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## Identification of Crystals Protruding from Surface of $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ Glass

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When a fresh fragment of  $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$  glass was bombarded with intense electron beams, in an electron microscope, needle-shaped crystals, about 10 nm in diameter, grew out from the glass surface. When the fragment was allowed to stand in the air saturated with water for three weeks before subjected to the electron bombardment, a little curved rod-shaped crystals, about 200 nm in diameter, grew out from the glass surface. Electron diffraction analysis of the needle- and rod-shaped crystals indicated that the former crystals are  $\text{Na}_2\text{O}$ , the latter being  $\text{NaHCO}_3$ . These results were supported by in-situ observation of the crystals during heating up to 800°C under the electron microscope. Formation of these crystals was interpreted as one of the phenomena of percrystallization.

### I INTRODUCTION

When fresh fragments of alkali silicate glasses are bombarded with intense electron beams, needle-shaped crystals, about 10 nm in diameter, grow from the surface of the fragments. If the fresh fragments are allowed to stand under a normal atmospheric condition for a few weeks before subjected to electron bombardment, a little curved rod-shaped crystals, about 200 nm in diameter, are formed. The rod-shaped crystals further grow in diameter by successive intense electron bombardment. The authors have observed these phenomena continuously under an electron microscope with a transmission technique and reported their results elsewhere.<sup>1-4</sup>

The present article deals with identification of these crystals. Limited-field electron diffraction analyses as well as electron microscopic observations during heating up to about 800°C were made on these crystals for this purpose.

### II EXPERIMENTAL PROCEDURE

A glass of the composition  $\text{Na}_2\text{O}$  25,  $\text{SiO}_2$  75 mole% was prepared from reagent grade  $\text{Na}_2\text{CO}_3$  and high purity  $\text{SiO}_2$  powders. Fragments of the glass <500 Å thick, obtained by shattering with a hammer,<sup>1,2</sup> were placed between two gold grids and brought into an electron microscope (Model HU-IID, Hitachi Ltd., Tokyo, Japan). Besides the fresh fragments, those kept in a desiccator filled with the air saturated with moisture at room temperature for three weeks were also subjected to the electron microscopic observations.

For the electron microscopic observation, the acceleration voltage and filament current were kept at 75 kV and 40  $\mu\text{A}$ , respectively. To keep the samples as clean

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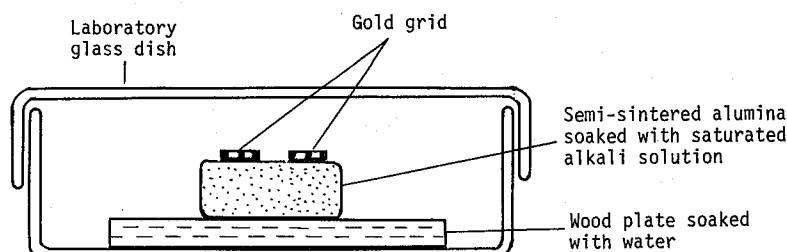


Fig. 1. Apparatus for preparation of needle-shaped crystals of alkali compounds.

as possible, the sample chamber in the electron microscope was cooled with liquid nitrogen to achieve a high vacuum. To provide a high electron beam density on the sample surface, the beam was focused to a diameter about  $5\ \mu\text{m}$ . To heat the sample at high temperatures a resistance heater (Model HH-2, Hitachi Ltd., Tokyo, Japan) attached to the electron microscope was used. Identification of crystals grown from the glass sample was made by the limited-field electron diffraction method. For determination of the camera constant gold was vacuumdeposited on the surface of the gold grids previously coated with a collodion film.

