

## Formation of Metastable $\delta$ -Form of $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ Crystal from Its Melt

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Levin *et al.* reported that the  $\gamma$ -form of  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  has an equilibrium melting temperature of  $900^\circ\text{C}$ , being most stable at least down to  $600^\circ\text{C}$ . The present authors, however, have found that the  $\gamma$ -form never precipitates from a thoroughly homogenized melt of the same composition even when the melt is cooled slowly, *e.g.* at a rate as low as  $0.2^\circ\text{C}/\text{min}$ : The melt is supercooled down to  $740^\circ\text{C}$ , where a metastable  $\delta$ -form of  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  precipitates in the supercooled melt in place of the  $\gamma$ -form.

The high energy barrier for formation of the  $\gamma$ -form as well as the low energy barrier for formation of the  $\delta$ -form were explained in terms of similarity in microstructure of the  $\gamma$ - and  $\delta$ -form with their melt: The  $\delta$ -form has a more open, defective and symmetric structure which is similar to that of the melt than that of the  $\gamma$ -form. Stability relationships of the  $\gamma$ - and  $\delta$ -form with their melt were determined detail.

### I. INTRODUCTION

The  $\gamma$ -form of  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  (mole ratio) crystal shows a high photoconductivity and strong electro-optic effect.<sup>1,2)</sup> It can be fabricated by the pulling technique<sup>3)</sup> from its melt using a  $\gamma$ -crystal as a seed.

According to the phase diagram of the  $\text{Bi}_2\text{O}_3$ - $\text{SiO}_2$  system determined by Levin *et al.*<sup>4)</sup> (Fig. 1), the  $\gamma$ -form of  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  crystal has its melting temperature at  $900^\circ\text{C}$  and is most stable from  $900^\circ$  to at least  $600^\circ\text{C}$ . It belongs to a space group  $I23$ .<sup>5)</sup>

G. Gattow and H. Schröder<sup>6)</sup> found that when a  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  melt was quenched without using a  $\gamma$ -crystal as a seed, the cubic  $\delta$ -form of  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  crystal (space group  $\text{Fm}3\text{m}$ ) formed from its melt in place of the  $\gamma$ -form. Their result suggests that the  $\delta$ -form is the metastable form, into which the melt can transform much easier than the  $\gamma$ -form. The present authors have found recently that the transformation of the  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  melt into the  $\delta$ -form occurs not only by quenching but also by slow cooling at a rate as low as  $0.2^\circ\text{C}/\text{min}$ , if the  $\gamma$ -crystals were not present in the melt before cooling.

The purpose of the present study is to find out exact conditions for formation of the  $\gamma$ - and  $\delta$ -form from the melt of the composition  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ . For this purpose, stability relationship among the  $\gamma$ -,  $\delta$ -form of  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  and their melt has been investigated.

### II. EXPERIMENTAL PROCEDURE AND RESULTS

#### 1. Conditions for Formation of $\delta$ - and $\gamma$ -Crystals from Their Melt

##### 1. 1. Formation of $\delta$ -Crystal from a Thoroughly Homogenized Melt

About 150 g of the batch mixture of the composition,  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  (mole ratio), was

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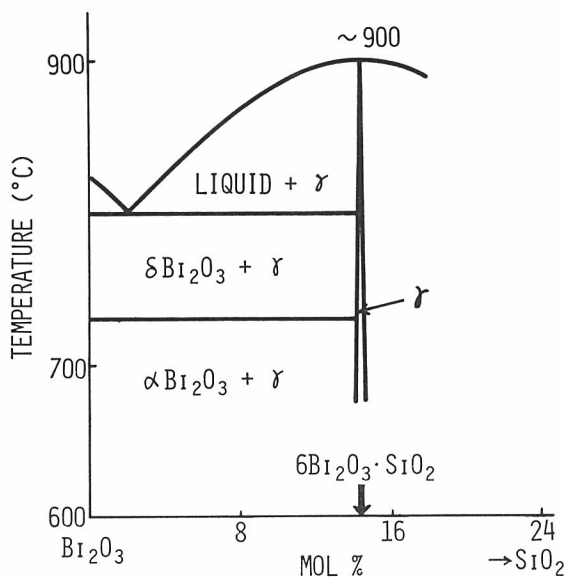


