

Transformation of Metastable δ -Form of $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ and Its Melt into Stable γ -Form Induced by Mechanical Tapping

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The supercooled $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ melt precipitated spontaneously only metastable δ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ crystals when cooled still in a Pt-crucible without giving any mechanical shock, while it precipitated stable γ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ crystals when the Pt-crucible was intensively tapped with a hard rod such as an alumina rod in the course of cooling. The δ -crystals once precipitated spontaneously from the melt never transformed into the γ -crystals on further cooling when cooled still, while they transformed into the γ -crystals when the crucible was intensively tapped in the course of cooling. The precipitation of the γ -crystals from the melt induced by the tapping was attributed to formation of cavities in the melt, and the transformation of the δ -crystals into the γ -crystals induced by the tapping was attributed to formation of dislocations in the δ -crystals; both the cavities in the supercooled melt and dislocations in the δ -crystals were thought to accelerate nucleation of the γ -crystals.

I. INTRODUCTION

The stable γ -form of $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ has an equilibrium melting temperature of 900°C .¹⁾ The present authors reported elsewhere²⁾ that a thoroughly homogenized melt of composition $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$, when cooled still in a Pt-crucible without giving any mechanical shock, never precipitates the γ -form but supercooled down to 740°C , where the melt begins to precipitate the metastable δ -form, and furthermore, the δ -form thus formed remained unchanged down to room temperature when quenched.

The present authors have newly found that the supercooled $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ melt or the metastable δ -crystals formed spontaneously transform into the stable γ -form, when the Pt-crucible containing the melt or the δ -crystals is tapped with a hard rod such as a sintered alumina rod in the course of cooling.

The present article describes phenomena of such transformations caused by the mechanical shock. Cause of these transformations are discussed.

II. EXPERIMENTAL PROCEDURE AND RESULTS

1. Conditions for Formation of the δ - and γ -Crystals

1. 1. Spontaneous Formation of δ -Crystals from a Supercooled $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ Melt

In the preceding article²⁾ it was reported that a thoroughly homogenized melt of

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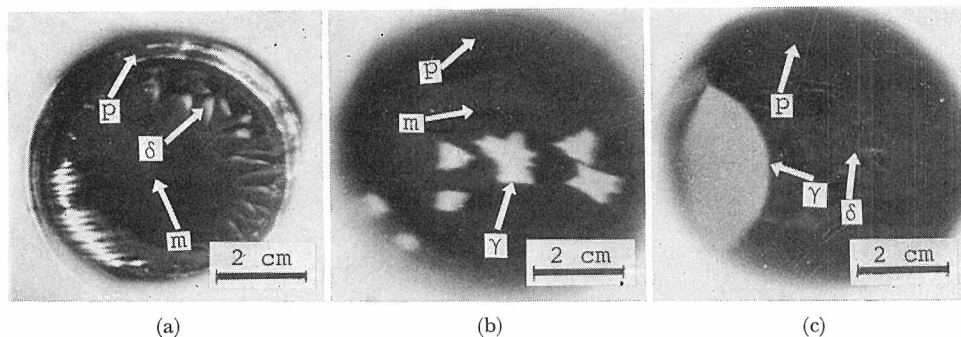


Fig. 1. Appearance of free surface of melt and δ -crystals in the middle of propagation of transformation.

(a) Spontaneous crystallization (melt \rightarrow δ , 740°C), (b) Tap-induced crystallization (melt \rightarrow γ , 745°C), (c) Tap-induced transformation (δ \rightarrow γ , 675°C).
 p, periphery of Pt-crucible; m, melt; δ , δ -crystal; γ , γ -crystal.

