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Identification of Crystals Protruding from Surface of $Na_2O \cdot 3SiO_2$ Glass

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When a fresh fragment of Na_2O3SiO_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 Na_2O, the latter being $NaHCO_3$. These results were supported by in-situ observation of the crystals during beating 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.[1~4].

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 Na_2O 25, SiO_2 75 mole% was prepared from reagent grade Na_2CO_3 and high purity SiO_2 powders. Fragments of the glass <500 Å thick, obtained by shattering with a hammer,[1,2] 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 desiccater 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 μA, respectively. To keep the samples as clean

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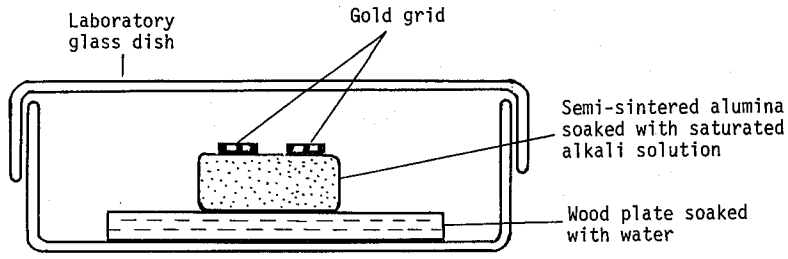


Fig. 1. Apparatus for preparation of needle-shaped crystals of alkali compounds.

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 μm. 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 grow 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 $NaHCO_3$, Na_2CO_3, or NaOH all of reagent grade, by a method similar to those used by Fells *et al.*[5] The apparatus used for this purpose is schematically shown in Fig. 1. As a substratum of the gold grid a semi-sintered alumina cylinder (Al_2O_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[1,2] 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 Na_2O crystals calculated from four d spacings of Na_2O crystals given in a literature[6] 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,

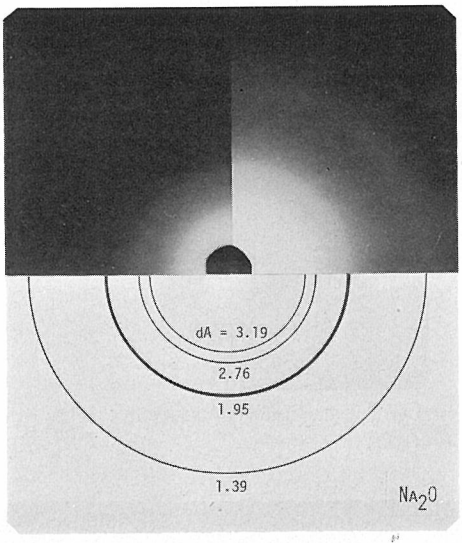
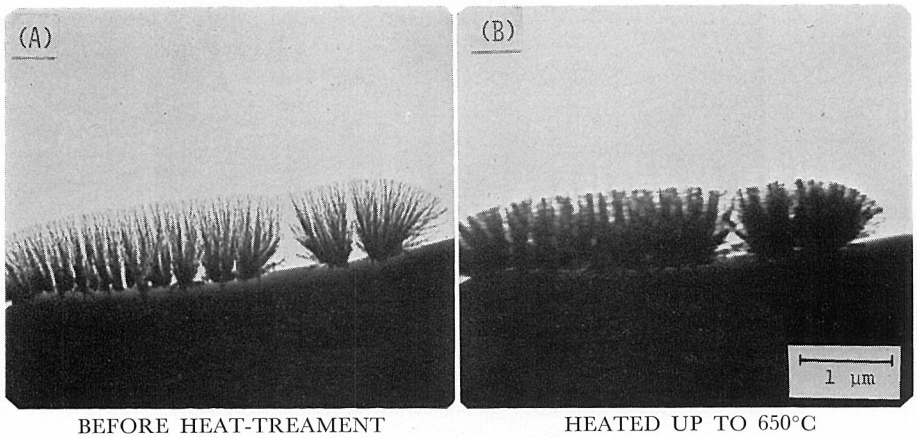


Fig. 2. Limited-field electron diffraction pattern of needle-shaped crystals formed on surface of $Na_2O \cdot 3SiO_2$ glass by subjecting to intense electron bombardment.



