HYDROTHERMAL AND FLUX GROWTH OF CASSITERITE (SnO_2) CRYSTALS

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1. INTRODUCTION

Synthesis of cassiterite was first reported by Daubree in 1849. Thereafter cassiterite syntheses have been mainly made by the chemical transport reaction method from the points of interest in optical and electrical properties as a semiconductor (Marley and MacAvoy (1961), Reed *et al.* (1962), Nagasawa *et al.* (1965), Morgan and Wright (1966), Fonstad *et al.* (1969) and Crabtree *et al.* (1969)), except for a report on morphological study by Frankel (1947). There are also several reports on the growth conditions and crystal morphology for the hydrothermal synthesis of cassiterite by Smith (1947), Michel-Levy *et al.* (1947), Havill and Roy (1966) and Kuzmina and Litvin (1963). On the other hand, this mineral was also synthesized by Kunkle and Kohnke (1965) from Cu_2O flux using thermal gradient method, though they did not give any description of morphological features.

It is the purpose of the present paper to find the most suitable solvent for hydrothermal synthesis of cassiterite, and to grow this mineral using suitable fluxes. Morphological features are also described.

2. EXPERIMENTAL

SnO_2 powder of 99.99% was pressed to form a plate of $10 \times 10 \times 1$ mm at the

room temperature under a pressure of 500 kg/cm^2 which was then sintered for 20 h at 1000°C under 1 atm in air. The pressure vessel was a standard tube of 1/4 in. in ID. The hydrothermal reaction was conducted in sealed Au capsules placed in this pressure vessel. A SnO_2 plate was sealed in a capsule of 4 mm in ID and 15 mm long having a very small hole. This capsule and solvent were placed in the dissolution zone in a larger capsule (6 mm in OD and 70 mm long), which was sealed by welding (Fig. 1). The small capsule served as a baffle plate. The temperature gradient between the crystallization and dissolution zones was controlled to be 60 to 70°C on the outside of the pressure vessel.

Fig. 1. Gold capsules in the pressure vessel

On the other hand, PbF_2 of 99.99% purity, $\text{Na}_2\text{B}_4\text{O}_7$ powder of 99.9% purity and KF of guaranteed reagent were used as the fluxes. The standard method of flux growth was applied in this study using platinum crucibles of 30 or 50 ml. The

crucible was weighed before and after a run, and SnO_2 crystals were separated by dissolving the flux in 20% hot nitric acid.

Identification was made by microscopic examination and X-ray diffraction analysis. Crystal morphology was investigated by the universal stage method.

3. RESULTS AND DISCUSSION

Hydrothermal growth

Cassiterite crystals were grown in various solvents. The experimental conditions and the results are summarized in Table 1. In oxyhydride and carbonate solvents, large crystals in acicular form were grown from the solutions of Na_2CO_3 and NaOH . The maximum crystal size attains up to 3 mm at 600°C and 1000 atm for 170 h using 10 wt % Na_2CO_3 solvent (Fig. 2). Smaller crystals were also formed from the solvents of KOH and K_2CO_3 . Irregular polyhedral grains were formed in KOH solvent, and an aggregation of irregular polyhedral grains and acicular crystals were obtained in K_2CO_3 solvent. Short prismatic crystals of smaller

size were grown from solvents of LiCl and NaCl (Fig. 3), polyhedral grains of irregular form usually coexisting in the latter solvent. Crystals are colorless.

On the other hand, cassiterite crystals were effectively grown from fluoride solutions of potassium, sodium hydrogen and ammonia. Crystals attaining 2 mm in sizes of polyhedral form were grown at 600°C and 1000 atm for 140 h using 10 wt % NH_4F (Fig. 4). It was found that SnO_2 is quite soluble in solutions of NH_4F and HF ; SnO_2 was usually transported from the cold zone to the hot zone, namely it has a retrograde solubility. It was also found that crystals grown from solvents of NH_4F and HF are always colored from bluish to black. The color is inferred to the oxygen deficiency, since, annealing of colored crystals at 700°C change their color to colorless or pale brown. When oxidizer such as a solution of 1 wt % KClO_3 were added to 10 wt % MH_4F solvent at 600°C and 1000 atm, crystals were grown in colorless to pale brown. The density of an aggregation of the black

Table 1. Comparison of cassiterites grown hydrothermally from various solvents.