Fig. 1. Phase diagram of  $\text{Bi}_2\text{O}_3\text{-SiO}_2$  system. (After Levin *et al.*<sup>4)</sup>)

prepared from reagent-grade  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$  powders, both of the 99.99% purity. The batch mixture was charged in a Pt crucible, 55 mm in diameter and 35 mm in height, and melted at  $910^\circ\text{C}$  for 30 min in an electric furnace with SiC heating elements. The melt was then cooled at a rate of  $60^\circ\text{C}/\text{min}$ . It was found that the melt did not crystallize at the equilibrium melting temperature,  $900^\circ\text{C}$ , but was supercooled down to  $740^\circ\text{C}$ , and at this temperature it started to crystallize from the periphery of its free surface attached to the inner surface of the Pt crucible (Fig. 2). After the whole melt in the Pt crucible crystallized at about  $700^\circ\text{C}$ , the crucible was taken out together with its content from the furnace and quenched by dipping its bottom in water. Powder X-ray diffraction analysis showed that the crystalline aggregate formed in the crucible consisted only of the cubic  $\delta$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystal, which was the same one already obtained by Gattow *et al.*<sup>6)</sup> by quench-

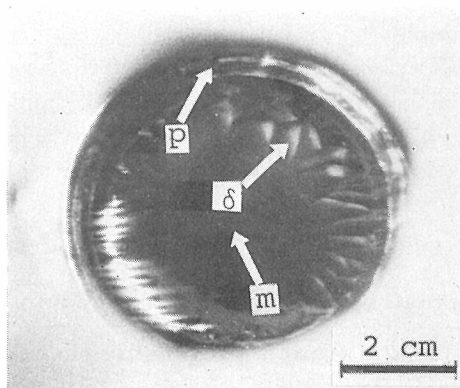


Fig. 2.  $\delta$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystal growing from the periphery of free surface of the melt at  $740^\circ\text{C}$ .

p, Pt crucible;  $\delta$ ,  $\delta$ -form crystal; m,  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt.

ing the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt: Its X-ray diffraction pattern consisted only of the sharp peaks characteristic of the  $\delta$ -form; no broad peaks indicating the presence of glassy phase was observed.

Experiments similar to the one described above were performed, varying the melting temperature of the batch from  $910^\circ$  to  $1000^\circ\text{C}$ , the melting time from 5 to 600 min., and the cooling rate from  $150^\circ$  to  $0.2^\circ\text{C}/\text{min}$ . In some cases,  $\text{SiO}_2$  crucibles were used in place of the Pt crucibles for melting the batch. In all cases, the same results as described above were obtained; *i.g.*, the  $\delta$ -form always formed from the supercooled melt at about  $740^\circ\text{C}$  but not the  $\gamma$ -form.

Figure 3 shows micrographs of an ingot consisting of  $\delta$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystals: Fig. 3(a) shows the free surface of the ingot photographed with a reflected light. Figures 3(b), (c)