composition $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ in mole ratio, when cooled still in a Pt-crucible without giving any mechanical shock, never precipitated the stable γ -form of $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ at or below its equilibrium melting temperature (900°C), but was supercooled down to 740°C, where it began to precipitate the metastable δ -form of $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$. In the experiment reported above, the melts were prepared from about 150 g of batch mixtures of reagent grade chemicals of Bi_2O_3 and SiO_2 by heating at 1000°C for 30 min. The melts were cooled at various rates ranging from 0.2° to 150°C/min. Figure 1 (a) is a photograph taken of the free surface of the melt at the time when the δ -crystals started to precipitate from the inner surface of the Pt-crucible. The crystallization started at 740°C and completed at about 700°C, when the melt was cooled at a rate of 60°C/min. In the present experiments, it was found that the metastable δ -form of $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ once formed remained unchanged down to room temperature when cooled at rates over 60°C/min, whereas they decomposed although partially, forming a small amount of α - Bi_2O_3 crystals when cooled at rates less than 60°C/min. At any cooling rates, however, no γ -form of $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ formed spontaneously from aggregates of δ -form of $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$. In all aggregates of δ -form of $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ containing no or a small amount of α - Bi_2O_3 crystals, many cracks were observed with the naked eye.

1. 2. Formation of γ -Crystals from the Supercooled Melt and the Aggregate of δ -Crystals Induced by Tapping

The present authors have newly found that when the supercooled $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ melt and the aggregate of the δ -crystals spontaneously formed at about 740°C were mechanically tapped with a sintered alumina rod through the crucible wall in the course of their cooling, they both transformed rapidly into an aggregate of the stable γ -crystals: The starting melt was the same as described in 1.1. The cooling rate was 60°C/min. The tapping was given against the outersurface of the crucible continuously at a rate of 2 to 3 times per second with a tip of sintered alumina rod until a new phase appeared in the crucible. For the tapping, the rod was moved horizontally back and forth through a hole bored the refractory side wall of the furnace. The tapping was given so intensely that the free surface of the melt was ruffled into many ripples. When the temperature of the melt reached to about 745°C, which is the temperature a little above the temperature where the spontaneous formation

of the δ -crystals was found to start, the melt, being tapped continuously, began to crystallize from some points on its free surface with the evolution of a large amount of heat. The crystals grew radially from each spot, shining bright. This crystallization phenomena was over looked through a silica glass plate, 2 mm thick, placed on the Pt-crucible. Figure 1 (b) is a photograph taken of the free surface of the melt at the time when the crystallization was induced by the tapping. The crystallization of the whole melt completed rapidly. Then the crucible was taken out immediately from the furnace and quenched by dipping its bottom into water. The crystals thus formed were identified as the γ -form of $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ by powder X-ray diffraction analyses.

Against the aggregate of δ -crystals once formed spontaneously at 740°C in the Pt-crucible, the tapping was given through the crucible wall continuously during further cooling. The tapping was given so intensely that some cracks were formed in the aggregate of the δ -crystals. When the temperature of the aggregate was lowered down to about 675°C , the δ -crystals started to transform into another form of crystals, shining bright, from a point of tapping. Figure 1 (c) is a photograph taken of the free surface of the aggregate of the δ -crystals at the time when the transformation described above started. The transformation of the δ -crystals into new crystals completed rapidly, being accompanied with the evolution of a large amount of heat. The new crystal thus formed was identified as the γ -form of $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ by X-ray diffraction analysis.

1. 3. Transformations of the δ -Crystals Caused by Reheating

About 3 g of a batch mixture yielding the composition $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ was melted at 1000°C for 30 min in a Pt-sample holder, 8 mm in diameter and 15 mm in depth, for use in a DTA apparatus (Shimadzu Ltd., Model DT-10B). The crucible was cooled down to room temperature at a rate of $60^\circ\text{C}/\text{min}$. The crystals thus formed in the crucible were identified as the δ -form, the same form as obtained in the experiment described in 1.1. Many cracks were observed with the naked eye in the aggregate of δ -crystals as formed in the Pt-sample holder, in this case, too. The aggregate of δ -crystals as-formed in the sample holder was subjected to DTA. Another aggregate of δ -crystals prepared in the same way as above was also subjected to DTA, after crushed and powdered to -200 mesh with an alumina mortar. Their thermograms are shown in Fig. 2 (a) and (b). A thermogram shown in Fig. 2 (c) was obtained for a droplet-form aggregate of the δ -crystals prepared by a method entirely different from the two described above. The method used is as follow; in the course of cooling the $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ melt from 1000°C described in 1.1, a tip of a Pt-wire 0.5 mm in diameter was dipped into the melt at 750°C about two or three times, until a droplet of the melt about 3 mm in diameter and about 0.1 g in weight was formed, being attached to the tip of the Pt-wire. The droplet of the melt was air-quenched at room temperature together with the Pt-wire. The solidified droplet was identified also as the δ -form of $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$. In contrast to the aggregate of δ -form as-crystallized in the crucible, no crack was observed in the solidified droplet thus formed. For DTA, the droplet was placed in the Pt-sample holder together with a portion of the Pt-wire stucked in the droplet; an excess portion of the Pt-wire outside of the droplet was previously cut off without giving any mechanical shock to the droplet.