BEFORE HEAT-TREAMENT HEATED UP TO 650°C

Fig. 3. Crystal growth on fresh surface of $Na_2O \cdot 3SiO_2$ glass subjected to 60 minutes intense electron bombardment followed by heat-treatment.

2.13, and 1.75 Å)[6], NaO_2(III) crystal (d=2.77, 2.68, and 1.93 Å) and Na_2O_2 crystal (d=3.79, 2.10, and 1.90 A), 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.

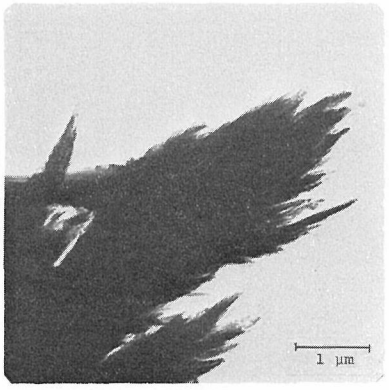


Fig. 4. Crystal growth on surface of $Na_2O \cdot 3SiO_2$ glass by exposing to moisture for three weeks.

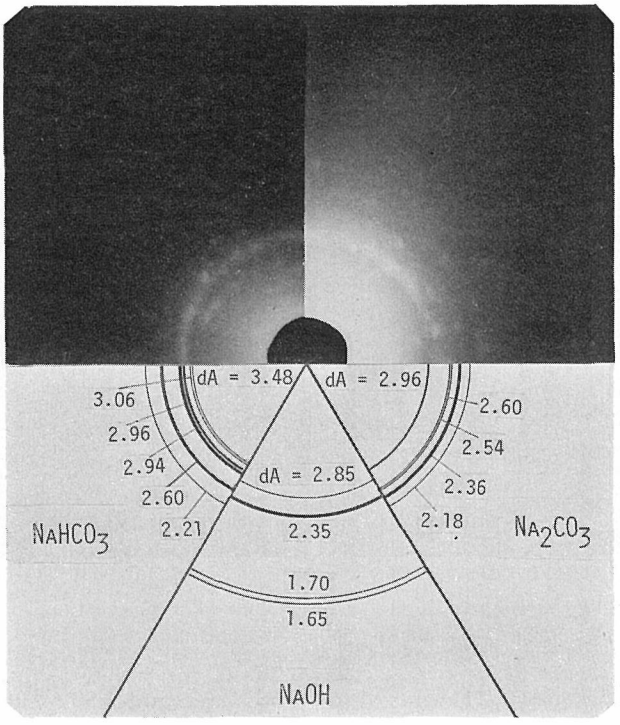


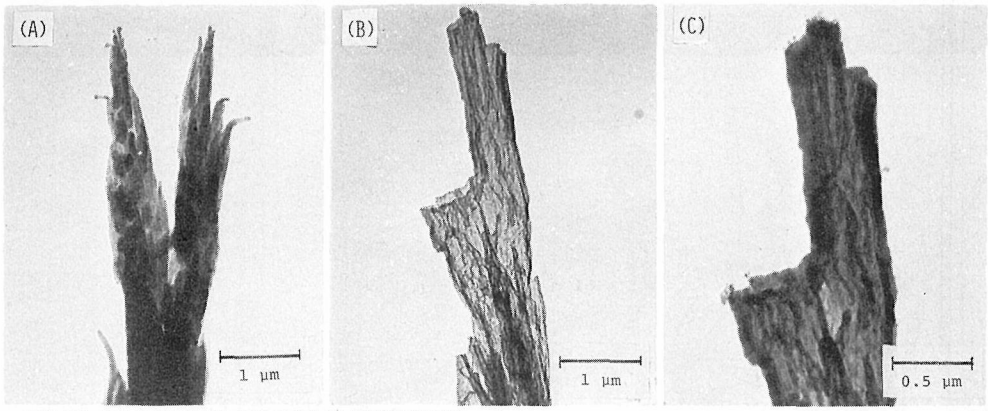
Fig. 5. Limited-field electron diffraction pattern of rod-shaped crystals formed on surface of $Na_2O \cdot 3SiO_2$ glass by exposing to moisture for three weeks.

