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DSC INVESTIGATION OF CAESIUM BORATE GLASSES

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ABSTRACT

The Thermodynamic properties of $XCs_2O\cdot(1-X)B_2O_3$ (X - molar fraction of Cs_2O, $0\leq X\leq 0.4$) glasses and crystals at 200-1100 K were DSC studied. The coincidence of heat capacity of stable and metastable melts of the same composition was observed. The variation of heat capacity per mol. with composition is connected with nonmonotonous change of the glass and crystal structure with increasing content of Cs_2O.

DSC study of glass forming systems gives the possibility to obtain the thermodynamic description of glass - metastable liquid- - crystal - stable melt transitions in a ran. This information is very useful for understanding of glass nature.

The thermal properties of caesium borate glasses and crystals were obtained using DSC 111 "Setaram" at heating rates 5 and 20 K/min. Preliminary results are communicated now.

The heat capacity (C_p) of caesium pentaborate in crystalline and glassy states as a function of temperature is shown in fig. 1. As shown there heat capacity of metastable liquid is temperature independent and its value coincides with the one for the stable melt obtained by fusion of the crystal.

Heat capacity for $0.33Cs_2O\cdot 0.67B_2O_3$ glass (composition was determined with chemical analysis) versus temperature is snown in fig. 2. The intensive exothermic effect following the glass transition is due to crystallization process. We observed the crystallization of glasses with X 0.25. In conformity to phase diagram three endothermic effects at 895, 970 and 1030 K are attributed to eutectic fusion, peritectic departure and going through liquidus curve accordingly. Hence the correct composition is 0.34- -0.345Cs_2O. This is convincing example of DSC application for the

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verification of composition as a problem inverse to the determination of phase diagram!

The variation of glass transition temperature (T_g) and crystallization temperature ($T_{cr.}$) with composition is shown in fig. 3. T_g variation resembles the liquidus line.

The variation of heat capacity with composition at three selected temperatures is shown in fig. 4. This C_p variation seems to be associated with the change in structure of glass and metastable liquid with increase of Cs_2O content. Now it is widely accepted [1] that the structure of alkali borate glasses (melts) up to 30 - 35 mol.% of alkali oxide would be defined as polymerized structure composed of boron-oxygen groups similar to groupings occur in crystalline borates. Modifier cations are at the voids of the disorded frame-

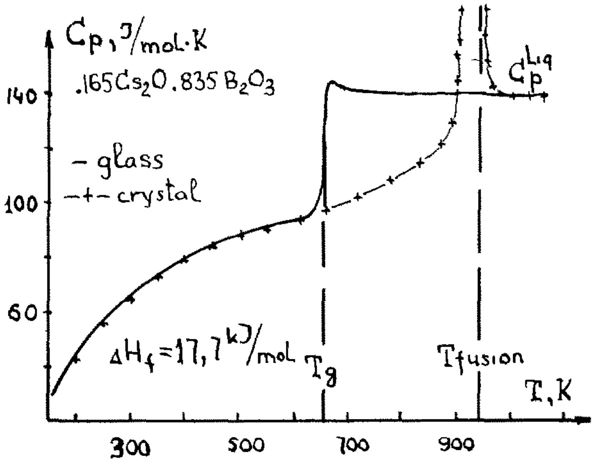

Fig. 1

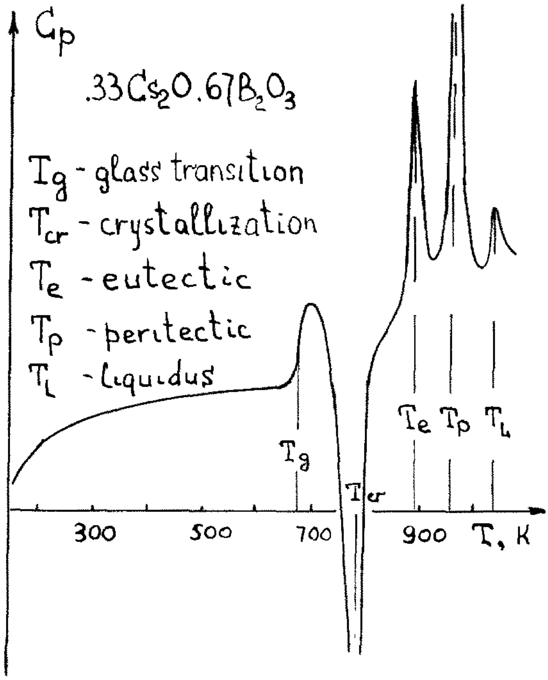

Fig. 2

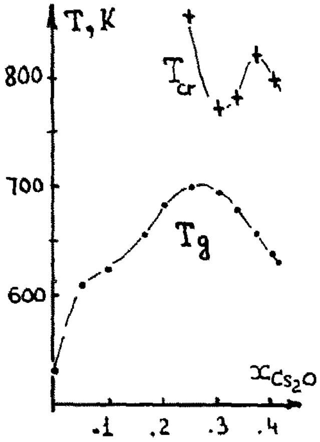

Fig. 3

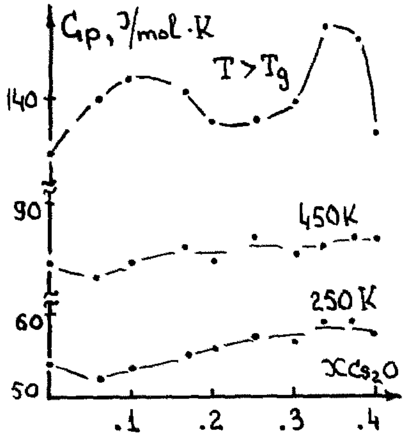

Fig. 4

work and are surrounded by bridging oxygens. The increase of alkali oxide content is followed by the appearance of nonbridging oxygens and destruction of the framework. The structure studies of crystalline caesium borates [1,2] show complicate change of their structure with composition. It is possible that similar effects may occur in glasses and melts. Variation of C_p with composition at $T < T_g$ doesn't show some singularities connected with the change of structure. This appears to indicate that only low frequency vibrations of Debye continium are excited at this temperatures. The vibrational modes of Cs - O bond seem to be excited completely already at 300 K [3] . At $T > T_g$ the excitation of the characteristic vibrations of different borate groupings becomes essential and as a result C_p is determined by them. So variation of C_p^L seems to reflect complicate changes of the melt structure with composition. It is noticeable that caesium triborate has the largest values of T_g, $T_{cr.}$ and T_{fusion} and the lowest C_p^L.

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