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# Crystallization of the Glasses in the $Li_2O$-$SiO_2$ System

By

**Satoru KAKITANI**

*with* 1 *Table,* 2 *Text-figures, and* 4 *Plates*

(Received May 30, 1972)

ABSTRACT: Heterogeneity of the $Li_2O$–$SiO_2$ glass and the process of crystallization through heating were investigated by using the electron- and ordinary microscopic techniques. Under the electron microscope the separated droplet phases of about 100 Å in diameter were observed comprised in the matrix of the opalescent glass composed of lithium trisilicate, while the parts of the colorless and transparent glass of lithium disilicate were also found to be slightly heterogeneous. In addition to above, the fact that the interfacial boundaries between two separated phases are not favorable for nucleation of the crystals was also confirmed. As a result of the differential thermal analysis, a small-scaled endothermic phenomenon assumed to be necessary for the atomic rearrangement was recognized just before the remarkable exothermic reaction ascribed to crystallization. Moreover, it is to be noted that devitrification of the glass rod accompanied with crystallization of lithium silicate and lithium metasilicate was markedly promoted in a short period of about two months.

CONTENTS

## I. INTRODUCTION

In spite of its mechanical properties as a true solid the glass is usually called an undercooled liquid, but surely differs from the crystalline substance owing to obscurity of its melting point. The atoms in the glassy structure are arranged in the manner similar to those in the liquid and combined with the permanent neighbors at a fairly definite distance, whereas in a liquid the neighbors about any atoms of molecules are continually changing. On the other hand, the glass is conveniently considered as a sort of liquid cooled below its freezing point existing in a state of metastable equilibrium with the free energy higher than that of the corresponding mixture of the crystalline phases under the same condition. In order to convert the glass from the metastable to stable state, two types of reactions such as nucleation and crystal growth are requisite.

The $X$-ray diffraction patterns of the glass consist of one or more broad and diffused rings. The structure of silica glass was analysed by WARREN (1937) according to ZACHARIASEN's framework theory (1932). WARREN's analysis was criticized on the basis of a comparison of the structure of $\alpha$-cristobalite with that of the silica glass by OBERLIES and DIETZEL (1957) pointing out that the short range order in the latter should be higher than was previously assumed and similar to that in the former. Not all of the six membered rings of [$SiO_4$] tetrahedra in this framework are complete and many of them may be "open" or incomplete state like those observed in the behavior in the transformation range, while the tetrahedra can not be strictly regular, but is more or less distorted in the glass.

The phenomenon concerning crystallization of the silicate glass is an interesting subject and also one of the fundamental problems to be inspected. The author wished to try to analyze the structure prior to that of the crystalline state through the radial atomic distribution function method and the infra-red absorption data, but sufficient information was unable to be obtained yet. In consequence only heterogeneity in the precrystalline state of the $Li_2O$–$SiO_2$ glasses observed under the optical and electron-microscopes and the thermal phenomena accompanied with crystallization were discribed in this paper.

## II. PREPARATION OF THE SPECIMENS

The glasses to be investigated were melted in the platinum crucible placed in a siliconit furnace, poured out on the platinum plate and quenched in the air but not annealed for excluding emergence of the stresses.

The compositions and characteristics of the prepared glasses are presented in Table 1. The glasses of this series considered as the object convenient for studying heterogeneity found in the original state and during the process of crystallization derived from the thermal treatments were subjected to the following experiments.

TABLE 1. COMPOSITIONS AND MEGASCOPIC CHARACTERISTICS OF THE GLASSES

| Composition $Li_2O$ : $SiO_2$ (Mole ratio) | Condition for preparation | Characteristics of Glass |
|---|---|---|
| 1 : 3 | Melt poured onto the platinum plate and cooled | Blue-colored, opalescent in moderate intensity |
| 1 : 2.5 | | Faint blue-colored, opalescent |
| 1 : 2.25 | | Transparent and colorless |
| 1 : 2 | | Same as above |
| 1 : 1.75 | | Same as above |
| 1 : 1.5 | | Partly crystallized |
| 1 : 1 | | Mostly crystallized |

## III. ELECTRON MICROSCOPY

Some of the small pieces were picked up out of the crushed specimens of glass and provided for the experiments after some procedures such as etching in 1–2% HF for the definite time (10 to 60 sec.) washing in the running distilled water and thorough drying for obtaining the fractures with the fresh surface. The specimens with the knife edges were used partly for the direct transmission microscopy and partly for the procedure with the replicas. The surfaces of the specimens subjected to the latter were coated simultaneously with carbon and platinum, and then the replicas obtained were peeled off in 10% HF solution.

