SHORT COMMUNICATION

PREPARATION AND SURFACE OBSERVATION OF BERNDTITE (SnS_2) SINGLE CRYSTALS

YOSHINORI FUJIKI and YOSHIO ISHIZAWA

*National Institute for Researches in Inorganic Materials,
Kurakake, Sakura-mura, Niihari-gun, Ibaragi, Japan*

Single crystals of berndtite (SnS_2) were first synthesized by Oftedal (1926, 1928) to determine the crystal structure. Recently single crystals of this mineral were prepared by the chemical transport reaction from the points of interest in optical and electrical properties (Greenaway & Nitsche, 1965; Domingo *et al.*, 1966; Conroy & Park, 1968; Lee *et al.*, 1969). However, these experiments had no description of the growth mechanism and surface observation of the single crystals. Though this mineral is not common in nature, some example of its occurrence have been reported by Moh and Berndt (1964) and Moh (1969).

In this paper we shall describe the preparation of the SnS_2 single crystals grown by the chemical transport reaction and the surface observation relating to the growth mechanism.

Preparation

Starting materials used in this experiment were massive tin and flake-like iodine of the 5N purity, and powdered sulfur of the 4N purity, which were supplied by the Rare Metallic Co. Japan. Iodine was used as a transport reagent. All reactions were carried out in

vycor tubes in a size of 1.1 cm i. d. and 12 cm in length. The sealing procedure was performed under vacuum in 3×10^{-5} mmHg, where the vycor tube was immersed into liquid nitrogen to prevent vapourization of iodine.

The best crystals were grown during the transport from the 675°C zone to the 575°C zone, with the reaction time of 90 hours, and with the iodine concentration of 5 mg/cm³ in an ampoule. Crystals grown by this method are classified into two types: large thick platy crystals (100 microns) in reddish brown and smaller thin platy crystals (several microns) in golden yellow. The maximum crystal size of the former was 10×15 mm² and the latter 5×3 mm². The reddish brown crystals have been transferred to the most distant zone in the ampoule, and they occur in random aggregation in a subhedral form. The crystal of this type has not been reported previously. The golden yellow crystals occur in wide distribution and an euhedral or a subhedral form with random aggregation in the vycor tube. These two crystals gave an identical X-ray powder pattern.

Surface observation

1) Golden yellow crystal

The {0001} surfaces of golden yellow crystals were observed under the differential interference microscope. Growth spirals originating from the points of emergence of screw dislocations were usually recognized (Fig. 1). There are generally two types: single and composite spirals. Patterns of these growth spirals show trigonal and hexagonal symmetries, and are more distinct at the center than towards the outside in many growth hillocks consisting of curved spiral arms (Fig. 1). Interlaced spirals emanating from the same or different centers are often recognized. Also, it is noticed that dislocations in the boundary formed along the junction between two different crystals play a very important role as

Fig. 1. Differential interference microphotograph showing growth spirals on the basal plane of an SnS_2 crystal of golden yellow type. The left spiral emanates from the boundary formed along the junction between two different crystals and the right one shows trigonal symmetry with a composite spiral.

Fig. 2. Differential interference microphotograph showing a growth hillock on the basal plane of an SnS_2 crystal of reddish brown type.

a source of growth steps (Fig. 1). It was tried to measure the heights of the growth steps directly by the two beam interferometer, but was unsuccessful because of the very low height ($<300\text{\AA}$).

2) Reddish brown crystal

The basal planes of reddish brown crystals are characterized by large growth hillocks and high growth steps. The general growth pattern of this type is shown in Fig. 2. Although perfect spiral patterns were rarely observed, some spirals originating from a center of a screw dislocation were sometimes observed, and the heights of the steps were shown to be about $600\text{\AA}$ or about $1,000\text{\AA}$ by two beam interferometry.

Discussion

It is inferred from the surface observation that the screw dislocations on the basal planes and the dislocations in the boundaries formed along the junction between two different crystals play an

important role as growth mechanisms in the crystals of the two types. The spirals originating from the dislocation in crystal boundaries have been discussed by Morgan and Dunning (1970) with carbon tetrabromide crystals.

Reddish brown crystals were not obtained when a transport reagent was not used in one run, although golden yellow crystals and ottemanite (Sn_2S_3) were transferred. Also, reddish brown crystals have not been described in the previous works which used the same amount of iodine as in the present work. The formation of reddish brown crystals may be related to the amount of iodine in the ampoule after the sealing procedure, which will certainly call for special care because of the high vapour pressure of iodine. On the other hand, the electrical conductivity in the basal planes of reddish brown crystals is much larger than those of golden yellow crystals ($\sigma \sim 10^{-1} \Omega^{-1} \text{cm}^{-1}$ at room temperature for reddish brown crystals), and the impurity states or defect levels exist in the extrinsic range. It is surmised from the sample preparation that the impurity states of iodine are most probably responsible for the formation of this type of crystal. If the impurity states in reddish brown crystals are confirmed, we might say, from the differences in the impurity amounts and surface observations between reddish brown and golden yellow (2H-type) crystals, that the crystal of this type is of a long-period structure of stacking layers. Moh (1969) has synthesized by the solid reaction $\alpha\text{-Sn}_{1+x}\text{S}_2$ which is dark reddish brown to brown, but the crystallographic relation between $\alpha\text{-Sn}_{1+x}\text{S}_2$ and SnS_2 of the reddish brown type in the present work is not clear yet.

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