All the thermograms shown in Fig. 2 were obtained by heating the specimens at a constant rate of $10^\circ\text{C}/\text{min}$. X-ray diffraction analyses made for various specimens taken

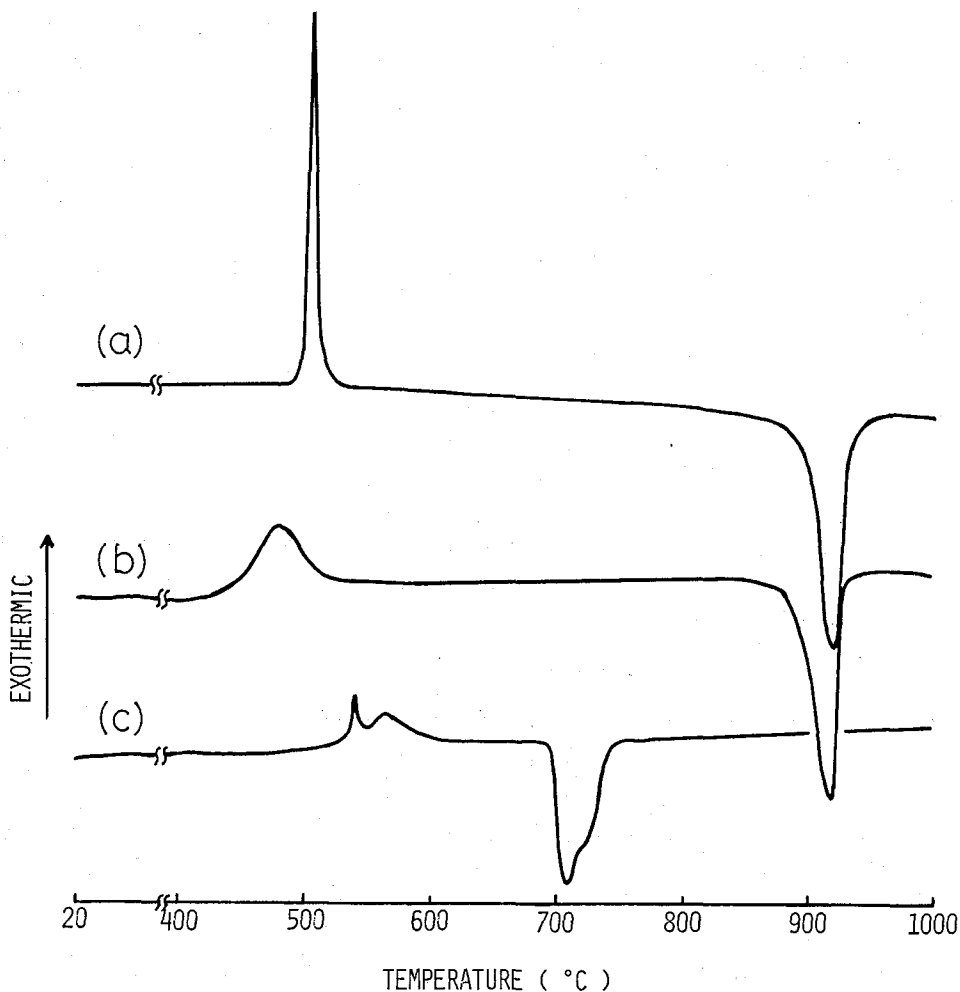


Fig. 2. DTA curves of δ -6 $\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ crystals (heating rate: $10^\circ\text{C}/\text{min.}$).
 (a) δ -form as-crystallized from the melt in the crucible. (b) δ -form of crystals once pulverized with Al_2O_3 mortar. (c) δ -form of crystals formed as a droplet at a tip of Pt-wire.