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

A rod-shaped material, 0.2–0.5 μm width and 2–8 μm in length, grew from fragments of the glass exposed to the air saturated with water for three weeks. Figure 4 shows its electron micrograph. Figuer 5 shows its elctron 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 $NaHCO_3$, Na_2CO_3, and NaOH calculated from their d spacings given in literatures.[6,7] The diffraction rings corresponding to d=3.48, 2.96, 2.94, 2.60, and 2.21 Å characteristic for $NaHCO_3$[7], d=2.96, 2.60, 2.54, 2.36, and 2.18 Å for Na_2CO_3[6], and d=2.85, 2.35, 1.70, and 1.65 Å for NaOH[6] 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



TIME OF ELECTRON BOMBARDMENT:
0min. 10min. 730min.

Fig. 6. Effect of intense electron bombardment on crystals formed on surface of $Na_2O{\cdot}3SiO_2$ glass by exposing to moisture.

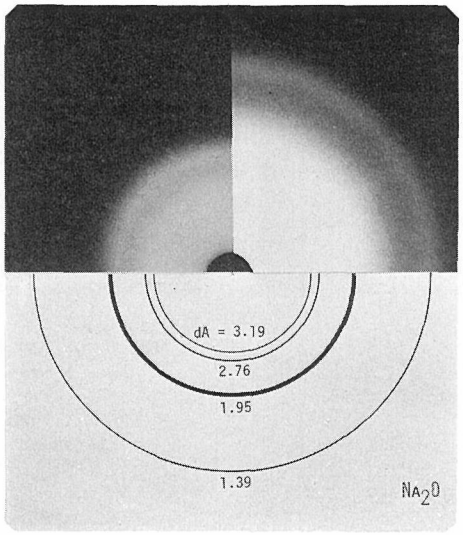


Fig. 7. Limited-field electron diffraction pattern of rod-shaped crystals formed on surface of $Na_2O{\cdot}3SiO_2$ glass by exposing to moisture. The pattern was obtained after the crystals were bombarded with intense electron beams for 30 minutes.

