FEATURES OF THE SKELETAL CRYSTALLIZATION OF NiAsS

CRYSTALLOGRAPHY

1970

SovietRxiv

Abstract

Full Text

UDC 548.524+575.546.74+19+221

CRYSTALLOGRAPHY

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FEATURES OF THE SKELETAL CRYSTALLIZATION OF NiAsS

IN GLASS OF As–S COMPOSITION

(A NEW FORM OF CRYSTAL GROWTH)

(Presented by Academician N. V. Belov, 9 IX 1969)

NiAsS was synthesized in a high-pressure chamber as a result of the interaction of glass of composition As–S with nickel at a temperature of 450–600° and a pressure of 30–70 kbar. Under these conditions, diffusion of nickel into the glass and crystallization of NiAsS are observed. The source of nickel was the walls of an ampoule made of nickel foil, or nickel plates introduced into the reaction volume. As a result of the experiments, cylindrical samples of glass (4×4 mm in size), or partially crystallized glass containing NiAsS crystals, were obtained. Polished sections were prepared from the samples obtained; their study showed similarity of the optical properties of the NiAsS crystals to those of the natural mineral gersdorffite. X-ray analysis showed the identity of the structure of synthetic NiAsS with the structure of gersdorffite.

As microscopic study showed, the NiAsS crystals are distributed in the glass mass along strictly definite directions. The size of individual grains varies rather considerably (from 0.5 to 50 μ). The shape of the grains is varied. Small grains are usually rounded or slightly elongated; larger grains have the shape of regular polyhedra (octahedra) or else the shape of skeletal octahedra, represented in section by crosses with forked ends (Fig. 1a, see insert facing p. 1035).

Single crystals of synthesized NiAsS are rare. Usually they form regularly oriented groups, in which the crystallographic orientation of all crystals, their sizes, and the distances between them remain constant. At the same time, the distances between crystals increase proportionally with the growth of the crystal sizes.

Three types of regular orientation of NiAsS grains may be distinguished.

Figure 1

Figure 1: Figure 1

1. Flat nets consisting of crystals arranged at equal distances (Fig. 1b). If the crystals have the shape of skeletal octahedra, it is clearly seen that in all of them the crystallographic axes are oriented identically. One of the fourth-order axes is always normal to the plane of the net. The size of the nets may reach 1.5 mm in length, with particles 2-3 μ in size. In individual areas, curvatures of the nets are observed.
2. The second group may include systems of two nets of the type described in point 1, intersecting at different angles. Systems of two nets intersecting at small angles and running almost parallel to one another are frequently encountered (Fig. 1c, d). In this group the crystallographic orientation of the crystals is somewhat different—in all the sections studied it is seen that the quaternary axes of the crystals lie in the planes of the bisectors of the angles formed by the nets.
3. Finally, the most frequently encountered are regular spatial lattices formed by systems of flat nets

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Fig. 1. *a* —a system of networks of cruciform crystals; *b* —a section of a network of cruciform crystals; *v* —a system of two intersecting networks; *g* —a distorted system of two networks; *d* —three-dimensional lattice of NiAsS; *e* —character of the grain boundaries of skeletal crystals; *zh* —orientation of crystals in intersecting networks; *z* —a twisted crystal. White —NiAsS, gray —As_2S_3 crystals, dark gray —glass of composition As_2S_3, black —polishing defects. Magnification: *a*, *b*, *v*, *g*, *d*, *e* —1000×; *zh* —200×; *z* —500×.

(Fig. 1d)*. The angles and distances between the networks are striking in their constancy and strict periodicity. All the component crystals have the same crystallographic orientation. The size of individual blocks with the same crystal orientation (such blocks may be called skeletal "single crystals") reaches 2 mm across, while the crystallites are 1-50 μ in size. The boundaries between the blocks are distinct (Fig. 1e); within them, foreign segregations of gersdorffite that do not fit into the system occur very rarely. A geometrical analysis of various sections of skeletal crystals showed that, most probably, the crystallites of the skeletal crystals are arranged along periodically repeating planes of the rhombododecahedron (011), with the direction of the quaternary axes of each of the crystallites coinciding with the direction of the quaternary axis of the rhombododecahedron. In those sections where the networks intersect at a right angle, one of the beams of the cross-shaped crystallites is always oriented along the direction of the chains (Fig. 1a), while in the chains forming a rhombic network the beams are oriented normal to the bisectors (Fig. 1g). If the networks intersect at an angle close to 60°, no crosses are observed.

Although we have studied a large number of sections, we still cannot say anything about the order of arrangement of the crystallites in the planar networks.

As in ordinary crystals, growth defects are observed in the formations described; moreover, it is not individual networks that undergo distortion (displacement, fracture, curvature, and twisting), but the entire skeletal crystal as a whole (Fig. 1z).

Thus, we have discovered a new form of crystal growth in the form of isolated crystallites, identically oriented crystallographically in space and forming a three-dimensional system of planar networks arranged in a strictly regular manner.

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Received
8 VIII 1969

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* Since the study was carried out only in plane sections, we can say nothing about the presence and distribution of one-dimensional chains of crystals.

Note: Figure translations are in progress. See original paper for figures.