out from the sample holders at intervals in each course of DTA revealed that exothermic peaks appearing at $500^\circ\sim 530^\circ\text{C}$ and $425^\circ\sim 520^\circ\text{C}$ on the curves (a) and (b), respectively, are both due to transformation of the δ -crystal to the γ -crystal and endothermic peaks appearing at $880^\circ\sim 920^\circ\text{C}$ on both the curves (a) and (b), respectively, are due to melting of the γ -crystal, and, furthermore, the two small exothermic peaks appearing in a short range from 535° to 580°C on the curve (c) is due to formation of a small amount of α - Bi_2O_3 crystals in the aggregate of δ -form of $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ and an endothermic peak appearing at $700^\circ\sim 735^\circ\text{C}$ on the same curve is due to melting of the δ -crystals containing a small amount of the α - Bi_2O_3 crystal. These results indicate that, (1) the metastable δ -form as-crystallized from the melt in the Pt-crucible and those once powdered with a mortar both transform easily into the stable γ -form on heating at relatively low temperatures, and the γ -form thus formed melts at its equilibrium melting temperature (900°C) on further heating, (2) the

temperature of transformation from the δ - to γ -form for the powdered δ -crystals is lower than that for their original aggregate, and (3) the droplet-form aggregate of δ -form prepared by dipping a piece of Pt-wire into the supercooled melt never transform into the γ -form on heating, until it melts at $700^\circ\sim 735^\circ\text{C}$.

1. 4. Transformation of the δ -Crystals Caused by Severe Milling Near Room Temperature

About 2 g of a piece of δ -crystals formed spontaneously from the melt by the method described in 1.1 was first powdered to -200 mesh with an alumina mortar, and then put into a mixer mill (Spex Industries Inc., Model 8000), 40 mm in inside diameter and 40 mm in inside length, together with one ball, 10 mm in diameter. The mill and ball were both