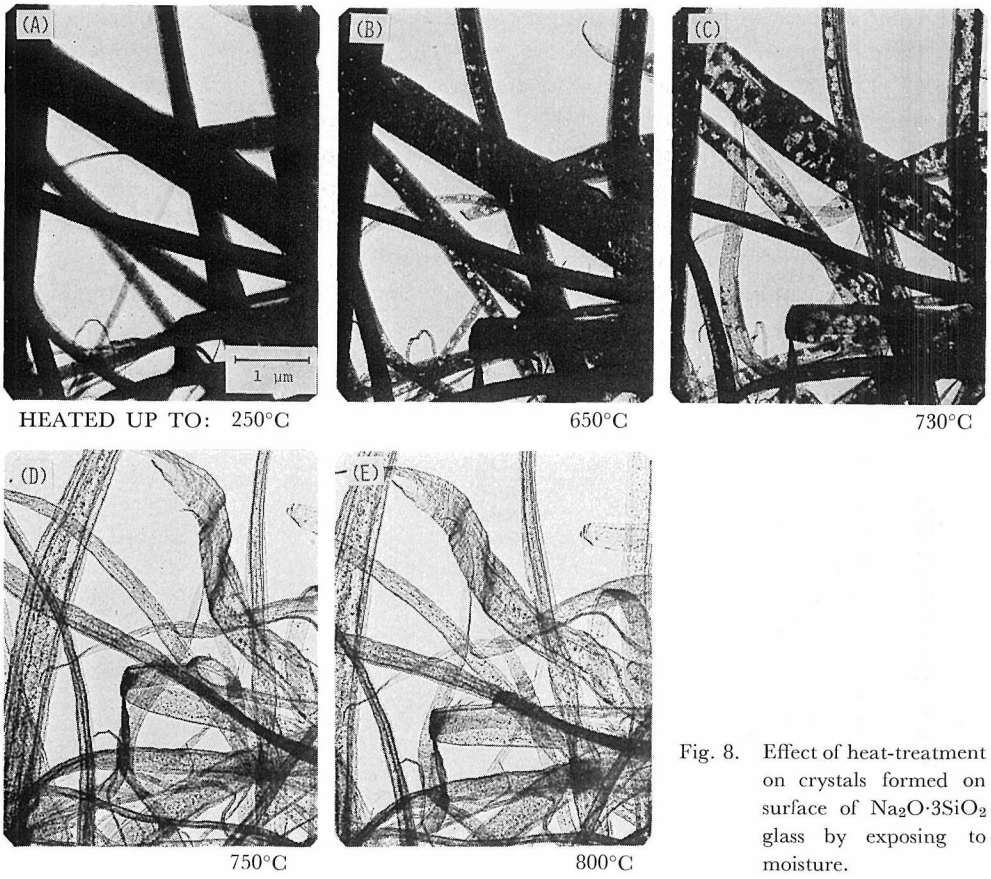


Fig. 8. Effect of heat-treatment on crystals formed on surface of $Na_2O \cdot 3SiO_2$ glass by exposing to moisture.

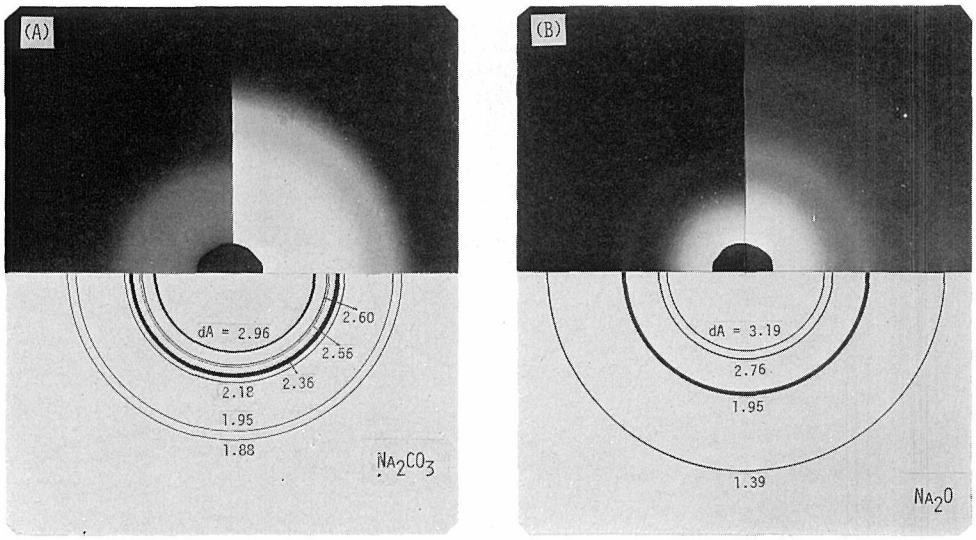
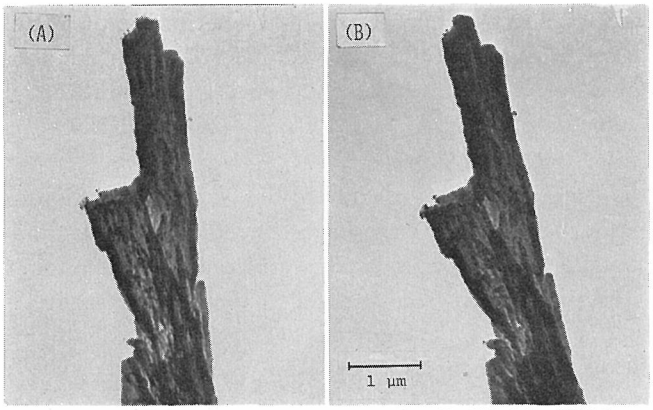