### 1) *Observation through Direct Transmission*

All of the photographs 1∼8 in Plate 18 show those obtained through the transmitted electrons radiated onto the thin edges of the etched specimens. As is shown in photo. 1 of Plate 18, heterogeneity is not clearly observable in the colorless and transparent glass with the ratio of lithium disilicate $Li_2O$ : $SiO_2$ (1 : 2) but slightly recognized merely with careful inspection. With ascension of the temperature from 550°C to 580°C, heterogeneity gradually become clear. In the case of the pale opalescent glass with the composition of $Li_2O$ : $SiO_2$ (1 : 2.5) the tiny droplets are formed in the texture as is revealed in photo. 4 of Plate 18. In the heterogeneous micro-structure of the opalescent glass composed of lithium trisilicate showing in photos. 5 and 8 of Plate 18, the separated droplets are discernible in the matrix. As elevation of the treating temperature, deformation of the droplets in more amount and development of the linkages among them become more conspicuous. The phase of the separated droplet is less soluble than that of the glassy matrix etched with HF solution. It is to be noticed that the dispersed phase appears stronger than the matrix against the absorption electrons and is rich in silica. This is well consistent with the results given by PHILLIPS, MCMILLAN (1965) and JAMES, MCMILLAN (1968). Judging from the pattern shown in photo. 8 of Plate 18, the matrix of glass with the composition of lithium trisilicate is considered to be constructed of the cellular textures.

### 2) *Observation with Replica*

Photo. 1 of Plate 19 shows the microfeature of the replica on the fracture surface of the colorless and opalescent glass with the ratio of $Li_2O$ : $SiO_2$ (1 : 2). The photos. 2, 3 and 4 indicate those of the same glasses heated respectively at 550°C, 580°C and 600°C. In each case the small-scaled relief is observable and its contrast is most clear on the specimen heated at 600°C. The hollows with different magnification are discernible in photo. 5 and assumed to be corresponding to the droplets obtained through the direct transmission method, while their deformation as well as variation of the texture are confirmable in photos. 6, 7 and 8.

## IV. ORDINARY MICROSCOPY

Heterogeneity of the glasses in the $Li_2O$–$SiO_2$ system is not discriminated under the ordinary microscope. In all glasses after heating at 550°C to 620°C for about two hours the beautiful sphelurites are observable. It seems common that the lithium silicate glasses have a characteristic tendency to crystallize easily. So the spherulites are formed even at the lower temperatures referred to above. In the temperature region from 550°C to 620°C the spherulites are isolated from each other, as is clearly observed in Plate 20 revealing various shapes formed in the glass. In the case of the glass with the composition rich in silica, high temperatures are necessary for their formation. Through heating at about 650°C, the spherulites disappear and the aggregates of crystals in all specimens of the glasses in this system appear, as are exhibited in photos. 1~4 of Plate 21. Although there are no evidences on observation of the process it seems obvious that the separated droplets give some apparent influence on formation of the crystals in the glasses.

## V. CRYSTAL GROWTH IN THE GLASS ROD

Through keeping the small rod made of the fused glass composed of lithium disilicate for about two months under the room condition, the aggregates of the crystals of lithium silicate and lithium metasilicate are discriminated on its surface and in the interior, as are displayed in photos. 2, 3 and 4 of Plate 21. With duration of time the glass rod become to bear an uneven surface and insensitive to light. From the fact of crystal growth in the glass rod it is deducible that because of the strong attraction of lithium atoms for oxygen atoms in the glasses of lithium silicate, their distance is kept shorter, resulting in unstable state of the structure and accordingly remarkable growth of the crystals even under the room condition and for a relatively short period.