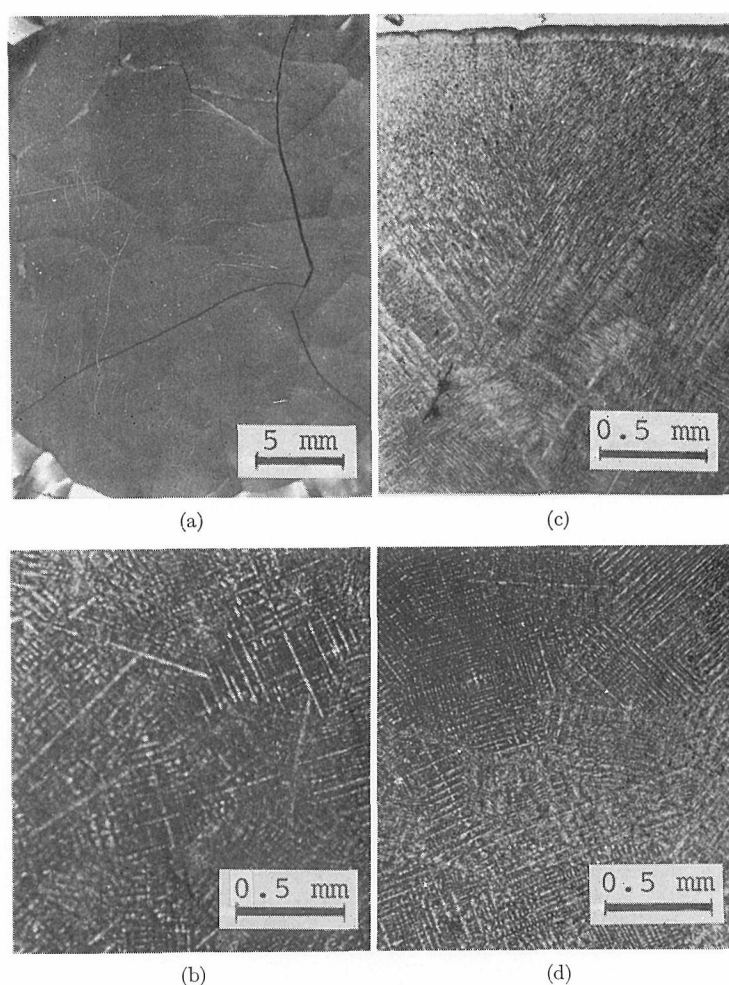


Fig. 3. Microstructures of  $\delta$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystals formed spontaneously at  $740^\circ\text{C}$  from its thoroughly homogenized melt.

(a) free surface overlooked; (b) transverse section 5 mm below the free surface; (c) longitudinal section near the free surface; (d) longitudinal section ranging from 4 to 6 mm from the free surface.

and (d) show microstructures of longitudinal and transverse sections of the ingot, all 0.1 mm thick, photographed with a transmitted light. These photographs indicate clearly that the crystals ( $\delta$ -form) grow dendritically not only from the free surface of the melt but also from many spots, which are homogeneously distributed at about 0.5 mm intervals, inside of the melt. This suggests that the crystals grew not only from the free surface of the melt, but also from many nuclei formed homogeneously inside of the melt at a fairly high rate during cooling.

## 1. 2. Formation of $\gamma$ -Crystal from a Partially Molten Batch

About 150 g of the same batch as described in 1.1 was packed in the Pt crucible and heated at 800°C, which was below the melting point of the  $\gamma$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ , for one hour. X-ray diffraction analysis showed that the batch transformed completely into an aggregate of the  $\gamma$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystals. The Pt crucible containing the aggregate of the  $\gamma$ -crystals were then transferred into an electric furnace with a vertical temperature gradient. Temperatures in the furnace were controlled, so that the temperature at the surface of the crystalline aggregate was raised up to 930°C and that at its bottom to 885°C. By this procedure the upper two-third of the crystalline aggregate was melted whereas its lower one-third was left in a solid state. The two temperatures at the upper surface of the melt (930°C) and the bottom of the crystalline aggregate (885°C) were then lowered both at a rate of 1.7°C/min down to room temperature, so that the interface between the melt and crystalline aggregate proceeded upwards at a constant rate of 33 mm/hr. After the whole melt crystallized, the ingot was examined with a petrographic microscope. It was found that many columnar crystals about 0.5 mm in diameter grew densely and uniaxially upwards from the surface of the original unmolten crystalline aggregate (Fig. 4). X-ray diffraction analyses showed that the columnar crystals having grown from the surface of the unmolten crystalline aggregate ( $\gamma$ -form) were also the  $\gamma$ -form. This indicates that if the  $\gamma$ -form crystals are left unmolten at the bottom of the crucible, they act as seeds and  $\gamma$ -form crystals newly grow from the seeds upwards in the melt.

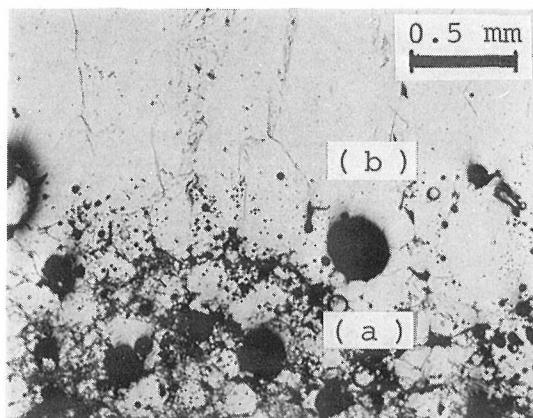


Fig. 4. Longitudinal section showing the interface between the original unmolten crystalline aggregate (a) and newly developed columnar crystals (b).