Fig. 9. Limited-field electron diffraction patterns of rod-shaped crystals formed on surface of $Na_2O \cdot 3SiO_2$ glass by exposing to moisture. The patterns (A) and (B) were obtained after the crystals were heated up to 500 and 730°C, respectively.

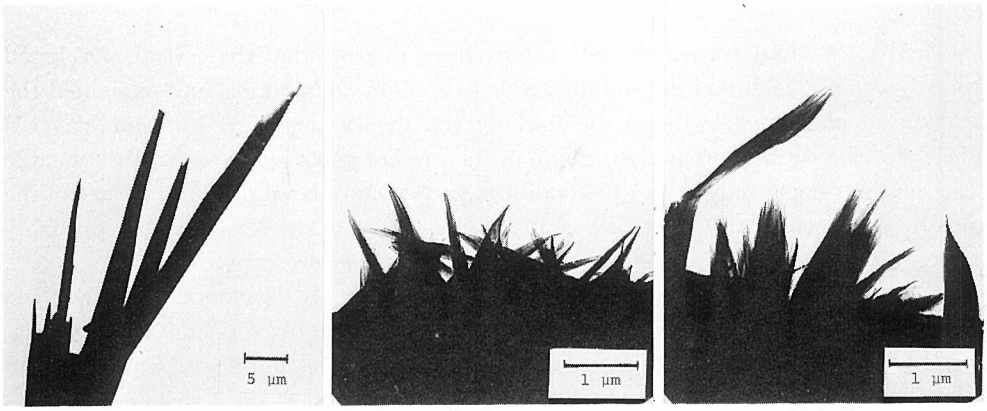
corners of the skeletonized crystal (Fig. 6(c)). Figure 7 shows an electron diffraction pattern of the skeleton crystal, which was very similar to that of the needle-shaped crystals grown from the fresh glass fragments, *i.e.*, to that of the Na_2O crystals.

When the rod-shaped crystals were heated in the electron microscope at a rate of about 20°C/min. without bombarding with intense electron beams, their skeletonization also occurred; it started from about 250°C and progressed very fast from about 800°C. Its process is shown in Fig. 8. Figure 9 is an electron diffraction pattern of the skeleton heated up to about 730°C. The pattern is very similar to that of the Na_2O crystals but not anyone of those of the $NaHCO_3$, Na_2CO_3, and NaOH crystals. The two rod-shaped crystals, one subjected to the intense electron beams followed by the heating up to about 600°C with the resistance heater, are shown for comparison in Fig. 10. Their diffraction pattern both consisted of fairly diffuse hallows but almost similar to that of the Na_2O.



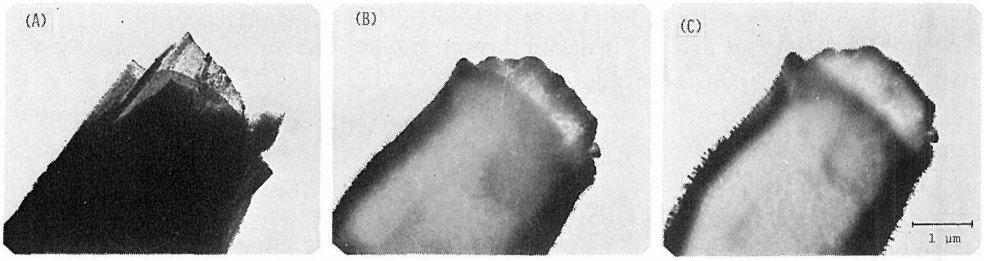
BEFORE HEAT-TREATMENT HEATED UP TO 600°C

Fig. 10. Effect of heat-treatment on rod-shaped crystals formed on surface of $Na_2O \cdot 3SiO_2$ glass by subjecting to intense electron beams for 30 minutes. Before heat-treatment the crystals were bombarded with intense electron beams for 30 minutes.