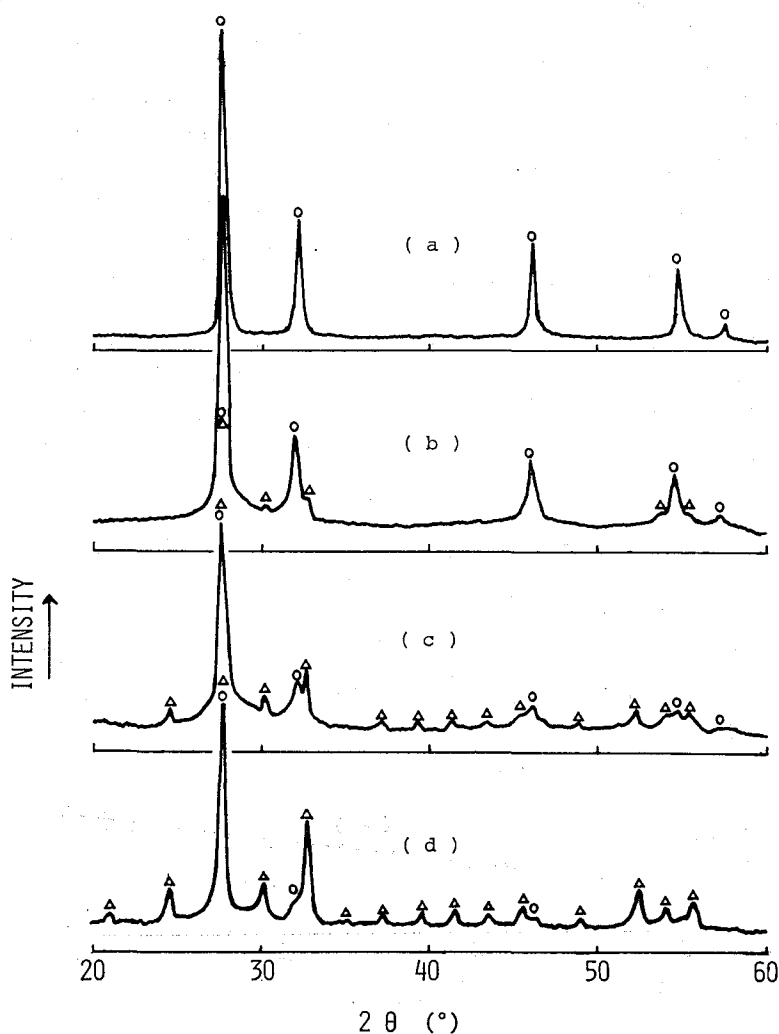


Fig. 3. X-ray diffraction patterns of δ -crystals milled successively. (a) Original powders (0 min.), (b) after 10 min milling, (c) after 20 min milling, (d) after 30 min milling.
 \circ δ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$, \triangle γ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$

made of WC. The mill was run at a rate of 1200 rpm for 30 min in all, but with intermissions of 30 min every 10 min run, in order to keep the temperature of the inside of the mill below at least 50°C. A small amount of the powders taken out from the cell at every intermission was subjected to the powder X-ray diffraction analyses. Their X-ray diffraction patterns are shown in Fig. 3, which indicates that the metastable δ -crystal powders first put in the mill transform gradually into the stable γ -form as the milling time increases.

1. 5. Velocity of Propagation of Phase-Transformation

The $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ melt prepared by the method described in 1.1 was cooled still in the Pt-crucible without giving any mechanical shock from 1000° to 740°C at a rate of 60°C/min, and its temperature was kept at 740°C. When the δ -crystals began to precipitate spontaneously from the periphery of the inner surface of the crucible inward, the propagation of the front of δ -crystals on the free surface of the melt was photographed with a movie camera at a rate of one frame per 10 seconds.

Another $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ melt prepared similarly as described above was cooled from 1000° to 745°C at a rate of 60°C/min, and after its temperature was kept at 745°C, the outside of the Pt-crucible was tapped with the alumina rod. Immediately after the γ -crystals began to crystallize from some points on the free surface of the melt, the tapping was stopped, and the propagation of the front of the γ -crystals, which proceeded radially outward from each point, was photographed with the camera at a rate of one frame per 0.5 seconds.

The aggregate of the δ -crystals spontaneously formed from the melt at 740°C in the Pt-crucible was further cooled down to 675°C at a rate of 60°C/min and after its temperature was kept at 675°C, the outside of the Pt-crucible was tapped with the alumina rod.

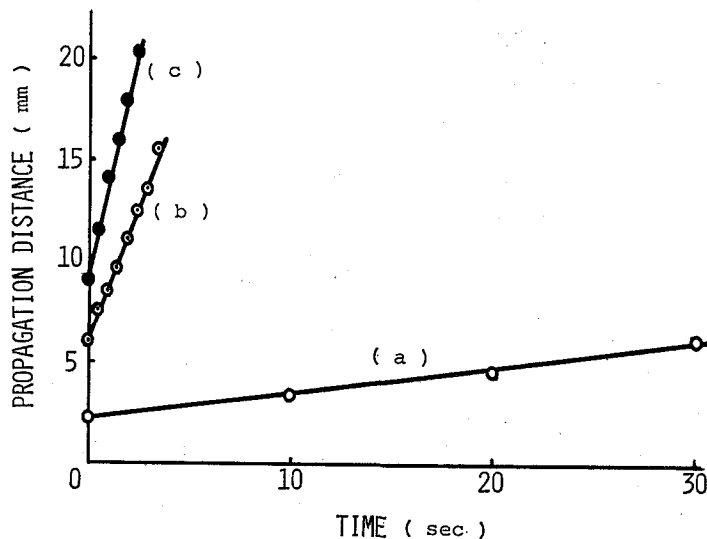


Fig. 4. Propagation of phase-transformation in the melt or δ -crystals. (a) Spontaneous crystallization of δ -crystals from melt at 740°C. (b) Crystallization of γ -crystals from melt at 745°C induced by tapping. (c) Transformation of δ -crystals into γ -crystals at 675°C induced by tapping.