In separate model experiments needle-shaped crystals resembling in appearance to those grown on the surface of the glass exposed to moisture were prepared from various aqueous solutions saturated with  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , or  $\text{NaOH}$  all of reagent grade, by a method similar to those used by Fells *et al.*<sup>5)</sup> The apparatus used for this purpose is schematically shown in Fig. 1. As a substratum of the gold grid a semi-sintered alumina cylinder ( $\text{Al}_2\text{O}_3 > 99.0\%$ ; 10 mm in diameter and 10 mm in length) was used. The alumina cylinder was soaked with one of the saturated solutions described above and a wood plate beneath it was soaked with pure water. These piled materials were allowed to stand in a laboratory glass dish covered with a glass lid for 70 hours, and needle-shaped crystals grown on the gold grid were subjected to electron microscopic studies.

### III EXPERIMENTAL RESULTS

#### 1. Crystal Grown from a Fresh Fragment of a Glass

It was reported<sup>1,2)</sup> that needle-shaped crystals grew outward from the surface when fresh fragments of the glass were bombarded with intense electron beams. Figure 2 is a limited-field electron diffraction pattern of the crystals obtained in the present experiments by projecting an electron beam at the tips of the crystals. The two types of patterns shown in the upper left and right are the results of printing an original negative to reveal preferentially either the inner or outer rings of the diffraction pattern, at the expense of the others. The schematic pattern below is that of  $\text{Na}_2\text{O}$  crystals calculated from four  $d$  spacings of  $\text{Na}_2\text{O}$  crystals given in a literature<sup>6)</sup>  $d=3.19$ , 2.76, 1.95 and 1.39 Å, as well as the camera constant. Although the diffraction rings experimentally obtained were fairly broad, main three rings were judged to coincide well with those corresponding to  $d=3.19$ , 1.95, and 1.39, respectively. The diffraction pattern experimentally obtained was also compared with those of Na metal ( $d=3.02$ ,

## Identification of Crystals from Glass Surface

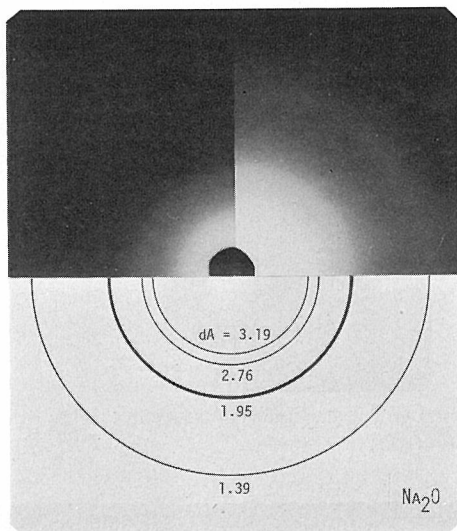


Fig. 2. Limited-field electron diffraction pattern of needle-shaped crystals formed on surface of  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$  glass by subjecting to intense electron bombardment.

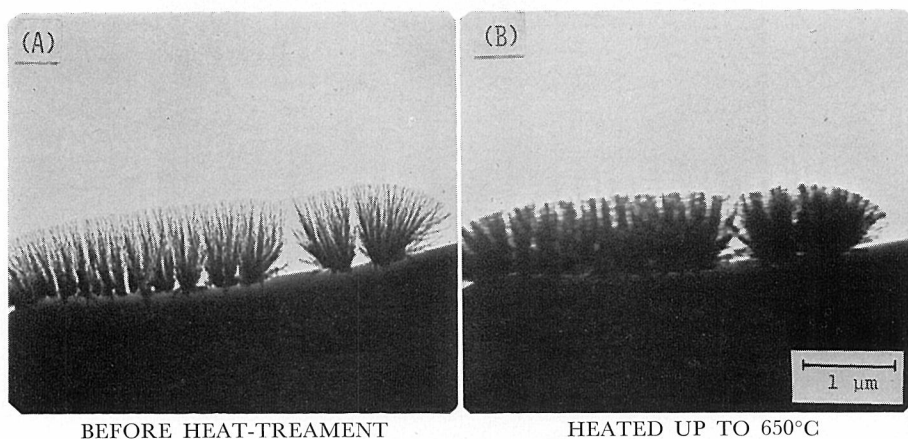


Fig. 3. Crystal growth on fresh surface of  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$  glass subjected to 60 minutes intense electron bombardment followed by heat-treatment.