Temperature	Pressure	Solvent	Duration	Comments
°C	atm	wt %	hours	
600	1000	10 % NaOH	138	acicular, 1 mm long
550	1000	10 % KOH	145	polyhedral grain, 0.2 mm
600	1000	10 % Na_2CO_3	168	acicular, 3 mm long
600	1000	10 % K_2CO_3	140	polyhedral grain and acicular, 0.1 mm
550	1000	10 % NH_4HCO_3	163	no reaction
550	1000	10 % NaCl	138	short prismatic, 0.3 mm long polyhedral grain, 0.2 mm
600	1000	10 % LiCl	190	short prismatic, 0.3 mm long
500	500	10 % NH_4Cl	65	polyhedral grain, 0.1 mm
600	1000	10 % NH_4F	140	polyhedral grain, 2 mm bluish to black
500	1000	10 % HF	160	polyhedral grain, 0.5 mm bluish to black
650	1000	10 % KF	187	polyhedral grain, 0.5 mm colorless to brownish
600	1000	3.5 % NaF	160	acicular, 0.1 mm long

Fig. 2. Acicular crystals of SnO_2 grown at 600°C under 1000 atm for 138 h using 10 wt % NaOH solvent

Fig. 3. Short prismatic crystals of SnO_2 grown at 600°C under 1000 atm for 190 h using 10 wt % LiCl solvent

Fig. 4. Twinned crystals of SnO_2 grown at 600°C under 1000 atm for 140 h using 10 wt % NH_4F solvent

crystals was measured to be 6.724 (the theoretical density is 7.082) by the Barman density balance, and the composition calculated from which was $\text{SnO}_{1.33}$.

An interesting mode of occurrence was observed in a run using 10 wt % KF solvent; relatively large polyhedral crystals are grown in the cold zone, whereas crystals

formed at the most distant portion from the nutrient were small and acicular. It is conjectured that the habit change from polyhedral to acicular is related to the temperature difference in the solvent, confirming the observation by Marley and MacAvoy (1965) on SnO_2 crystals grown from the vapor phase.

Acicular crystals grown from alkali solvents are characterized by the well development of $\{100\}$ and $\{101\}$ faces, elongated parallel to the c -axis (Fig. 5-(a)). Short prismatic crystals grown from LiCl solvent also show similar combination of faces. These often show rutile-law twinings with composition plane of $(01\bar{1})$ (Fig. 5-(b)). Crystals grown from fluoride solutions are rather complicated, with well developed $\{110\}$, $\{111\}$, and $\{322\}$ faces, and most of them are twinned after rutile-law (Fig. 5-(c)).

Although crystal surfaces were examined under the differential interference microscope, clear patterns were not detected, except for the $\{100\}$ faces of some acicular crystals, on which spiral-like growth layers develop (Fig. 6).

Harvill and Roy (1966) have reported that the SnO_2 crystals grown hydrothermally from a KOH solvent show only (110) and (101) faces, which are in accordance with the prediction of Hartman's theory (Hartman and Perdok (1955)). According to Hartman (1966) the (110) and (101) faces are a F -face; the (100) , an S -face; and the (111) , a K -face in rutile type oxides such as SnO_2 . In the present work, it was found that the external form of crystals is remarkably affected by the nature of solvents, though some crystals may be related to the temperature difference. The habit change of SnO_2 crystals seems to be composition

Fig. 5. Typical habits of SnO_2 crystals grown hydrothermally; (a) Acicular and short prismatic crystals, (b) Twinned crystal from alkali solvents, (c) Twinned crystal from fluoride solvents

Fig. 6. Growth pattern on {100} faces of acicular crystal grown at 600°C under 100 atm for 168 h using 10 wt % Na_2CO_3 solvent

Fig. 7. SnO_2 crystals growth from the $\text{Na}_2\text{B}_4\text{O}_7$ flux

sensitive. Typical habits of these crystals are characterized by the development of S- and K-faces rather than F-face.

