SYNTHESIS OF BINARY PGE SULFARSENIDES

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Sulpharsenides of Platinum-Group Elements (PGE) except Pd are known as minerals with variable composition. The most common among them are irarsite, IrAsS, and hollingworthite, RhAsS. Although many data are published the limits of isomorphous replacements PGE-PGE are not determined till now. Very often the natural PGE sulpharsenides are heterogeneous and contain tiny inclusions of other minerals that hamper the solution of this question. For study the problem of isomorphous replacement between different PGE in "binary" sulfarsenides the preliminary experiments have been carried out within the systems RhAsS-PtAsS, RhAsS-RuAsS, RhAsS-PdAsS, PtAsS-IrAsS, and OsAsS-IrAsS.

The synthesis was made in vacuumed quartz ampoules. Every series consisted from 11 samples (through 10 mol.%). Charges (100mg) prepared from pure elements were dried during 2 hours in hot Ar (400°C) flow. Samples prepared were gradually heated till 1150°C and preheated at these Tº 12 hours. Then they were annealed at 760°C during 21 days, and quenched in ice water. RhAsS-PdAsS samples were slowly cooled from 1150°C with the furnace.

Because of the presence of very fine powder As, S, or AsS in the upper part of quartz tubes it is obvious that the synthesis was carried out under condensed conditions and at high S- and As-fugacities (Fig.1a). Small crystals, 1-20μ, present samples synthesised. They were studied using optic microscope, microprobe (SX-500), and scanning electron microscopy (JSM-5300 + LINK ISIS). The grain dimension of compound synthesised depends on PGE (Fig.1a-d). For example, crystals of sulpharsenides rich in Rh are smaller than sulpharsenides of other PGE.

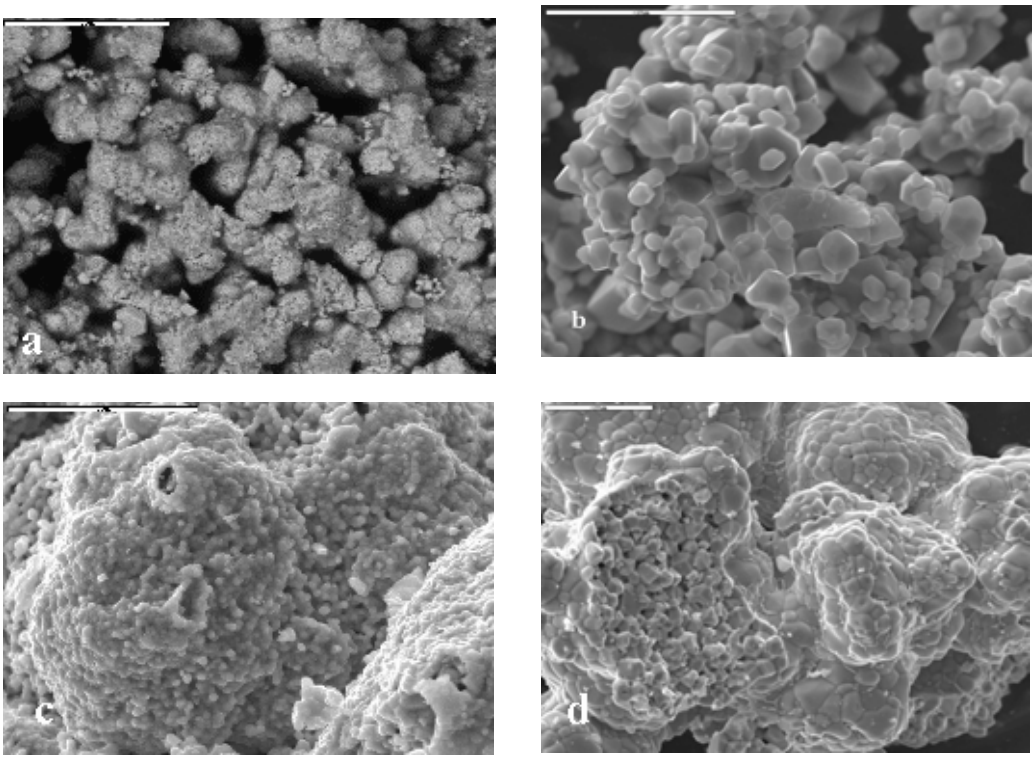

Fig.1. PGE sulpharsenides, synthesised in pseudobinary systems: a) PtAsS with 18.1 wt.% Ir; "spherules"– AsS. Scale – 20 μ; б) RuAsS с 5.77 мас.% Rh, Scale – 10 μ; c) RhAsS с 5.6 wt.% Ir, small crystals - IrAsS с 12.75 wt.% Rh, Scale – 10 μ; d) RhAsS с 15.06 wt.% Pt, Scale – 10 μ.

The solid solution series of different expansion are established in all systems studied. In hollingworthite-irarsite: RhAsS – $(Rh_{0.75}Ir_{0.25})$ AsS and IrAsS – $(Ir_{0.5}Rh_{0.5})$AsS. For hollingworthite - platarsite (RhAsS-PtAsS) the solid solutions are limited by 20 mol. % RhAsS in PtAsS, and 52 mol. % PtAsS in RhAsS. The limited solid solutions in the system RhAsS – RuAsS are RuAsS – $(Ru_{0.8}Rh_{0.2})$AsS and RhAsS – $(Rh_{0.9}Ru_{0.1})$AsS. The most narrow composition fields of end members are determined in the system OsAsS – IrAsS: (Os,Ir)AsS with ~3.5 mol.% IrAsS and (Ir,Os)AsS with ~5 mol.% OsAsS. The system PdAsS – RhAsS is characterized by two narrow miscibility gaps (~10 mol. %) at ~ 30 and 70 mol. % RhAsS. The direct correlation Pt-As and Rh-As found in sulpharsenides enriched in Rh and Pt possibly is due to the submicroscopic inclusions of $PtAs_2$ and Rh_2As. The elevated concentration of S found in some tiny crystals of sulpharsenides are caused by the sulphur powder covered synthesised material.

The comparison of experimental and natural PGE sulpharsenide shows the difference in composition of solid solution, especially in PtAsS-RhAsS and IrAsS-RhAsS series. Natural PGE sulpharsenide composition correspond to more large solid solution series: $(Pt_{0.7}Rh_{0.3})$AsS - RhAsS and IrAsS - $(Pt_{0.8}It_{0.2})$AsS correspondingly. But the series of synthesizes solid solutions have PtAsS as the end member. This fact needs the additional study, but the main reason resides in the heterogeneity of natural minerals and in limitation of investigation methods. It is necessary to control the mineral homogeneity simultaneously with the composition (i.e. SEM+LINK ISIS).