## 2. Stability of $\delta$ - and $\gamma$ -Crystals

The same batch mixture as described in 1.1 was compressed at  $2000\text{ kg/cm}^2$  into disk form, 2 mm thick and 16 mm in diameter, heated at various temperatures in the range  $350^\circ$  to  $850^\circ\text{C}$  for one hour in an electric furnace and then taken out from the furnace to be allowed to cool in air. The same heat-treatment as above was also given to fragments of the ingot consisting of  $\delta$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystals prepared by the method described in 1.1. Powder X-ray diffraction analyses showed that (1) the compressed batch mixture transformed into an aggregate of the  $\gamma$ -form crystal particles when heated above  $650^\circ\text{C}$ , and (2) the ingot consisting of the  $\delta$ -form crystal particles transformed also into an aggregate of the  $\gamma$ -form crystal particles when heated above  $400^\circ\text{C}$ .

## 3. Melting Temperatures of $\delta$ - and $\gamma$ -Crystals

Figure 5 shows results of differential thermal analyses of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  composition: About 3 g of a compressed batch mixture yielding the composition  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  was sintered at  $800^\circ\text{C}$  for one hour in a Pt crucible. An aggregate of the  $\gamma$ -form crystal particles thus obtained was placed in a Pt sample holder, 8 mm in diameter and 15 mm in depth, of the DTA apparatus (Shimadzu Ltd., Model DT-10B). A thermogram shown in Fig. 5 was obtained when the aggregate of the  $\gamma$ -form crystal particles was heated from room temperature to  $1000^\circ\text{C}$  [curve (a)], then cooled to  $650^\circ\text{C}$  [curve (b)] and again heated to  $1000^\circ\text{C}$  [curve (c)]. The heating and cooling rates were all set at  $10^\circ\text{C}/\text{min}$ . X-ray diffraction analyses made for various specimens taken out from the sample holder at intervals in the course of DTA revealed that a big endothermic peak appearing at  $890^\circ\sim 920^\circ\text{C}$  on the heating curve (a) is due to melting of the  $\gamma$ -form, a small exothermic peak appearing at  $745^\circ\sim 710^\circ\text{C}$  on the cooling curve (b) is due to crystallization of the  $\delta$ -form from the supercooled melt and a small endothermic peak appearing at  $720^\circ\sim 755^\circ\text{C}$  on the reheating curve (c) is due to melting of the  $\delta$ -form. These results indicate that the equilibrium melt-

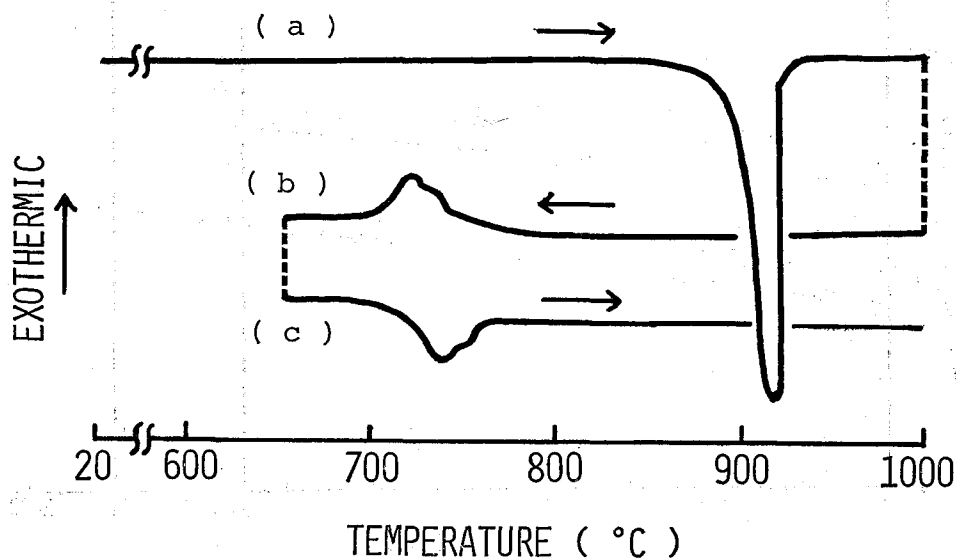


Fig. 5. DTA curves of  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystal on heating and cooling at a rate of  $10^\circ\text{C}/\text{min}$ .