Flux growth

(a) $\text{Na}_2\text{B}_4\text{O}_7$ and $\text{Na}_2\text{B}_4\text{O}_7$ -KF flux

Both $\text{Na}_2\text{B}_4\text{O}_7$ and $\text{Na}_2\text{B}_4\text{O}_7$ -KF fluxes were tried. It was found that $\text{Na}_2\text{B}_4\text{O}_7$ did not fit well as a flux because of its low degree of convective mixing in a very viscous liquid. However, if KF is added, SnO_2 dissolves remarkably, since viscosity of the melt decreases. Thus, $\text{Na}_2\text{B}_4\text{O}_7$ -KF system was mainly used as fluxes. SnO_2 crystals grown spontaneously from a $\text{Na}_2\text{B}_4\text{O}_7$ flux are in tabular form (Fig. 7). By adding KF

in the flux, crystals change gradually their habit from tabular, through short prismatic, to acicular with the increase of KF component. The growth conditions and the results are given in Table 2.

Relatively large crystals were obtained in the system of a starting composition, SnO_2 15 wt %, $\text{Na}_2\text{B}_4\text{O}_7$ 42.5 wt % and KF 42.5 wt %; flux loss was 10 wt % during cooling from 1000°C to 870°C at a rate of 2°C per hour. Crystals formed in this system were mostly acicular, attaining the maximum size of $0.2 \times 0.2 \times 5$ mm on edge length (Fig. 8). They usually coexist with a small amount of dendritic crystals.

(b) PbF_2 flux

SnO_2 crystals were also grown from

Table 2. Growth conditions and morphology of SnO_2 crystals grown in some fluxes.

Starting composition				Maximum temp.	Cooled to	Cooling rate	Weight loss of flux	SnO_2 crystals
SnO_2	$\text{Na}_2\text{B}_4\text{O}_7$	KF	PbF_2					
wt %	wt %	wt %	wt %	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	wt %	mm
7.7	92.3	—	—	1200	860	4	5.5	tabular, 0.5×0.3
8.2	88.5	3.3	—	1100	820	4	1.8	tabular, 1×0.3
18.5	74.7	6.8	—	1200	890	4	1.2	tabular, 1×0.3 acicular
13.0	43.5	43.5	—	1000	870	2	9.2	acicular, 5×0.1
5.7	—	—	94.3	990	820	2	25.0	acicular, 2×0.2
7.2	—	—	92.8	1000	790	2	26.4	acicular, 2×0.2

Fig. 8. SnO_2 crystals grown from the $\text{Na}_2\text{B}_4\text{O}_7$ -KF flux Fig. 9. SnO_2 crystals grown from the PbF_2 flux

PbF_2 flux (Table 2). Relatively large crystals were obtained in the system of a starting composition of SnO_2 8 wt % and PbF_2 92 wt %; flux loss was about 25 wt % during cooling from 1000°C to 800°C at a rate of 2°C per hour. Crystals attained $0.4 \times 0.4 \times 2$ mm on edge length (Fig. 9). They usually grow on the crucible wall near the surface of the flux melt, and are mostly acicular in form, and coexist with a small amount of dendritic crystals.

