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THERMAL ANALYSIS OF CERTAIN SULPHIDE-SODIUM SYSTEMS

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Abstract

Our studies have shown that in the systems studied complex sulphides(thiosalts) of non-ferrous metals and sodium were formed.

The results of the study of double sulphide systems Na_2S-MeS(Me- ZN, Cd Tl, In,Sb) conducted with the aim of defining of regionsof existence of possible interconnections and plotting of phase diagrams are given in this paper.

The study of the systems was conducted by the methods of differencial thermal analysis(DTA) on the cooling curves, X-ray phase and microscopic analysis.

Na_2S-ZnS system. On the basis of received experimental data phase diagram of the system was made. It was found only two compounds $ZnS \cdot Na_2S$ and $ZnS \cdot 3Na_2S$, crystallisation of which proceeds according to peritectic at the temperatures 615±5° C and 820±5°C, respectively. Compounds $ZnS \cdot Na_2S$ and $ZnS \cdot 3Na_2S$ at 605±5°C form eutectic with the composition 49% of Na_2S and 51 % of ZnS.

The study has confirmed the character and temperature of phase transition α - ZnS ⇄ β - ZnS. It was found out the fact of forming in the system with porphyrous structure of initial crystallization with polytype modification from the system melts at the temperatures 900-620°C. Formation of other compounds was not confirmed(for example $2Na_2S \cdot ZnS$, $ZnS \cdot 5Na_2S$)(1).

Na_2S-CdS system. Presence of 3 unknown before individual compounds and of 4 biphase groups of melts in this system was succeeded to find out. Compounds $Na_2S \cdot Cd$ S and 3 $Na_2S \cdot CdS$ are crystallized according to peritectic at the temperatures 900±5 and 850±5°C respectively and the compound $2Na_2S \cdot Cd$ S is melted at the temperature 840± 5°C.

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Compounds $3Na_2S \cdot CdS$ and $2 Na_2S \cdot CdS$ form at $805 \pm 5°C$ eutectic containing 45 % CdS and compounds $2Na_2S \cdot CdS$ and $Na_2S \cdot CdS$ at $790 \pm 5°C$ form eutectic containing 52 % CdS.

New X-ray diffraction and mineralogic characteristics for these compounds are received(2).

Small quantity of cubic modification of CdS-hawlyite was found out in immersion preparation. Consequently phase transition greenockite $\rightleftarrows$ hawlyite takes place during CdS and Na_2S melting. Most intensely tis process takes place at the contents of 15 % of Na_2S in the system. Line intensity redistribution on the diffractogramm is observed in this case and hawlyite lattice parametre is a= 5,73 A, at standard data a= 5,818 A. Analoguous phenomenon was noted and in the system $Na_2S - ZnS$ where wurtzite transforms into sphalerite at the small contents of Na_2S.

Na_2S-Tl_2S system. System state diagram was constructed on the basis of received experimental data. It was found only two compounds $2Na_2S \cdot Tl_2S$ and $Na_2S \cdot Tl_2S$, crystallization of which proceeds according to peritectic at the temperatures $615 \pm 5°C$ and $400° \pm 5°C$ respectively. Compound $Na_2S \cdot Tl_2S$ and primary compound Tl_2S form eutectic characterized by melting temperature $300 \pm 5°C$ and Tl_2S contents 91 %.

The systems melts containing more than 85 % of Tl_2S consist of the mixture of thiosalt Na_2S Tl_2S and Tl_2S which is presented by three modifications.

Na_2S-In_2S_3 system. State diagram of the Na_2S-In_2S_3 system was constructed according to the results of analysis of cooling thermograms and X-ray phase studies. Occurence of 3 chemical compounds was found out. The compound $Na_2S \cdot In_2S_3$ with melting temperature 920°C is formed when the system contains 19.5 % Na_2S. Results received by us deviate a little from the data given in the literature where according to the results of optical analysis the sulphoindate sodium crystals are related to rhombic syngony. X-ray structural analysis allowed to find out that $Na_2S \cdot In_2S_3$ crystals belong to hexagonal syngony with the lattice parameters a= 3,79, b=19,80 A (3).

Two other compounds are unknown from the literature. The first of them containing 49 % Na_2S fits the formula $4 Na_2S \cdot InS_3$

This compound melts incongruently at 690°C, the second compound fitting the formula 5 $Na_2S \cdot In_2S_3$ melts incongruently at 700± 5°C. The most low melting eutectic is formed by the compounds $Na_2S \cdot In_2S_3$ and 4 $Na_2S \cdot In_2S_3$. It contains 42 % of Na_2S melts at 660°C. In_5S_6 presence is found in the melts containing 3-15 % Na_2S with the help of X-ray structure analysis. It is possible that in this region takes place S redistribution among original sulphides, in the result of which sodium polysulphide and In_5S_6 are formed(4).

Na_2S- Sb_2S_3 system. Three chemical compounds were found during the study of this system. The melting of compounds Na_3SbS_3 and $Na_2S \cdot 2\ Sb_2S_3$ takes place incongruently at the temperatures 550 and 480°C respectively and compound $NaSbS_3$ melts congruently at the temperature 700°C.

We failed to find other compounds in the system studied. Compound Na_3SbS_4 was synthesized from Na_2S and Sb_2S_5 under certain conditions. Its X-ray structural and mineralogical Characteristics were defined. The presence of compound $Na_6Sb_4S_9$ was not confirmed.

REFERENCES

1 Kopylov N.I., Polyvyanny I.R., Ivakina L.P., Antonyuk V.I. Zhurnal neorganicheskoy himii 23 (1978) 3095
2 Polyvyanny I.R., Lata V.A., Ivakina L.P., Antonyuk V.I., Zhurnal neorganicheskoy himii 26 (1981) 1038
3 Antonyuk V.I., Klyuchnikov Yu.F., Lata V.A., Zhurnal neorganicheskoy himii 25 (1980) 1404
4 Polyvyanny I.R., Lata V.A., Antonyuk V.I., Zhurnal neorganicheskoy himii 22 (1978) 192.