## VI. DIFFERENTIAL THERMAL ANALYSIS

As is clear in Fig. 1, a noticeable exotherm ascribed to crystallization of the glass is observed at about 600°C in association with a tiny-scaled endotherm just before the marked exotherm related to crystallization of lithium metasilicate.

In contrast to the exotherm, the thermal absorption on crystallization in the glass, though to a slight extent, is considered of significance. At this stage of the endothermic reaction the atoms in the structure of the glass may be most actively movable for reaching the crystalline state. It appears remarkable that the positions of the exothermic peaks are variable with the chemical composition of galsses.

## VII. CONSIDERATION

For variation of the structure from the unstable state of glass in the system of lithium silicate to the stable crystalline state, two processes such as nucleation and crystal growth are indispensable. TAMMAN (1925) pointed out already that these processes have different mechanics controlling the rate of reaction and the maximum nucleation often occurs at a temperature lower than that for the critical rate of growth. In the special cases devitrification based upon nucleation and growth of the crystals is recognizable at a negligible rate, since there are certain kinds of the natural glasses such as obsidian without the remarkable progress of devitrification subsequent to their formation. Some of the glasses composed of lithium silicate however suggest the rapid nucleation and crystal growth.

Be it so, it is most desirable, if possible, to find out some information concerned with movement of the atoms in the structure of the glass through analysis with use of the radial

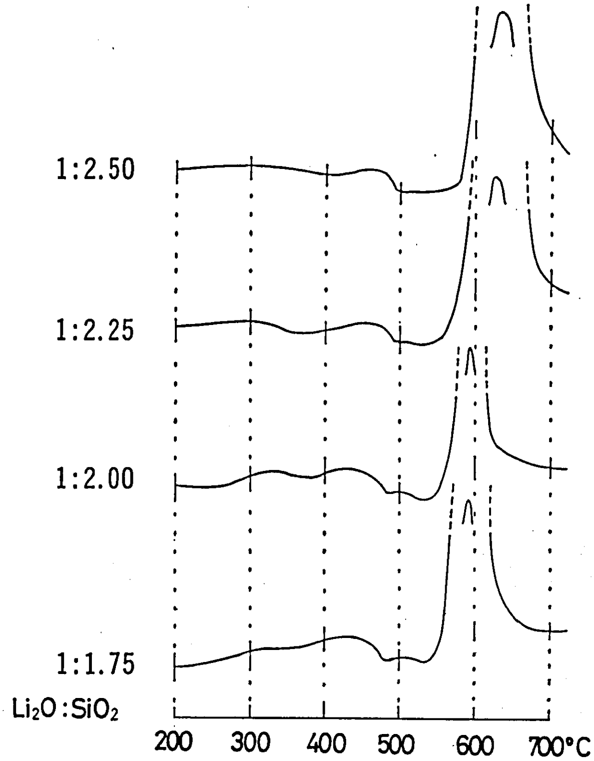

Fig. 1. DTA curves for the glasses with some mol. ratios of the compositions in the $Li_2O$–$SiO_2$ system.

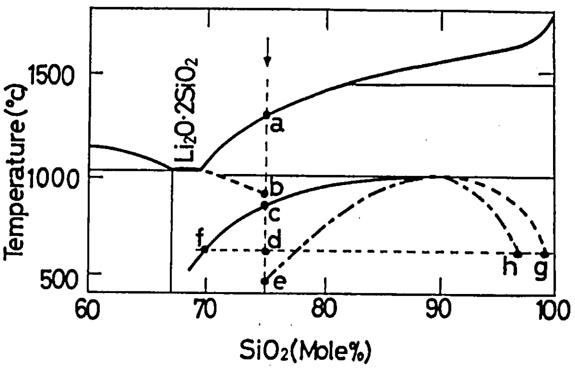

Fig. 2. A part of the phase diagram of the $Li_2O$-$SiO_2$ system.

distribution function for obtaining directly the inter-atomic distance together with the numbers of the neighboring atoms around the respective atoms, whereas the present data seem insufficient for the purpose.

Fig. 2 shows a part of the phase diagram given for the system $Li_2O$–$SiO_2$ showing the miscibility line (f–c–g), the spinodal line (e–h) and an immiscibility region surrounded by the solid line (f–c–g) determined experimentally by MORIYA, WARRINGTON, and DOUGLAS (1967).