2.13, and 1.75 Å)<sup>6)</sup>,  $\text{NaO}_2(\text{III})$  crystal ( $d=2.77$ , 2.68, and 1.93 Å) and  $\text{Na}_2\text{O}_2$  crystal ( $d=3.79$ , 2.10, and 1.90 Å), respectively, but none of them was coincident with the experimentally obtained pattern.

A fragment of the glass once bombarded with intense electron beams was heated to about 650°C using the resistance heater in the electron microscope. Electron microscopic observation during the heat-treatment indicated that the needle-shaped crystals grow markedly in width but little in length. Figure 3 shows the appearances of the crystals before and after this heat-treatment. The diffraction patterns taken before and after the heat-treatment were the same. From a fragment of the fresh glass not bombarded with intense electron beams, no needle-shaped crystals formed when subjected to the same heat-treatment as described above.

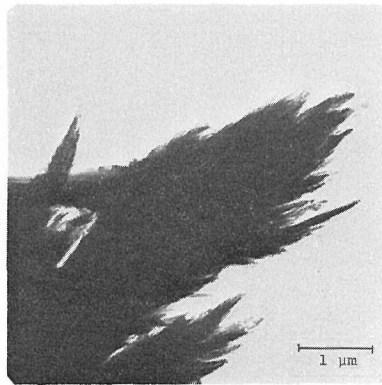


Fig. 4. Crystal growth on surface of  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$  glass by exposing to moisture for three weeks.

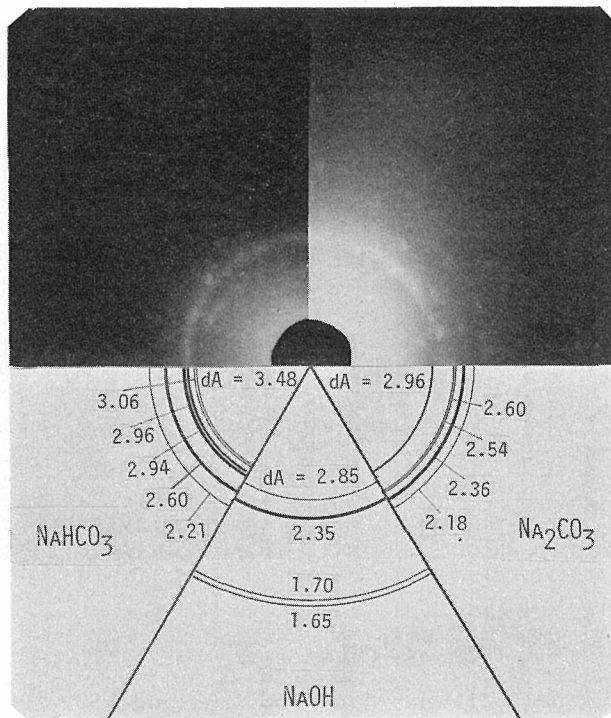


Fig. 5. Limited-field electron diffraction pattern of rod-shaped crystals formed on surface of  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$  glass by exposing to moisture for three weeks.

