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CALORIMETRIC STUDY OF VITREOUS AND CRYSTALLINE RUBIDIUM AND CAESIUM BORATES

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ABSTRACT

Calorimetric study of vitreous and crystalline rubidium and caesium borates at 298 K was carried out. The enthalpies of formation from oxides for glasses and crystals as well as the heats of crystallization for glasses were calculated.

RESULTS AND DISCUSSION

The enthalpies of solution (ΔH_{sol}) in 2 N nitric acid at 298 K were measured for borate glasses containing 0 - 34.7 mol % Rb_2O, 0 - 42.5 mol % Cs_2O /1/ and for crystals of the $Me_2O \cdot n\ B_2O_3$ type, where Me = Rb n = 1,2,3,4,5; Me = Cs n = 1,2,3,4,5,9 (fig. 1a, 1b). The accuracy of thermal effect measurements is ± 0.1 kcal/mole.

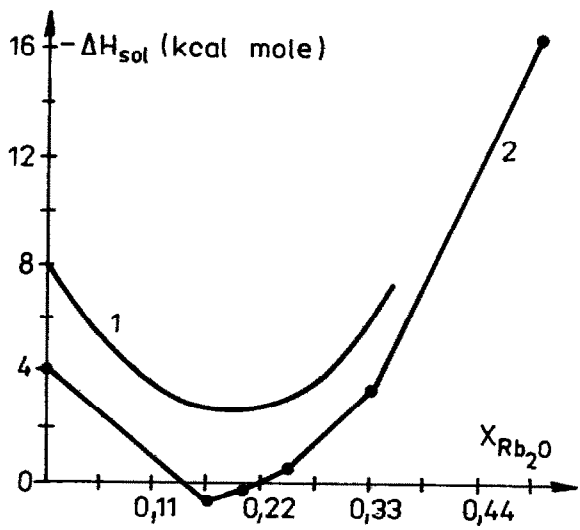

Fig. 1a. Enthalpies of solution for rubidium borate glasses and crystals.
1 - glasses
2 - crystals

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The samples studied were made by fusing chemically pure boric acid and alkali carbonates in a platinum crucible at 1200° C for 3 hours. The glasses were obtained by quenching the melts, the crystals were produced by annealing the glasses.

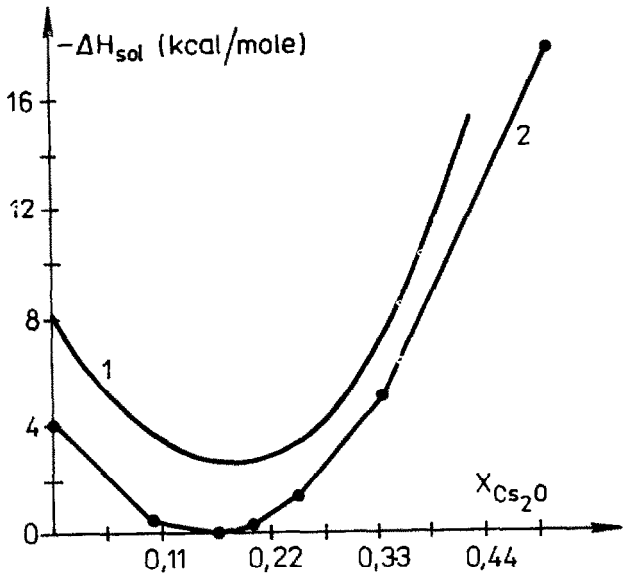

Fig. 1b. Enthalpies of solution for caesium borate glasses and crystals.
1 - glasses
2 - crystals

From the experimental data the enthalpies of formation (ΔH_{form}) from vitreous boron oxide and crystalline rubidium and caesium oxides were calculated for all glasses and crystals studied (fig. 2a, 2b). The accuracy of this computation is $\pm$ 0.2 kcal/mole. The results obtained reveal that the formation of vitreous and crystalline rubidium and caesium borates is highly exothermal. This negative deviation from ideality is due to the strong chemical interaction of the components.

