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"Synthesis of vanadate and molybdate phases with participation of ZnO and ZrO_2"

In recent years vanadium and molybdenum containing compounds are the subject of a number of studies, mainly due to their interesting physical properties and have received much attention in order to create manyfunctional attractive materials. They have been widely used as amorphous semiconductors, solid electrolytes, catalysts, lasers, and materials with negative thermal expansion. The MoO_3 and V_2O_5 oxides are known as non-conventional network formers and series of two- and multicomponent glasses with their participation have been synthesized. These glasses are mainly of academic interest as a suitable object for the solution of certain problems of the glassy state. From the fundamental point of view it is interesting to study the influence of third component on the glass forming ability in the selected V_2O_5-MoO_3 model system. In the present investigations as third component were chosen ZnO and ZrO_2, which belong to the group of intermediate oxides, according to the classic concepts of glass formation tendency.

The main purposes of this work are: i) to compare the possibilities of two synthesis methods – melt quenching method and mechanochemical activation for preparation of vanadate and molybdate phases and ii) to determine glass formation region in the V_2O_5-MoO_3-ZnO and V_2O_5-MoO_3-ZrO_2 systems and to obtain information of the main structural units forming amorphous networks.

The obtained amorphous and crystalline phases were characterized by x-ray diffraction (XRD), differential thermal analysis (DTA), infra-red spectroscopy (IR), x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

In consequence of experimental work and profound analysis of the obtained results it can be made some basic conclusions on dissertational work:

1. For the first time, the glass formation regions in the V_2O_5-MoO_3-ZnO and V_2O_5-MoO_3-ZrO_2 systems were determined applying melt quenching method at fast cooling rates. The glass

formation area in the V_2O_5-MoO_3-ZnO system is situated in the central part of the Gibb's triangle in the composition range 65–10 mol% V_2O_5, 65-10 mol% MoO_3 and 50-10 mol% ZnO. The glass formation area is situated near binary MoO_3-V_2O_5 system up to 10 mol% ZrO_2. Experimental results concerning glass forming ability shown that V_2O_5 is stronger network former than MoO_3. The reason for wider glass formation region in the V_2O_5-MoO_3-ZnO system in comparison with the glass formation area in the V_2O_5-MoO_3-ZrO_2 system can be connected with crystal chemistry of these two oxides. It's well known that ZnO and V_2O_5 form large number of compounds: ZnV_2O_6, $Zn_2V_2O_7$, $Zn_3(VO_4)_2$ and $Zn_4V_2O_9$, while in the system with participation of ZrO_2 only one compound is formed - ZrV_2O_7. From crystal chemistry point of view it can be say that in the system V_2O_5-ZnO exist larger number of structures and the opportunity of different kind of amorphous network to be realized with participation of different structural units is bigger. In the system with ZrO_2 participation in the crystal structures participate only isolated pyrogroups which is difficult to be frozen in an amorphous state.

2. On the base of spectral investigations, it was establish that amorphous network of the obtained glasses is build up mainly of polyhedra with high coordination number (VO_5 и MoO_6) and small amount of isolated $(V/Mo)O_4$ tetrahedra.

3. It was demonstrated the different influence of MoO_3, ZnO and ZrO_2 on the vanadate network. A transformation of amorphous network from vanadate constituting of meta- and pyro-complexes to molybtate one build up mainly of MoO_6 octahedra is established. The incorporation of MoO_3 into vanadate network, leads to increase of the connectivity of the structural units by forming of new bridging bonds V-O-Mo. Zinc ions stimulate the gradual transformation of layered vanadate structure into meta-, to pyro- and orthovanadate one. Accumulation of isolated $(V/Mo)O_4$ tetrahedra deteriorate the glass formation ability in compositions containing ZnO above 50 mol%. This is the reason three-component $Zn_{2.5}VMoO_8$ and $Zn_3V_2MoO_{11}$ phases building up from isolated $(V/Mo)O_4$ could not be vitrified. ZrO_2 acts as modifier in the realized amorphous networks. It stimulate direct $(V/Mo)O_6 \rightarrow (V/Mo)O_4$ transition and increases crystallization ability of the melts above 10 mol%.

4. For the first time monoclinic $Zn_2V_2O_7$ and monoclinic $Zn_3V_2MoO_{11}$ were obtained by melt quenching technique. It is proven that melt quenching technique is an appropriated method for the synthesis of polycrystalline materials with congruent melting character.

5. For the first time, by direct mechanochemical method following phases were synthezed: ZnV_2O_6, $Zn_2V_2O_7$ и $Zn_{2.5}VMoO_8$, while applying mechanochemically assisted solid state synthesis $Zn_3(VO_4)_2$, $ZnMoO_4$ and ZrV_2O_7 were produced. By mechanochemical activation the temperature and the time of solid state synthesis of above mentioned compounds are significantly decreased (≈ 200 ^{o}C and 60 hours).

6. It was establish that ZrO_2-V_2MoO_8 line is a real quasi-binary section in the system ZrO_2-MoO_3-V_2O_5. The binary ZrO_2-V_2MoO_8 system is a simple eutectic one with eutectic point situated at 74 mol% V_2MoO_8 and T_e = 520 ^oC.

Main contributions of dissertation work

1. New non-traditional vanadate and molybdate glasses without participation of classical network former were obtained at high cooling rates.

2. Structural models concerning amorphous network of the obtained vanadate glasses were developed. New knowledge about the main structural units (short range order) building glass network and their connectivity (middle range order) were accumulated. In the obtained non-traditional glasses Zachariasen's rule about the dominant participation of units with small coordination number (3 or 4) which are only corner shared is not satisfied. Mixed V-O-Me (Me= Mo, Zn) bonds are crucial for the glass formation.

3. It was extended the possibility for the synthesis of vanadate and molybdate phases applying melt quenching technique (bottom - up) and mechanochemical synthesis (up-down).