## 2. Crystals Grown from Glass Fragments Exposed to Moisture for Three Weeks

A rod-shaped material,  $0.2\text{--}0.5\ \mu\text{m}$  width and  $2\text{--}8\ \mu\text{m}$  in length, grew from fragments of the glass exposed to the air saturated with water for three weeks. Figure 4 shows its electron micrograph. Figure 5 shows its electron diffraction pattern, in which the diffraction rings appear to consist of many diffraction spots. In the lower portion

of Fig. 5 are drawn the diffraction patterns of  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaOH}$  calculated from their  $d$  spacings given in literatures.<sup>6,7)</sup> The diffraction rings corresponding to  $d=3.48, 2.96, 2.94, 2.60,$  and  $2.21 \text{ \AA}$  characteristic for  $\text{NaHCO}_3$ <sup>7)</sup>,  $d=2.96, 2.60, 2.54, 2.36,$  and  $2.18 \text{ \AA}$  for  $\text{Na}_2\text{CO}_3$ <sup>6)</sup>, and  $d=2.85, 2.35, 1.70,$  and  $1.65 \text{ \AA}$  for  $\text{NaOH}$ <sup>6)</sup> were all contained in the diffraction patterns experimentally obtained.

When the rod-shaped crystals were bombarded with intense electron beams, they became transparent from their periphery to inside, indicating that some of their constituent materials were vaporizing (Fig. 6(a) to 6(b)). Further continued electron bombardment caused new small needle-shaped crystals to grow outside from sharp

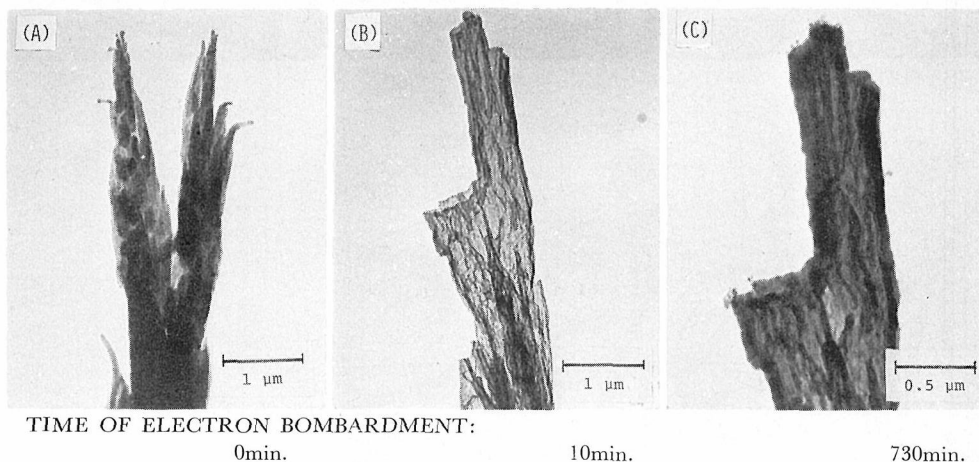


Fig. 6. Effect of intense electron bombardment on crystals formed on surface of  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$  glass by exposing to moisture.

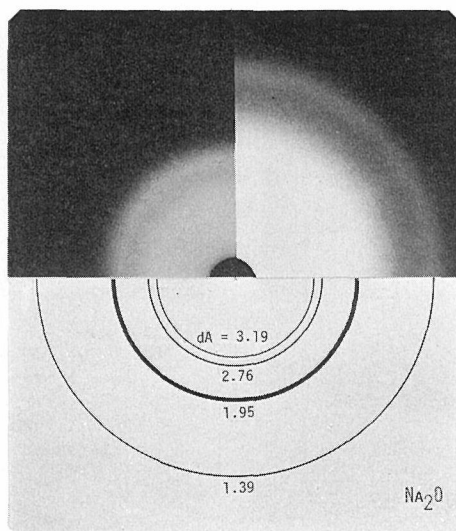


Fig. 7. Limited-field electron diffraction pattern of rod-shaped crystals formed on surface of  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$  glass by exposing to moisture. The pattern was obtained after the crystals were bombarded with intense electron beams for 30 minutes.