ing temperature of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  composition is about  $900^\circ\text{C}$  and the melting temperature of the metastable  $\delta$ -form crystal is about  $750^\circ\text{C}$ , and furthermore the  $\delta$ -form crystals once formed transform directly into its melt without transforming into the  $\gamma$ -form when heated. Comparison of the area of the endothermic peak of the  $\delta$ -crystal with that of the  $\gamma$ -crystal suggests that the heat of fusion of the  $\delta$ -crystal is about one-fifth of that of the  $\gamma$ -crystal.

#### 4. Specific Volume of the Melt, $\delta$ - and $\gamma$ -Crystals.

Specific volume of the melt of the composition  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  was measured at various temperatures in the range from  $760^\circ$  to  $1020^\circ\text{C}$  by the Archimedean two bob method,<sup>7)</sup> using two Pt balls, 8 and 10 mm in diameter. These bobs were suspended by a Pt wire, 0.1 mm in diameter, respectively. Immersion of the Pt bob into the supercooled melt did not cause its crystallization at least down to  $760^\circ\text{C}$ , if the surface of the Pt ball and Pt wire had previously been cleaned thoroughly first by washing with HCl and then heating up to  $800^\circ\text{C}$ . The errors caused by surface tension acting on the suspension wire and the buoyant effect of the liquid on the Pt wire were eliminated.

The specific volume of the  $\delta$ - and  $\gamma$ -crystals at room temperature were measured by the pycnometric method, and those at elevated temperatures were calculated from their specific volumes at room temperature and their thermal expansion of lattice constants determined by high-temperature X-ray diffraction analyses, in which platinum powders were used as an internal standard. The results are given in Fig. 6. The specific volumes of the  $\delta$ -crystal lie between those of the melt and  $\gamma$ -crystal near the melting temperatures of the  $\delta$ - and  $\gamma$ -crystals.

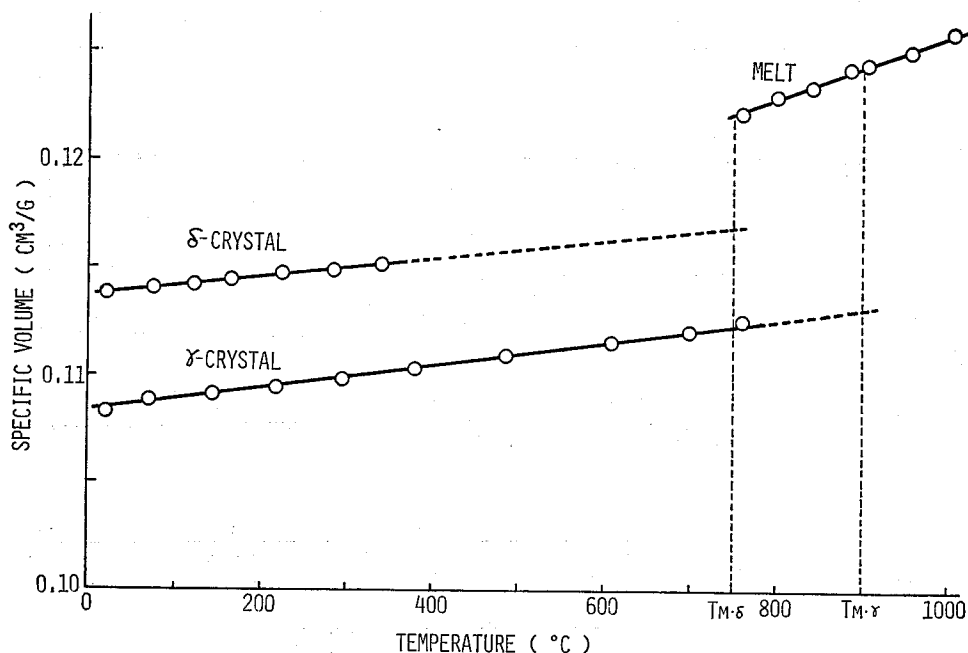


Fig. 6. Specific volume of  $\delta$ -,  $\gamma$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystal and their melt.