$NaHCO_3$ Na_2CO_3 NaOH

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



TIME OF ELECTRON BOMBADMENT:
0min. 15min. 30min.

Fig. 12. Changes of $NaHCO_3$ 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 $NaHCO_3$, Na_2CO_3, and NaOH, respectively, by the method described in the section II are shown in Fig. 11. The crystals grown from the $NaHCO_3$ 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 $NaHCO_3$, Na_2CO_3, and NaOH crystals given in literatures.[6,7]

When the rod-shaped crystals grown from the $NaHCO_3$ 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 Na_2O crystals but none of those of the $NaHCO_3$, Na_2CO_3, and NaOH crystals. Intense electron beams were also bombarded to the crystals developed from the Na_2CO_3 and 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,[1~4] 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.[8] Their electron diffraction analysis made in the present work indicates with reasonable certainly that they are Na_2O: The sodium atoms accumulated near the surface of the glass by the mechanism suggested by Lineweaver will form the Na_2O 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 $NaHCO_3$, Na_2CO_3, and 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 $NaHCO_3$: Decomposition or melting

temperatures of $NaHCO_3$, Na_2CO_3, and NaOH crystals at the atmospheric pressure are as follows[9]:

$$2NaHCO_3 \longrightarrow Na_2CO_3+H_2O+CO_2 \quad \text{at } 273°C$$
$$Na_2CO_3 \longrightarrow Na_2O+CO_2 \quad \text{at } 852°C$$
$$NaOH \text{ crystal} \longrightarrow NaOH \quad \text{melt at } 318°C$$

The skeletonization of the rod-shaped crystals started from about 230°C and progressed very fast from about 700°C. This would indicate that the decomposition of the $NaHCO_3$ crystals into the Na_2CO_3 crystals began from the former temperature and their further decomposition into the Na_2O crystals from the latter. The electron diffraction analysis of the two rod-shaped crystals heated up to about 500°C and about 730°C showed that they were probably the Na_2CO_3 and Na_2O crystals, respectively. The decomposition temperatures described above, *i.e.*, about 230°C and 700°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 Na_2CO_3 or NaOH, since the crystals were skeletonized from a much lower temperature than the decomposition temperature of the Na_2CO_3 and, furthermore, kept their shape over the temperatures much higher than the melting temperature of the NaOH.

Formation of $NaHCO_3$ crystals on the surface of the glass exposed to moisture was already confirmed by Tsuchihashi *et al.* for some Na_2O-containing commercial glasses by electron diffraction techniques.[10] To the authors knowledges, however, their morphological studies by transmission electron microscopic techniques have not yet been reported.

Why do the $NaHCO_3$ 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.[11] Especially, the present case seems to be analogous in principle to a case of percrystallization of sodium chloride first found by Hinegardne;[12] 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; Na^+ ions originally present in the silica-rich layer diffuse through this layer, reach the outside, combine with H_2O and CO_2, forming the rod-shaped $NaHCO_3$ crystals extending to one direction. The mechanism of the percrystallization, itself, have already been explained by several researcher.[13~15] There should be the same opportunity for the Na_2CO_3 and NaOH crystals to form in rod-shape as for the $NaHCO_3$ crystals. The fact that the rod-shaped crystals obtained were consisted mostly of the $NaHCO_3$ can be explained by the high growth rate of the $NaHCO_3$ crystals compared to those of the other two crystals (see Fig. 11).

The cause for the formation of needle-shaped Na_2O 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[1,2] would diffuse through the SiO_2 network-former in glass structure, reach the surface and combine with traces of oxygen in the electron microscope.

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