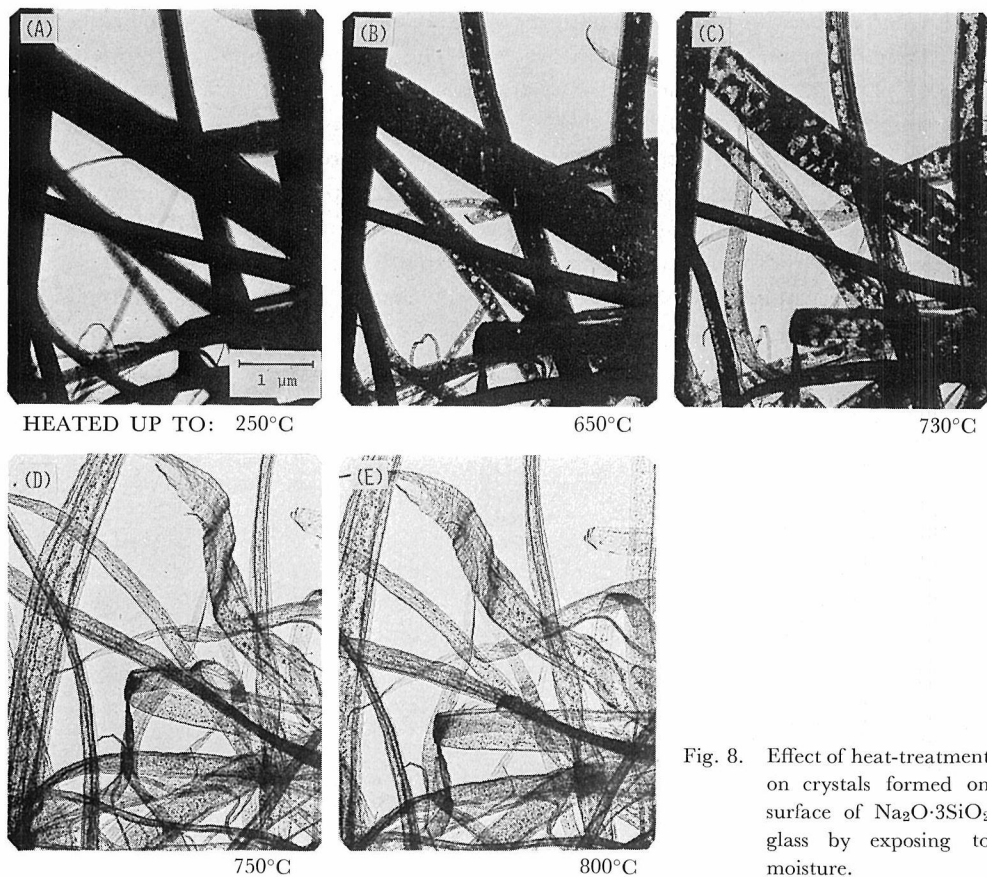


Fig. 8. Effect of heat-treatment on crystals formed on surface of  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$  glass by exposing to moisture.