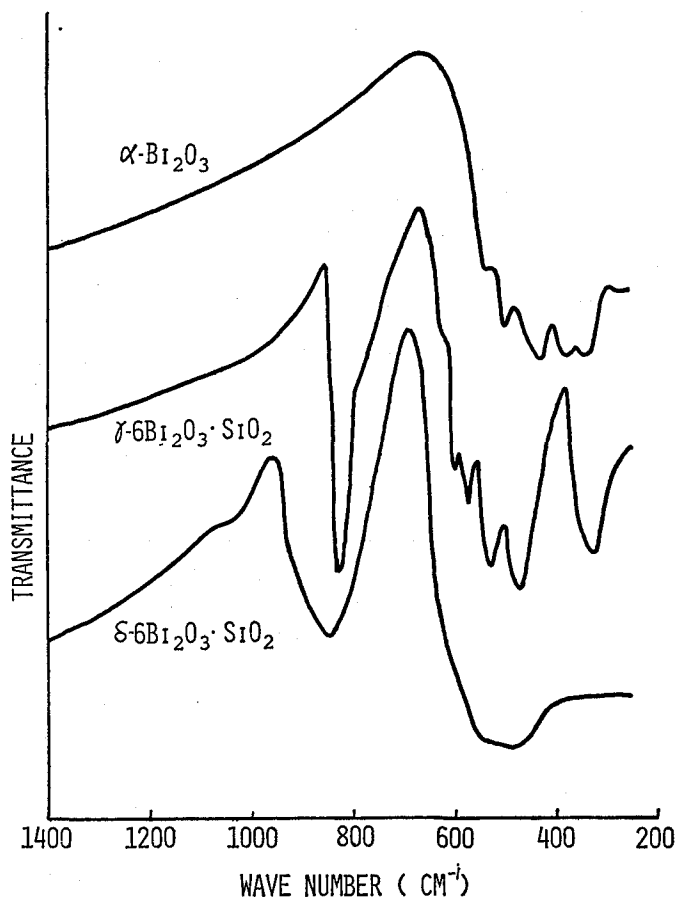


Fig. 7. Infrared spectra of  $\delta$ -,  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  and  $\alpha$ - $\text{Bi}_2\text{O}_3$  crystals.

### 5. Infrared Spectra of $\delta$ - and $\gamma$ -Crystals

Infrared absorption spectra of the  $\delta$ - and  $\gamma$ -crystals prepared by the methods described in 1.1 and 1.2, respectively, were obtained using their KBr-pelletized discs. The results are given in Fig. 7, in which a datum for  $\alpha$ - $\text{Bi}_2\text{O}_3$  crystal is also given for comparison.

Since the absorption bands due to Si-O stretching and bending vibrations are reported to occur at  $1100\sim 900\text{ cm}^{-1}$  and about  $475\text{ cm}^{-1}$ ,<sup>8)</sup> respectively, the bands at  $900\sim 800\text{ cm}^{-1}$  and  $475\text{ cm}^{-1}$  observed for both the  $\delta$ - and  $\gamma$ -crystals are ascribed also to these two vibrations, respectively. The bands at  $600\sim 300\text{ cm}^{-1}$  observed in both of the spectra of  $\delta$ - and  $\gamma$ -crystals are ascribed to the Bi-O bond vibrations, since the similar bands appear for the  $\alpha$ - $\text{Bi}_2\text{O}_3$  crystals. Generally, all of the absorption bands of the  $\delta$ -crystal are much broader than those of the  $\gamma$ -crystal.

