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GROWTH OF TIN (IV) OXIDE CRYSTALS FROM FLUX OF B_2O_3-V_2O_5 SYSTEM

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Needle crystals of SnO_2 were grown from the melt of B_2O_3-V_2O_5 system containing Zn_2SnO_4. Increasing the soaking temperature and the V_2O_5 content of B_2O_3-V_2O_5 system tended to increase the size of crystals. The growth direction of the crystals was along the c-axis of SnO_2.

The single crystals of tin (IV) oxide have been grown from the vapor phase by several authors.[1-3] On the other hand, none is reported on the flux growth except for the case of Cu_2O flux,[4] the use of which makes it difficult to operate above 1250°C owing to the reaction of Cu_2O with Pt crucible.

We reported the effects of B_2O_3 or V_2O_5 additive on the sintering of Zn_2SnO_4[5]; the sintering of Zn_2SnO_4 is accelerated via the dissolution process of Zn_2SnO_4 in the molten oxide of B_2O_3 or V_2O_5. It can be thought on the basis of the result that the oxide B_2O_3 or V_2O_5 is a suitable flux for dissolving Zn_2SnO_4. As a result of the solubility measurements of Zn_2SnO_4 in B_2O_3 and/or V_2O_5 melts, it was found that Zn_2SnO_4 could be dissolved in the molten oxides mixture with the composition of $2B_2O_3.V_2O_5$ in contrast with the very poor solubility of Zn_2SnO_4 in the one composition melt of B_2O_3 or V_2O_5 at 1300°C. As the temperature was cooled down, SnO_2 crystals were obtained in the melt of $2B_2O_3.V_2O_5$-Zn_2SnO_4 system. This report describes the growth of SnO_2 single crystals from the melts of B_2O_3-V_2O_5 system containing Zn_2SnO_4.

The starting materials were of G.R. grade. Zn_2SnO_4 samples were prepared by calcining the mixed powders of ZnO and SnO_2 in the stoichiometric ratio of Zn_2SnO_4 at 1300°C for 4 hrs. Mixed powders of Zn_2SnO_4, B_2O_3 and V_2O_5 were placed in a 30 ml Pt crucible. These were soaked at various temperatures between 1210°C and 1340°C for 10 - 16 hrs in air and then the SnO_2 crystals were grown by cooling from the soaking temperature to 900°C with cooling rate of 1.8 - 5°C/hr. The crystals were removed from the remaining flux by leaching in a hot 50 % nitric acid.

Figure 1 shows the needle crystals of SnO_2 grown at the surface of B_2O_3-V_2O_5 flux. Table 1 illustrates the experimental results of the SnO_2 crystals grown under the various conditions. From Table 1, it can be found that the higher the soaking temperature (runs 1-4), the lower the cooling rate (runs 3 and 7) and the higher the V_2O_5 content of B_2O_3-V_2O_5 system (runs 3, 5

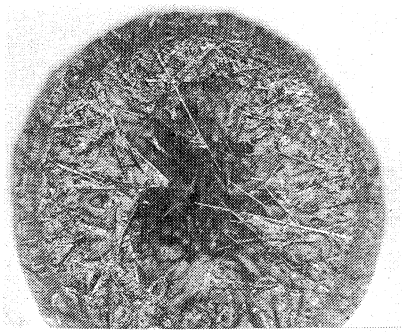

Fig. 1 The needle crystals of SnO_2 at the surface of B_2O_3-V_2O_5 flux (run 3).

and 6), the larger the needle crystal of SnO_2 in both length and width. The SnO_2 crystal was pale brown. The SnO_2 crystals grown at higher soaking temperature or under higher V_2O_5 content tended to become brown. The result of X-ray rotation photograph indicated that the long dimention was the c-axis direction. The cross section of as-grown crystal perpendicular to the growth direction was square.

The pellet of Zn_2SnO_4 or ZnO could be dissolved in the $2B_2O_3.V_2O_5$ melt at 1300°C, while the SnO_2 pellet was hardly dissolved in this melt (these pellets of 20 mm width and 2 mm thick were sintered at 1300°C). From this result, it is concluded that the dissolution of the ZnO component in Zn_2SnO_4 into the $2B_2O_3.V_2O_5$ melt results in the dissolution of the other hardly dissolved SnO_2 component in it. The fact that the larger SnO_2 crystal has been grown at the higher soaking temperature and under the higher V_2O_5 content (Table 1) suggests that increasing the soaking temperature or the V_2O_5 content becomes increasing the solubility of SnO_2 in the melt of B_2O_3-V_2O_5 system.

Table 1 Experimental results for the crystal growth

run	crystal	starting composition	soaking temp. (°C)	cooling rate (°C/hr)	size (max.) (mm)	color	habit
1	SnO_2	$2B_2O_3.V_2O_5$ (16.1g) Zn_2SnO_4 (1.5g)	1210	5	2.5 x 0.05	pale brown	needle
2	"	"	1250	5	4.0 x 0.05	"	"
3	"	"	1300	5	8.0 x 0.06	"	"
4	"	"	1340	5	12.0 x 0.08	brown	"
5	"	$B_2O_3.V_2O_5$ (15.2g) Zn_2SnO_4 (1.5g)	1300	5	10.0 x 0.3	"	"
6	"	$B_2O_3.2V_2O_5$ (17.4g) Zn_2SnO_4 (1.5g)	1300	5	15.0 x 0.4	"	"
7	"	$2B_2O_3.V_2O_5$ (32.1g) Zn_2SnO_4 (3.0g)	1300	1.8	12.0 x 0.1	pale brown	"

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