The heats of crystallization of glasses (ΔH^{glass}_{cryst}) were calculated as a difference between the ΔH_{sol} values for vitreous and crystalline borates of the same composition (fig. 3, 4). The accuracy of this computation is $\pm$ 0.2 kcal/mole. The straight lines in fig.3,4 characterize the partial contribution of boron oxide ($\Delta H^{B_2O_3}_{cryst}$) to the heats of crystallization. The $\Delta H^{B_2O_3}_{cryst}$ values may be attributed to the ordering of the boron-oxygen units caused by crystallization. It is evident (fig. 3, 4) that

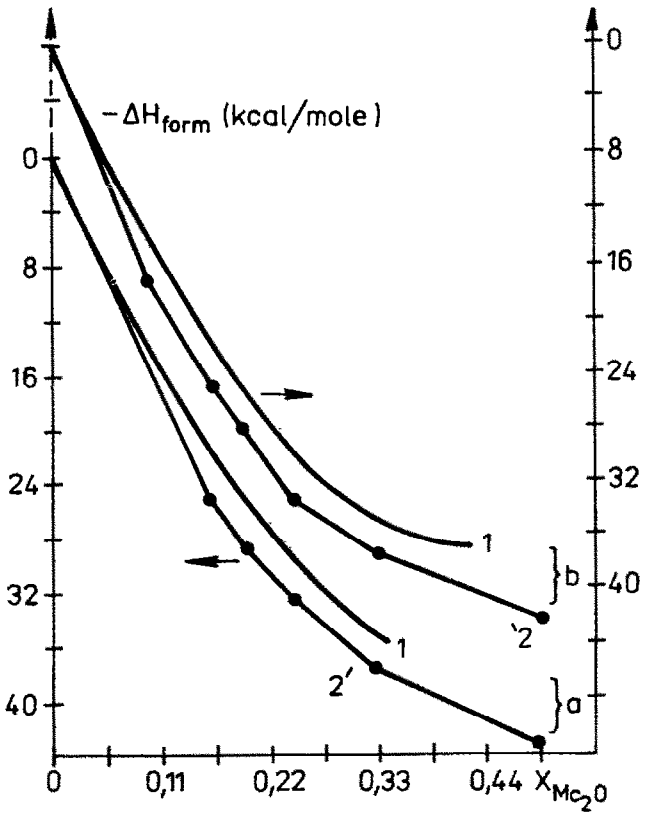

Fig. 2a, 2b. Enthalpies of formation for rubidium (a) and caesium (b) borate glasses and crystals
1 - glasses
2 - crystals

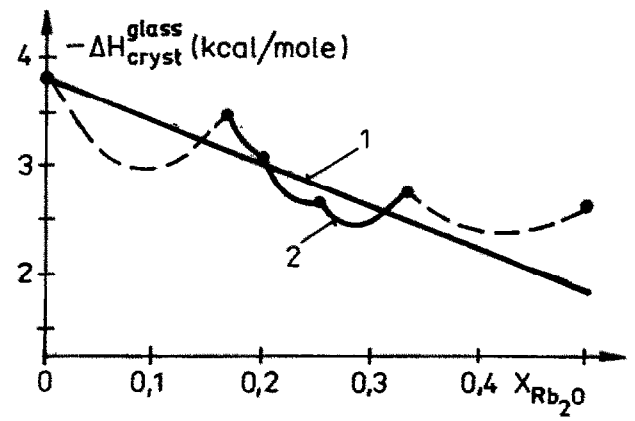

Fig. 3. Partial contribution of boron oxide (1) to the heats of crystallization of rubidium borate glasses (2)

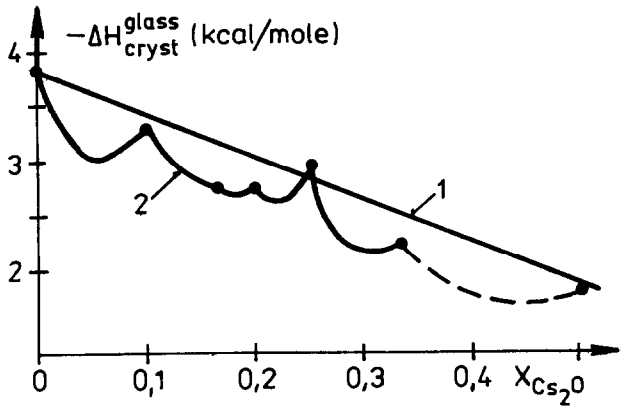

Fig. 4. Partial contribution of boron oxide (1) to the heats of crystallization of caesium borate glasses (2)

the $\Delta H^{B_2O_3}_{cryst}$ values make the main contribution to the heats of crystallization of glasses, because the ΔH^{glass}_{cryst} values (~ 2 - 4 kcal/mole) differ from the $\Delta H^{B_2O_3}_{cryst}$ values by 0.5 kcal/mole at most. This difference might result from the ordering of the cation-oxygen units in the course of crystallization. The small thermal effects of the ordering process indicate that the cation ordering in glasses is rather high. This is consistent with the results given in /2/.

CONCLUSIONS

The rubidium- and caesium-borate systems are characterized by considerable negative deviation from ideality resulting from strong acid-base interaction of the components. The heats of crystallization of alkali borate glasses are mainly determined by the crystallization effects for boron oxide.

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