When the system is cooled the melt with such a composition of the lithium trisilicate as is marked with an arrow is saturated with silica at the temperature below the point a. When the melt in question is undercooled without crystallization, the immiscibility region is obtained at and below the point c. The immiscibility region is divided into two areas by spinodal line passing through the point e. In the temperature range from c to e the undercooled melt tends to be disintegrated into the glassy phases with different compositions. For instance, at 600°C, the melt bears a tendency of being separated into two glassy phases with the compositions represented by the point f and g. It is common that one of two phases bears a droplet form.

In the immiscibility region of the $Li_2O$–$SiO_2$ system mentioned above, the glasses separated into two phases are often formed prior to nucleation of the crystalline material. Two glassy phases are separable through the process of nucleation and growth of the droplets, as were proposed by OHLBERG et al. (1965) and HALLER (1965), or spinodal decomposition, as was suggested by CHAN and CHARLES (1965). There are some experimental data given by MORIYA, WARINGTON, and DOUGLAS (1967) and MORIYA (1968) using the electron microscope, while the small angle scattering *X*-ray study on the spinodal decomposition in the soda-silica glass was obtained by NEILSON (1969). After heating the decomposed glass for long time the interconnecting phases are separated into the bulk of droplets.

As was pointed out by MUKHERJEE and ROGERS (1967) it may be thought that separation of the glass into two liquidus phases gives a favorable condition for nucleation of the crystals, although the intimate connection of phase separation with nucleation of the crystals is remained not to be clarified in the course of the present experiment. The crystallizing temperature of the opalescent glass with the ratio of $Li_2O : SiO_2$ (1 : 3) including the phase of the scattered droplets is slightly higher than that of the glass composed of lithium disilicate and the spherulite appear at about 600°C. With the detailed inspection under the electron microscope, a sort of the network textures were observed in the matrix of the glass composed of $Li_2O : SiO_2$ (1 : 3), while even in the case of the colorless and transparent glass composed of $Li_2O : SiO_2$ (1 : 2) uncertain one were recognizable. As for the separated phase of the droplets it is a matter of course that all specimens of the glasses in the $Li_2O$–$SiO_2$ system reveal more or less heterogeneity. With elevation of temperature, a contrast of heterogeneity become more clear even in the glasses such as those of silica with high crystallizing temperature and the heterogeneous microtexture are considered to be produced just before crystallization.

## VIII. SUMMARY

In the light of the complicated factors controling the $Li_2O$–$SiO_2$ system heterogeneity recognizable electron-microscopically in the glasses concerned and arrangement of the atoms in the state prior to crystallization, though without any reference to their behavior accompanied with variation, were subjected to research in the present study. Either in the opalescent glass separated into the droplet and matrix phases or even in the colorless and transparent one, heterogeneous microtextures were discriminated.

In the related glasses with the characteristics likely to crystallize a sort of heterogeneity is assumed to exist even at the initial stage before crystallization and clearly to be more accelerated by heating. Since through the processes of nucleation and crystal growth the interfacial effects between the droplet and matrix phases could hardly be recognized, the investigation concerning this kind of problem is necessary in the future.

In conclusion, the author would like to thank the staffs of the Mineralogical Laboratory of Hiroshima University for their considerable assistance during this investigation.

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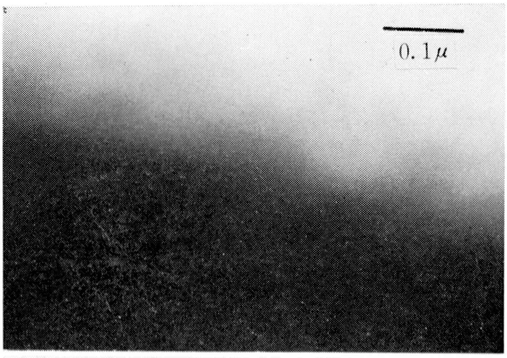
## EXPLANATION OF PLATE XVIII

Photomicrographs obtained through direct transmission under the electron-microscope.