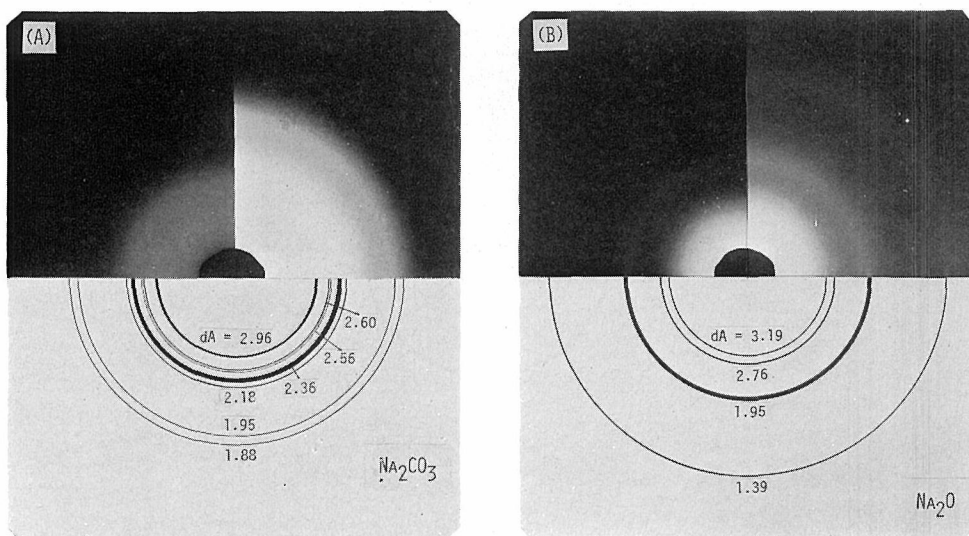


Fig. 9. Limited-field electron diffraction patterns of rod-shaped crystals formed on surface of  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$  glass by exposing to moisture. The patterns (A) and (B) were obtained after the crystals were heated up to 500 and 730°C, respectively.

corners of the skeletonized crystal (Fig. 6(c)). Figure 7 shows an electron diffraction pattern of the skeleton crystal, which was very similar to that of the needle-shaped crystals grown from the fresh glass fragments, *i.e.*, to that of the  $\text{Na}_2\text{O}$  crystals.

When the rod-shaped crystals were heated in the electron microscope at a rate of about  $20^\circ\text{C}/\text{min}$ . without bombarding with intense electron beams, their skeletonization also occurred; it started from about  $250^\circ\text{C}$  and progressed very fast from about  $800^\circ\text{C}$ . Its process is shown in Fig. 8. Figure 9 is an electron diffraction pattern of the skeleton heated up to about  $730^\circ\text{C}$ . The pattern is very similar to that of the  $\text{Na}_2\text{O}$  crystals but not any one of those of the  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaOH}$  crystals. The two rod-shaped crystals, one subjected to the intense electron beams followed by the heating up to about  $600^\circ\text{C}$  with the resistance heater, are shown for comparison in Fig. 10. Their diffraction pattern both consisted of fairly diffuse hallos but almost similar to that of the  $\text{Na}_2\text{O}$ .

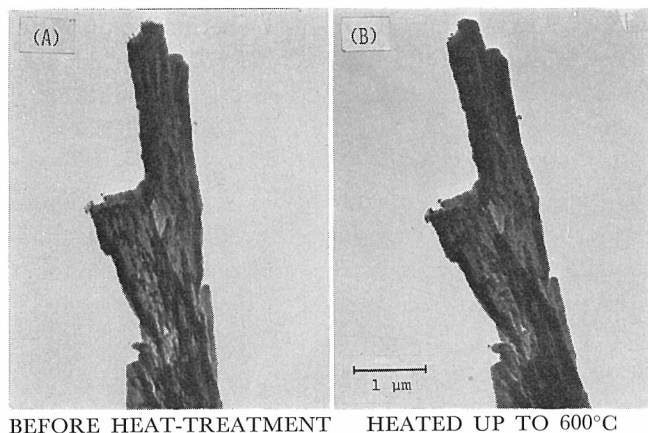


Fig. 10. Effect of heat-treatment on rod-shaped crystals formed on surface of  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$  glass by subjecting to intense electron beams for 30 minutes. Before heat-treatment the crystals were bombarded with intense electron beams for 30 minutes.

