THE THERMODYNAMIC MODELLING OF SYNTHESIS OF CRYSTALS IN MULTICOMPONENT BORATES SYSTEMS

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The present work is showing the thermodynamic modelling of crystallization of compound $Pb_2B_5O_9Br$ in hydrothermal conditions in system $PbCO_3 – B_2O_3 – KBr – H_2O$ is based on experimental data. This method has allowed to allocate areas of formation of phases and has helped to plan a way on which it is possible to have purposeful synthesis of compounds. A series of experiments has lead and thus we have received the scheme of areas crystallization $Pb_2B_5O_9Br$.

The theoretical calculations required thermochemical researches of $Pb_2B_5O_9Br$ and definition thermodynamic constants. The received constants of thermodynamic constants $Pb_2B_5O_9Br$ are presented in table 1.

Table1. Thermodynamic constants of $Pb_2B_5O_9Br$

$\Delta_f H^o_{el}$(298.15 K)[a], kJ/mole	S^o(298.15 K)[b], kJ/mole	$\Delta_f G^o_{el}$(298.15 K)[b], kJ/mole
-3826.1± 9.2	319	-3576

[a] – It was certain in this work
[b] – It was estimated in this work

We used the 7-componental system (H-B-C-O-K-Br-Pb) for thermodynamic calculation of experiments. The model has a 7 solid phases ($Pb_2B_5O_9Br$, PbO, $PbCO_3$, H_3BO_3, KBr, $Pb(BO_2)_2$, PbB_4O_7) and a water solution containing of 36, ions and complexes. The calculation of balance carried out by program complex HCh [1]. Thermodynamic properties of solid phases and components of a water solution took from database UNITHERM from the same software package. The composition of system set in an interval of the received experiments, but was more widely as much as possible to characterize area of stability of the phase.

Calculation results show that PbO and cerussite are stabile in boron free system. Only cerussite is stabile without bromine. Addition of boron with presence of KBr produces the crystallization of $Pb_2B_5O_9Br$ by reaction:

$$2PbCO_3+5H_3BO_3+Br^-=Pb_2B_5O_9Br+2HCO_3^-+6H_2O+H^+ \quad (1)$$

This reaction, besides concentration of B and Br, depends from pH and activity bicarbonate-ion. Fig. 1 shows the calculation values of pH. All values of pH are alkaline, that corresponds to a carbonate buffer. The values of pH in the field of $Pb_2B_5O_9Br$ are practically constant. At the correlation of components close to stehiometry, for reaction (1) crystallization $Pb_2B_5O_9Br$ is fullest. The calculation maximal output of a phase is observing at B_2O_3 – 1500–2000 g/kg H_2O and $PbBr_2$ – 200 – 600 g/kg H_2O.

Fig. 2 shows conditions of the experiments which lead with considering of thermodynamic modelling in which formed good crystals $Pb_2B_5O_9Br$ are suitable for diagnostics and definition of properties put to the scheme. All of them are close to border of disappearance cerussite and stehiomethry of reaction (1). The comparison of results of experimental and theoretical research of system has showed that they are identical and allowed to establish optimum conditions of crystallization of phases.

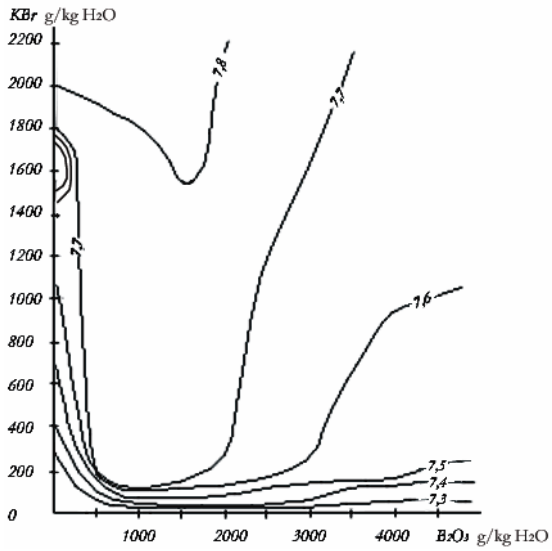

Fig.1. The calculation values of pH at 280°C for system $PbCO_3 – B_2O_3 – KBr – H_2O$

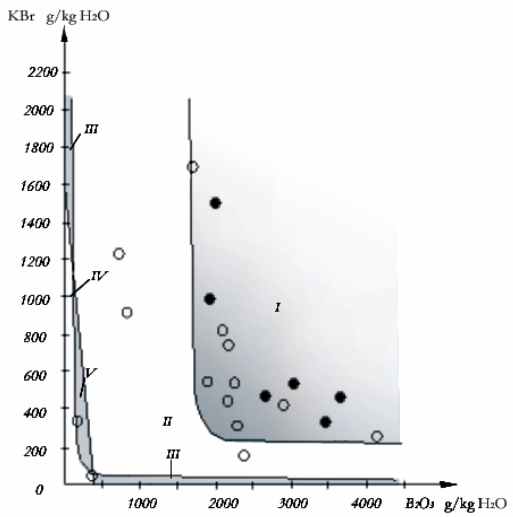

Fig.2. Calculate phase associations at temperature 280º C depending on structure of system $PbCO_3 – B_2O_3 – KBr – H_2O$.
I – $Pb_2B_5O_9Br$, II – $Pb_2B_5O_9Br$ and cerussite ($PbCO_3$), III – cerussite ($PbCO_3$) and PbO, IV – PbO, V – $Pb_2B_5O_9Br$, cerussite ($PbCO_3$) and PbO

○ the date of the experiments
● the date of the experiments which lead with considering of thermodynamic modeling

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