1. A part of the piece of the colorless and transparent glass with the composition of $Li_2O$: $SiO_2$ (1: 2).
2. Glass with the compostion of $Li_2O$: $SiO_2$ (1: 2) after heating at 550°C.
3. Glass with the composition of $Li_2O$: $SiO_2$ (1: 2) after heating at 580°C.
4. Pale opalescent glass with the composition of $Li_2O$: $SiO_2$ (1: 2.5).
5. Separated droplets in the matrix of glass with the composition of $Li_2O$: $SiO_2$ (1: 3).
6. Glass with the composition of $Li_2O$: $SiO_2$ (1: 3) after heating at 550°C.
7. Glass with the composition of $Li_2O$: $SiO_2$ (1: 3) after heating at 580°C.
8. Separated droplets and matrix showing the net-like textures of the glass with the composition of $Li_2O$: $SiO_2$ (1: 3).

1



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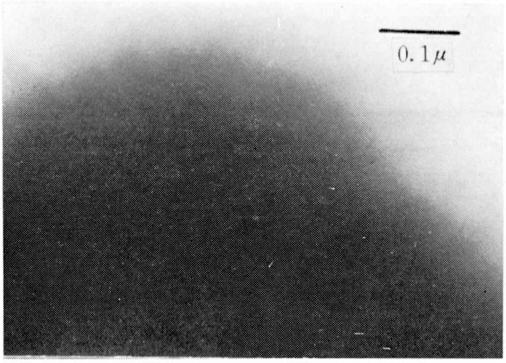

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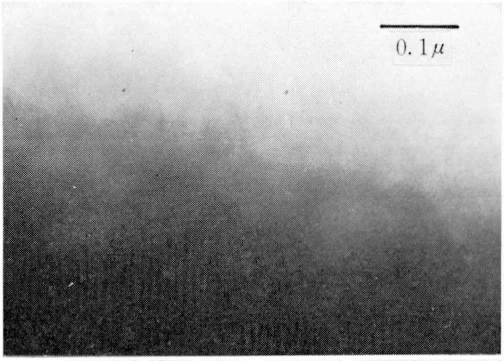

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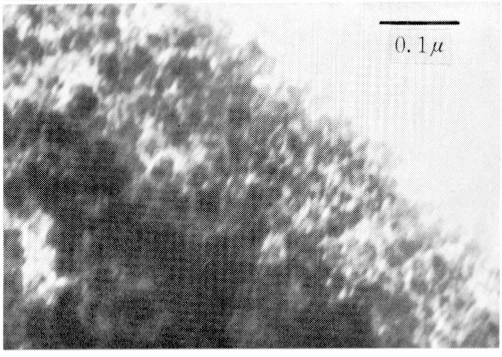

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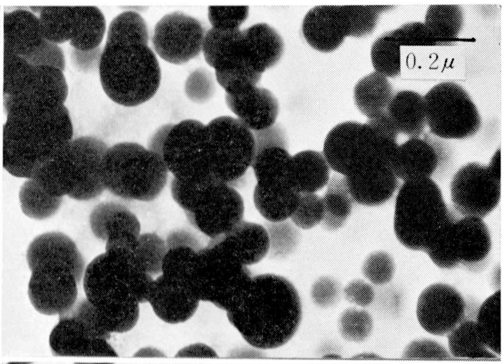

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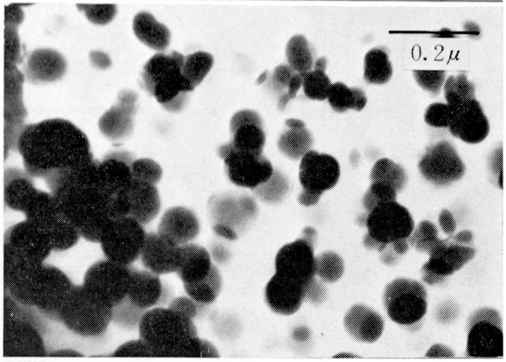

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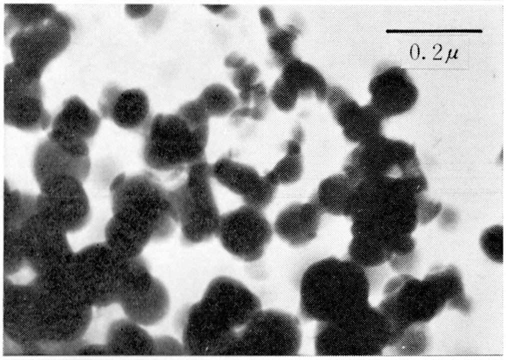