## III. DISCUSSION

### 1. Stability Relationship of $\delta$ -, $\gamma$ -Crystals and Melt

The ingot obtained from the thoroughly homogenized melt of the composition  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$

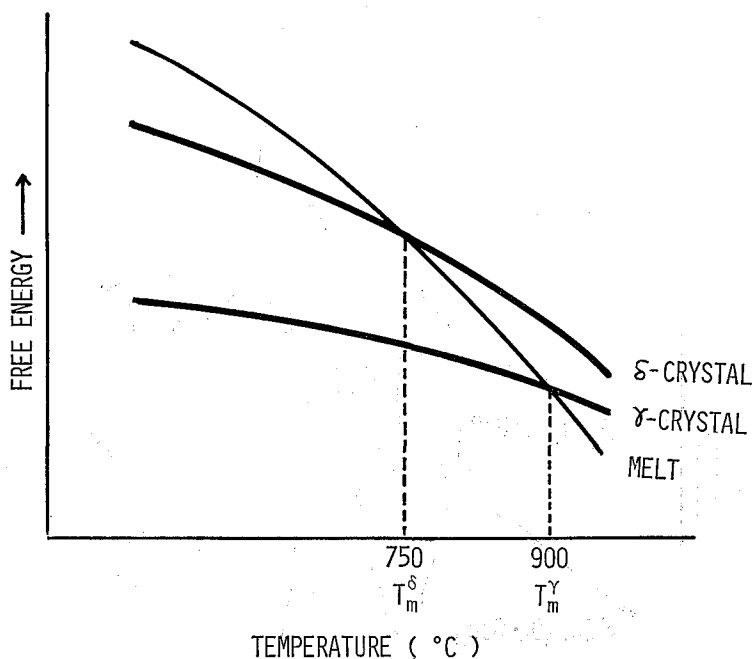


Fig. 8. Relationship among free energies of melt,  $\delta$ - and  $\gamma$ - $\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystals.  $T_m^\gamma$ , melting Temperature of  $\gamma$ -crystal;  $T_m^\delta$ , melting temperature of  $\delta$ -crystal.

$\text{O}_3\cdot\text{SiO}_2$  consisted only of the  $\delta$ -crystal, having no glassy phase. This indicates that the composition of the  $\delta$ -crystal is the same as that of the mother melt. On the other hand, the  $\gamma$ -crystal also has the same composition as that of the mother melt, since it melts congruently on heating. Thus, the solidification of the melt into the  $\delta$ - or  $\gamma$ -crystals on cooling described in II. 1.1 and II. 1.2, and the change of the  $\delta$ -crystal into the  $\gamma$ -crystal on heating described in II. 2 are all phase transformations which occur without compositional change. Causes of such transformations can be explained systematically, if we consider free energy changes of the  $\delta$ -,  $\gamma$ -crystals and the melt with temperature. Figure 8 is the diagram schematically drawn on the basis of the results obtained in the present study. The two temperatures,  $750^\circ$  and  $900^\circ\text{C}$ , at which the curve of free energy versus temperature for the melt intersects with those for the  $\delta$ - and  $\gamma$ -crystals, correspond to the melting temperatures of the  $\delta$ - and  $\gamma$ -crystals, respectively. The curve for the  $\delta$ -crystal was intentionally drawn so that it is situated higher and its slope is more rapid than that for the  $\gamma$ -crystal over all temperatures, since the measurements of the specific volumes of the  $\delta$ - and  $\gamma$ -crystals indicated that the  $\delta$ -crystal had a more open structure than the  $\gamma$ -crystal; generally, a Gibbs free energy of the more open structure is larger than that of a compact structure at  $0^\circ\text{K}$ , and it decreases more rapidly with increasing temperature than that of the latter structure.<sup>9)</sup>

The compressed powders of  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$  mixed in a mole ratio of 6:1, when heated, started to form the  $\gamma$ -crystals from  $650^\circ\text{C}$ , and the  $\delta$ -crystal obtained from its thoroughly homogenized melt, when reheated from room temperature, started to form the  $\gamma$ -crystals from  $400^\circ\text{C}$ . In both cases, the  $\gamma$ -crystals once formed never transformed into the  $\delta$ -crystals on further heating. These facts support that the  $\delta$ -crystal has higher free energy



than the  $\gamma$ -crystal, being metastable over all temperatures.