Immediately after the δ -crystals began to transform into the γ -crystals from the portion, where the tapping was given through the crucible wall, the tapping was stopped, and the propagation of the front of the γ -crystals on the free surface of the aggregate of δ -crystals was photographed at a rate of one frame per 0.5 seconds.

Figure 4 shows relations between the propagation distance and the time elapsed, all of which were obtained on the photographs. Rates of the front propagation of the δ -crystal in the melt, the γ -crystal in the melt and the γ -crystal in the aggregate of δ -crystals were calculated from the slope of those lines shown in Fig. 4; they were 0.14, 3.2 and 4.7 mm/sec, respectively.

To measure the temperature rise caused by the generation of heat of crystallization or transformation, the tip of a thin Pt-13Rh thermocouple was attached to the surface of the melt or the aggregate of the δ -crystals before the crystallization or transformation started. The maximum temperature rises attained with this thermocouple were $10\sim 15^\circ\text{C}$ for the spontaneous crystallization of the δ -form from the melt, about 150°C for the tap-induced crystallization of the γ -form from the melt and about 125°C for the tap-induced transformation of the δ -form into the γ -form.

III. DISCUSSION

It has been found that the $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ melt precipitates the stable γ -form of $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ when the Pt-crucible containing the melt is tapped with a hard rod in the course of cooling, while it precipitates the metastable δ -form of $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ spontaneously when cooled still in the crucible, without giving any mechanical shock. Furthermore, it has been found that the aggregate of the δ -crystals once formed spontaneously in the crucible transforms into the aggregate of the γ -crystals when the crucible is tapped on further cooling, while the same aggregate of the δ -crystals never transforms into the γ -crystals when cooled still in the crucible down to room temperature.

The spontaneous precipitation of the metastable δ -crystals from the melt on cooling was already explained elsewhere²⁾ by the energy barrier for the nucleation of the stable γ -crystal much higher than that of the metastable δ -crystal. Therefore, the formation of the γ -crystals from the melt caused by the tapping is considered to be a result of lowering of the energy barrier for nucleation of the γ -crystal.

It is well known that nucleation of a crystal in supercooled water or some metallic liquids is accelerated by mechanical shock, such as high intensity ultrasonic vibration or friction.³⁾ One of the well accepted theories used for explaining this phenomenon is the cavitation mechanism theory;⁴⁾ when liquids are vibrated intensely, cavities are formed in the liquids, and when they collapse, very high pressure pulses occur, rising equilibrium melting temperature and consequently lowering the thermodynamic energy barrier for nucleation of a new crystal. The formation of the γ -crystals from the melt caused by the tapping occurred probably by this cavitation mechanism; the tapping given against the melt through the crucible wall would cause formation of cavities in the melt, resulting in lowering of the energy barrier for nucleation of the γ -crystals. Here, it should be taken into consideration that the formation of cavities in the supercooled melt may also lower the energy barrier for nucleation of the metastable δ -crystal. However, even when many nuclei of the δ -crystal were formed together with those of the γ -crystal in the supercooled melt by the tapping, the

rate of growth of the δ -crystal in the melt is much lower than that of the γ -crystal as shown in Fig. 4. Hence, the nuclei of the γ -crystal will grow much faster than that of the δ -crystal, and the whole melt will transform mostly into an aggregate of the stable γ -crystals. This will explain the reason why the supercooled $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ melt transforms into the aggregate of the γ -crystals by the tapping.

The fact that the aggregate of the δ -crystals once formed spontaneously never transformed into the stable γ -crystals when cooled still in the crucible is explained by the high energy barrier for nucleation of the γ -crystal in the aggregate of the δ -crystals. The transformation of the δ - to γ -form caused by the tapping is therefore considered as a result of lowering of the energy barrier for the nucleation of the γ -crystal.

