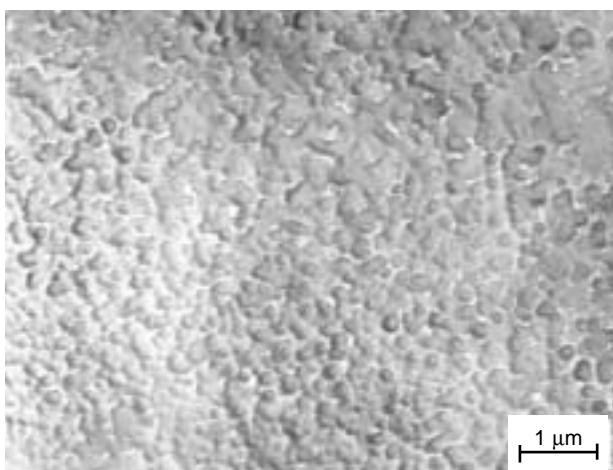


Figure 3. TEM micrograph of droplet-like structure of slowly cooled samples having composition $80V_2O_5.20B_2O_3$ (mol.%).

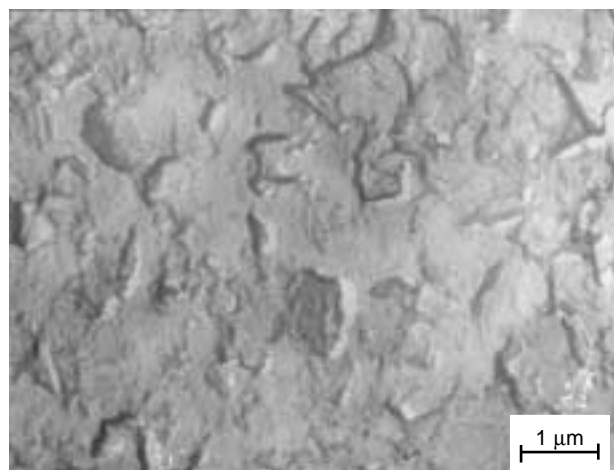


Figure 5. TEM micrograph of hydrated slowly cooled sample having composition $20V_2O_5.80B_2O_3$ (mol.%).

variation in glass composition leads to change in the intensity of the peaks. More precise experiments will be carried out to determine whether the mixed bridging bonds are formed.

The network of glasses rich in V_2O_5 consists of VO_5 groups with $V=O$ short bond. The formation of VO_4 groups is under question because the band at 1020 cm^{-1} corresponding to the vibration of $V=O$ bond is shifted only to 980 cm^{-1} and the intensity of band at 800 cm^{-1} decreases with increasing of B_2O_3 content. There is no spectral proof for formation of more complicated borate complexes with BO_4 units. Obviously the V_2O_5 does not stimulate the formation of BO_4 units. The B atoms are incorporated into vanadate network as isolated triangular BO_3 groups or other units containing only BO_3 groups. Probably, this is a reason for the difficult formation of an aperiodic amorphous network. Therefore, the immiscibility takes place below liquidus temperature as a more favourable process.

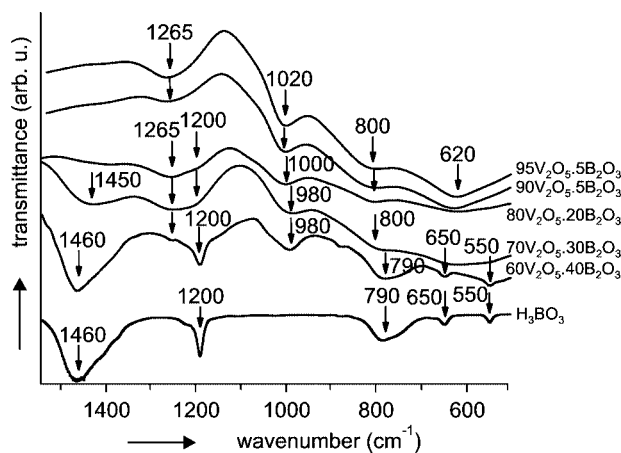


Figure 6. Infrared spectra of glasses.

CONCLUSIONS

The single - phase glasses are formed in all the concentration range of the B_2O_3 - V_2O_5 system only at high cooling rates. Based on the IR spectra the existence of BO_3 and VO_5 structural units in the wide concentration range was proved. It was found that the microheterogeneous structure is due to high crystallization ability of the V_2O_5 , liquid phase separation and hydratation processes.

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SKLA SYSTÉMU B_2O_3 - V_2O_5
PŘIPRAVENÁ RYCHLÝM CHLAZENÍM

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Sklotvornost systému B_2O_3 - V_2O_5 byla zkoumána při rychlostech chlazení 10^2 - 10^5 K s^{-1} . Připravená skla byla charakterizována RTG fázovou analýzou, diferenční termickou analýzou, infračervenou spektrometrií, transmisní elektronovou mikroskopií (TEM) a RTG fotoelektronovou spektroskopií. Byla dokázána existence strukturálních jednotek BO_3 a VO_5 tvořících skelnou strukturu. Metodou TEM byla pozorována mikroheterogenní struktura v centrálních oblastech vzorků, kterou tvořily krystalky V_2O_5 , formace kapiček a produkty hydratace.