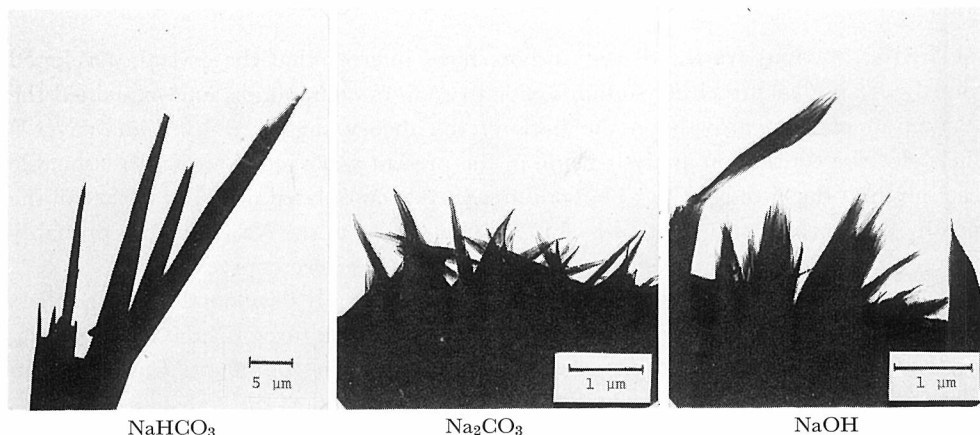


Fig. 11. Crystals of sodium compounds grown from saturated aqueous solutions.



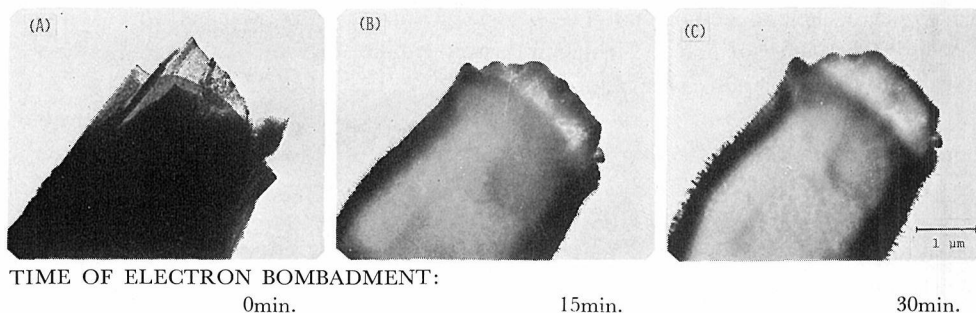


Fig. 12. Changes of  $\text{NaHCO}_3$  crystals caused by intense electron bombardment.

### 3. Crystals Grown from Aqueous Solutions Saturated with Sodium Compounds

The rod-shaped crystals grown from aqueous solutions saturated with  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaOH}$ , respectively, by the method described in the section II are shown in Fig. 11. The crystals grown from the  $\text{NaHCO}_3$  solution were about five times as large as those grown from the other solutions. Their electron diffraction patterns were respectively the same as those of the  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaOH}$  crystals given in literatures.<sup>6,7)</sup>

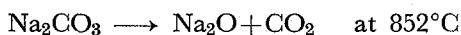
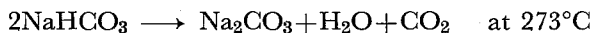
When the rod-shaped crystals grown from the  $\text{NaHCO}_3$  solution were bombarded with intense electron beams, they were first reduced to skeletons and then new tiny needle-shaped crystals grow outward from the surface of the skeletons in the same way as observed for the crystals grown from the glass exposed to moisture. (Fig. 12) The electron diffraction pattern of the skeletons was coincident with that of the  $\text{Na}_2\text{O}$  crystals but none of those of the  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaOH}$  crystals. Intense electron beams were also bombarded to the crystals developed from the  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  solutions, respectively. The former crystals showed no change in appearance whereas the latter crystals were first markedly bent and finally disappear from sight under the electron microscope.

## IV DISCUSSION

In the previous works,<sup>1-4)</sup> the authors have inferred that the crystals developed from the fresh glass are either sodium oxide or sodium compounds, and explained the mechanism of their growth on the basis of the theory suggested by Lineweaver.<sup>8)</sup> Their electron diffraction analysis made in the present work indicates with reasonable certainty that they are  $\text{Na}_2\text{O}$ : The sodium atoms accumulated near the surface of the glass by the mechanism suggested by Lineweaver will form the  $\text{Na}_2\text{O}$  crystals probably by combining a trace of oxygen present in the electron microscope.