(c) Morphological features

The tabular crystals grown spontaneously from the $\text{Na}_2\text{B}_4\text{O}_7$ flux are composed of $\{100\}$, $\{120\}$ and $\{101\}$ faces, with characteristic development of $\{100\}$ (Fig. 10-(a)). The direction of their elongation inclines at 57° to the c-axis. This sort of habits has not been reported among natural cassiterite. In contrast, the acicular crystals grown

in the $\text{Na}_2\text{B}_4\text{O}_7$ -KF flux usually elongate parallel to the c-axis, and are mainly composed of $\{100\}$, $\{110\}$ and $\{101\}$ faces (Fig. 10-(b)). It is noticed that the habit of the acicular crystals is characterized by the development of the $\{110\}$ faces in comparison with those grown hydrothermally, which are composed of the well developed $\{100\}$ and $\{101\}$ faces. Some crystals are twinned, whose composition plane is $(01\bar{1})$ (Fig. 10-(c)).

Crystals grown in the PbF_2 flux are rather complicated, mainly bounded by $\{111\}$, $\{131\}$, $\{421\}$, $\{121\}$ and $\{411\}$ faces (Fig. 10-(d)). They do not elongate in the c-axis direction. This sort of habits has also not been reported among natural cassiterite.

The $\{111\}$ surfaces of SnO_2 crystals grown in the PbF_2 flux were observed under the differential interference microscope. Growth patterns consisting of polygonal

Fig. 10. Typical habits of SnO_2 crystals grown in the fluxes; (a) $\text{Na}_2\text{B}_4\text{O}_7$ flux, (b) $\text{Na}_2\text{B}_4\text{O}_7$ -KF flux, (c) twinned crystal, $\text{Na}_2\text{B}_4\text{O}_7$ flux, and (d) PbF_2 flux.

bunched layers are usually observed (Fig. 11). Their step heights were measured by the two-beam interferometer to be several hundred to several thousand angstrom.

Fig. 11. Growth pattern on the $\{111\}$ surface of SnO_2 , PbF_2 flux

4. SUMMARY

Cassiterite crystals were hydrothermally grown from various solvents. In order to grow large crystals, it was found that the solvents of Na_2CO_3 and NH_4F were the most suitable, followed by the solutions of NaOH , HF and KF . Crystals grown from the solvents of NH_4F and HF , in which SnO_2 has a retrograde solubility, were bluish to black due to the oxygen deficiency. Morphological features of these crystals were divided into acicular, short prismatic and equidimensional polyhedral. Most polyhedral

crystals grown in the fluoride solvents are twinned after rutile-law.

Cassiterite crystals were grown by the slow cooling method using the fluxes of $\text{Na}_2\text{B}_4\text{O}_7$, $\text{Na}_2\text{B}_4\text{O}_7$ -KF and PbF_2 . It was observed that SnO_2 crystals change their habit systematically from tabular, through short prismatic, to acicular by adding KF component into $\text{Na}_2\text{B}_4\text{O}_7$. Crystals grown from the PbF_2 flux also acicular, whose $\{111\}$ faces exhibit polygonal thick growth layers.

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水熱およびフラックス法による Cassiterite (SnO_2) 単結晶の育成

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水熱法では SnO_2 単結晶を種々溶媒を用いて育成した Na_2CO_3 と NH_4F の溶媒から最も大きい結晶が育成され、次いで NaOH , HF , KF の各溶媒が育成に適することがわかった。とくに、 NH_4F と HF 溶媒中では逆溶解現象を示し、かつ育成された結晶は酸素欠損の程度により淡青から黒色を呈する。全体として結晶の形態は溶媒により異なり、主に針状、短柱状、粒状のいずれかを呈する。なお、 NH_4F , HF 溶媒で育成した結晶の大部分はルチル型双晶を示す。

フラックス法では $\text{Na}_2\text{B}_4\text{O}_7$, $\text{Na}_2\text{B}_4\text{O}_7\text{-KF}$, PbF_2 の各フラックスを用いて徐冷法で育成した。とくに、 $\text{Na}_2\text{B}_4\text{O}_7$ の単独で育成すると、板状であるが、 KF 成分を混合すると、その添加量に応じて短柱状から針状へと形態変化をする。また、 PbF_2 から育成すると針状であるが、非常に複雑な形態を示し、かつ $\{111\}$ 面には厚い成長層が特徴的に観察される。