It has long been known that transformation of a solid from one to another phase is accelerated by mechanical stress applied to the solid. Explanations given hitherto to its cause are as follows: (a) A mechanical compressive stress applied to a crystal increases its free energy change accompanied with its phase transformation, thus lowering the thermodynamic barrier for nucleation of a new phase.⁵⁾ This occurs only when the molar volume of the new phase is smaller than that of the original phase. (b) A severe stress forms dislocations in a crystal, and a strain energy stored at the dislocations lower the thermodynamic barrier for nucleation of a new phase.⁶⁾

The fact that the molar volume of the γ -crystals is smaller than that of the δ -crystal has already been confirmed by the authors and reported elsewhere.²⁾ Formation of dislocations in the δ -crystals by the tapping is also considered possible since the tapping given against their aggregate through the crucible was so severe that many cracks were formed at the point of tapping. Therefore, it appears that the two theories (a) and (b) described above, are both applicable to the lowering of energy barrier for nucleation of the γ -crystals in the aggregate of the δ -crystals. However, the theory (a) is not applicable to the phenomena observed, for example, in the DTA: The aggregate of the δ -crystals once formed spontaneously at 740°C from the melt in the Pt-sample holder never transformed into the γ -form in the original cooling process down to room temperature whereas the aggregate of the δ -crystals, when reheated from room temperature, transformed spontaneously into the γ -form at about 500°C (Fig. 2). These phenomena can not be explained by the theory (a): If the transformation occurring at about 500°C on reheating is simply due to the formation of big stresses resulting from a difference in thermal expansion between the aggregate of the δ -crystals and the Pt-crucible, the transformation must occur at the same temperature also in the original cooling process, since the magnitude of thermal stresses applied on the aggregate of the δ -crystals must be the same at the same temperature whether the aggregate is in the course of cooling or reheating.

In contrast with the theory (a), the theory (b) is also applicable to the above phenomena: When the aggregate of the δ -crystals is cooled down to about 500°C , thermal stresses may be so small that formation of dislocations in the aggregate is almost impossible. However, when the aggregate is cooled down to room temperature, the thermal stresses in the aggregate would reach the magnitude large enough to form many dislocations in the aggregate, and the dislocations thus formed would act as the sites for nucleation of the γ -crystal when the aggregate is reheated to about 500°C . The fact that large thermal stresses were applied to the aggregate cooled down to room temperature was confirmed by the existence of many cracks in the aggregate.

Transformation of $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ Crystal Induced by Tapping

The droplet-form aggregate of δ -crystals prepared at the tip of the Pt-wire never transformed into the γ -form even when reheated from room temperature. This seems natural since the droplet had never strained from its outside in the course of its original cooling down to room temperature, and consequently dislocations effective enough to act as the sites for nucleation of the γ -crystal were probably not formed in the droplet. Actually, no crack was observed in the droplet cooled down to room temperature.

The temperatures of the transformation of the aggregate of the δ into the γ -form decreased by 75°C by crushing and powdering the aggregate with the mortar. When the δ -crystal powders were crushed intensely in the mixer mill, they gradually transformed into the γ -form even at the temperatures below 50°C . These phenomena are possibly explained if it is assumed that dislocations are formed in the δ -crystals by crushing these aggregate or powders with the mortar or mill, and the dislocations thus formed will lower the thermodynamic barrier for nucleation of the γ -crystals, accelerating the transformation of the δ - into the γ -form.

When the δ -crystal powders are crushed severely in the mixer mill, dislocations formed in the δ -crystals become so effective in lowering the thermodynamic barrier for nucleation of the γ -crystals that transformation of the δ - into γ -form readily occurs even near room temperatures. Of course, in the course of milling near room temperatures, the lowering of thermodynamic barrier noted above is not satisfactory enough for the δ - into γ -form transformation: The kinetic energy large enough to go over the kinetic barrier for nucleation of the γ -crystal must also be given from the crushing work in the mill to atoms in the crystals for their rearrangement, although its detailed mechanism is still ambiguous. Any way, the theory (b) can be used most effectively for explanation of the primary cause of various transformation phenomena observed in the present experiments.

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