Electron diffraction analysis of the rod-shaped crystals developed from the glass exposed to moisture suggested that the crystals were the mixture of  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaOH}$  crystals, but did not clearly indicated which compound was the main constituent of the rod-shaped crystals. The skeletonization of the rod-shaped crystals caused by the intense electron bombardment or by heating with the resistance heater suggests that they were mainly composed of  $\text{NaHCO}_3$ : Decomposition or melting

temperatures of  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaOH}$  crystals at the atmospheric pressure are as follows<sup>9)</sup>:



The skeletonization of the rod-shaped crystals started from about  $230^\circ\text{C}$  and progressed very fast from about  $700^\circ\text{C}$ . This would indicate that the decomposition of the  $\text{NaHCO}_3$  crystals into the  $\text{Na}_2\text{CO}_3$  crystals began from the former temperature and their further decomposition into the  $\text{Na}_2\text{O}$  crystals from the latter. The electron diffraction analysis of the two rod-shaped crystals heated up to about  $500^\circ\text{C}$  and about  $730^\circ\text{C}$  showed that they were probably the  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{O}$  crystals, respectively. The decomposition temperatures described above, *i.e.*, about  $230^\circ\text{C}$  and  $700^\circ\text{C}$ , are both a little lower than those at the atmospheric pressure, respectively. This is probably due to the high vacuum (less than  $10^{-5}$  torr) in which the crystals were heated.

It is unlikely that the major constituent of the rod-shaped crystals is either the  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$ , since the crystals were skeletonized from a much lower temperature than the decomposition temperature of the  $\text{Na}_2\text{CO}_3$  and, furthermore, kept their shape over the temperatures much higher than the melting temperature of the  $\text{NaOH}$ .

Formation of  $\text{NaHCO}_3$  crystals on the surface of the glass exposed to moisture was already confirmed by Tsuchihashi *et al.* for some  $\text{Na}_2\text{O}$ -containing commercial glasses by electron diffraction techniques.<sup>10)</sup> To the authors' knowledge, however, their morphological studies by transmission electron microscopic techniques have not yet been reported.

Why do the  $\text{NaHCO}_3$  crystals take rod-shape when formed on the glass fragment exposed to moisture is the problem of great interest. The authors consider that it may be caused by the mechanism of the so-called percrystallization.<sup>11)</sup> Especially, the present case seems to be analogous in principle to a case of percrystallization of sodium chloride first found by Hinegardner;<sup>12)</sup> he noticed a thick mat of fine needle-shaped crystals covering a semi-dry silica gel prepared from sodium silicate and hydrochloric acid. In the present case, a silica-rich layer would be first formed on the surface of the glass fragment as a result of the chemical corrosion by moisture, and this layer would play the same role as that of the silica gel in the case of Hinegardner's experiment;  $\text{Na}^+$  ions originally present in the silica-rich layer diffuse through this layer, reach the outside, combine with  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , forming the rod-shaped  $\text{NaHCO}_3$  crystals extending to one direction. The mechanism of the percrystallization, itself, have already been explained by several researchers.<sup>13-15)</sup> There should be the same opportunity for the  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  crystals to form in rod-shape as for the  $\text{NaHCO}_3$  crystals. The fact that the rod-shaped crystals obtained were consisted mostly of the  $\text{NaHCO}_3$  can be explained by the high growth rate of the  $\text{NaHCO}_3$  crystals compared to those of the other two crystals (see Fig. 11).

The cause for the formation of needle-shaped  $\text{Na}_2\text{O}$  crystals on the fresh glass fragments can also be explained by the same mechanism; in this case, however, the sodium atoms formed near the glass surface by intense electron bombardment<sup>1,2)</sup> would diffuse through the  $\text{SiO}_2$  network-former in glass structure, reach the surface and combine with traces of oxygen in the electron microscope.

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