Using the diagram of Fig. 8, the formation of the  $\delta$ - or  $\gamma$ -crystals from the melt can be explained as follows: When the melt is cooled to its equilibrium melting point,  $T_m^\gamma$ , the most stable  $\gamma$ -crystal may form. However, if the rate of nucleation of the  $\gamma$ -crystal is low, the melt will continue to cool (supercooled), and at or below the melting temperature,  $T_m^\delta$ , the metastable  $\delta$ -crystal could form. This is actually the case when the thoroughly homogenized melt was cooled; homogeneous nucleation of the  $\gamma$ -crystal did not actually occur in the melt at or below  $T_m^\gamma$ , and the melt was supercooled down to  $T_m^\delta$ , where the formation of the metastable  $\delta$ -crystal commenced. When the  $\gamma$ -crystals were left unmolten at the bottom of the melt (section II. 1.2), however, the undissolved  $\gamma$ -crystals acted as seeds and as a result the whole melt transformed directly into the  $\gamma$ -form at the equilibrium melting temperature,  $T_m^\gamma$ .

## 2. Energy Barriers for Formation of $\delta$ - and $\gamma$ -Crystals

Generally, the metastable phase is formed when the energy barrier for formation of the stable phase is much higher than that for formation of the metastable phase.<sup>10)</sup> The energy barrier is low when the crystal is alike the mother melt in structure. The crystal with a more open, defective and symmetric structure, therefore, would be formed from the melt much easier than the crystal with a compact, complete and asymmetric structure. The fact that the  $\delta$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  has a more open structure than the  $\gamma$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  has already been confirmed by the specific volume measurements of the present study. According to the literatures, the  $\delta$ -form has a defective structure in which oxygen vacancies are randomly distributed, and, furthermore, its structural unit is more symmetric than that of the  $\gamma$ -form: The  $\delta$ -form has a fluorite defect structure, in which each bismuth atom is surrounded by eight or less oxygen atoms situated at the corner of a symmetrical cubic unit.<sup>9)</sup> The  $\gamma$ -form, however, has a structure of sillenite type, in which each bismuth atom is surrounded asymmetrically by seven oxygen atoms: five oxygen atoms form an incomplete octahedron and two further oxygen atoms are more weakly bonded.<sup>5)</sup> The defective structure of the  $\delta$ -form in which oxygen vacancies were reported to be randomly distributed was confirmed by the measurement of infrared absorption spectra of the  $\delta$ -form in the present study; variations in bond distance and bond angle of bismuth and oxygen atoms caused by the presence of oxygen vacancies are well represented by the broad absorption bands of the  $\delta$ -form. The fact that the metastable  $\delta$ -form is formed more easily from the melt than the  $\gamma$ -form is thus explained by an extraordinary similarity in structure between the  $\delta$ -form and the melt and by a big difference in structure between the  $\gamma$ -form and the melt.

## ACKNOWLEDGMENT

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REFERENCES

- (1) S. L. Hou and D. S. Oliver, *Appl. Phys. Letters*, **18**, 325 (1971).
- (2) R. E. Aldrich, S. L. Hou, and M. L. Harvill, *J. Appl. Phys.*, **42**, 493 (1971).
- (3) J. C. Brice, T. M. Bruton, O. F. Hill, and P. A. C. Whiffin, *J. Crystal Growth*, **24/25**, 429 (1971).
- (4) E. M. Levin and R. S. Roth, *J. Research NBS.*, **68A**, 197 (1964).
- (5) S. C. Abrahams, P. B. Jamieson, and J. L. Bernstein, *J. Chem. Phys.*, **47**, 4034 (1967).
- (6) G. Gattow and H. Schröder, *Z. anorg. allg. Chem.*, **318**, 197 (1962).
- (7) J. L. White in "Physicochemical Measurements at High Temperatures," J. O'M Bockris *et al.* Ed., Butterworths, London, (1959), p. 193.
- (8) P. Tarte in "Physics of Non-Crystalline Solids," J. A. Prince, Ed., North-Holland Publishing Co., Amsterdam, (1965), p. 549.
- (9) V. Raghavan and M. Cohen in "Treatise on Solid State Chemistry," Vol. 5, N. B. Hannay, Ed., Plenum Press, New York, (1975), p. 71.
- (10) W. D. Kingery *et al.*, "Introduction to Ceramics," 2nd ed, John Wiley & Sons, New York, (1976), p. 314.