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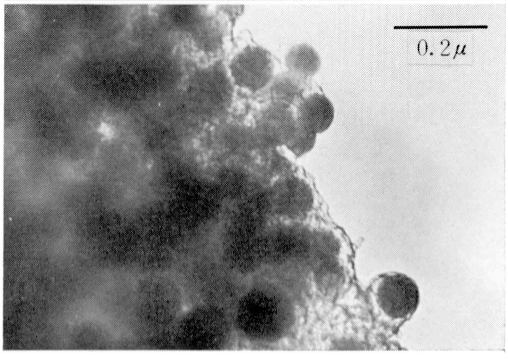
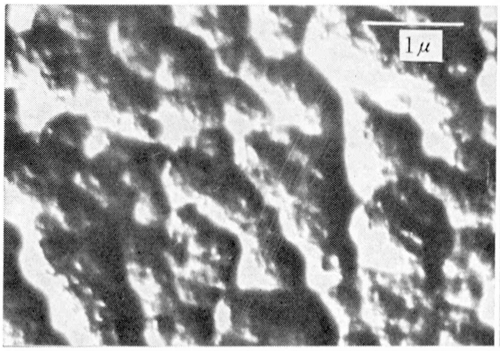


## EXPLANATION OF PLATE XIX

Photomicrographs obtained for the replicas under the electron-microscope.

1. Glass with the composition of $Li_2O : SiO_2$ (1 : 2).
2. Glass with the composition of $Li_2O : SiO_2$ (1 : 2) after heating at 550°C.
3. Glass with the composition of $Li_2O : SiO_2$ (1 : 2) after heating at 580°C.
4. Glass with the composition of $Li_2O : SiO_2$ (1 : 2) after heating at 600°C.
5. Glass with the composition of $Li_2O : SiO_2$ (1 : 3).
6. Glass with the composition of $Li_2O : SiO_2$ (1 : 3) after heating at 550°C.
7. Glass with the composition of $Li_2O : SiO_2$ (1 : 3) after heating at 580°C.
8. Glass with the composition of $Li_2O : SiO_2$ (1 : 3) after heating at 600°C.

1



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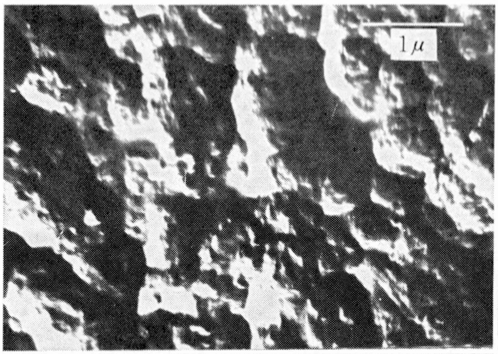

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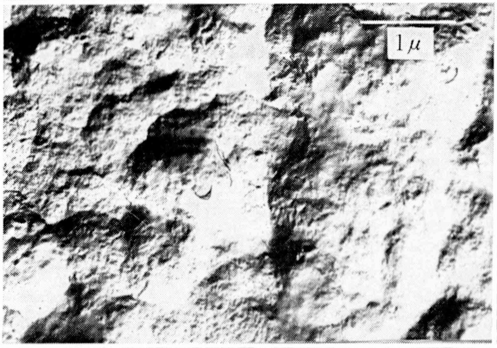

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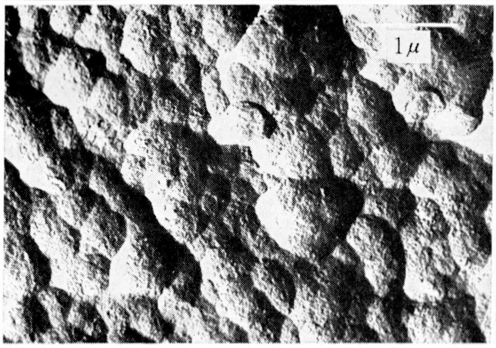

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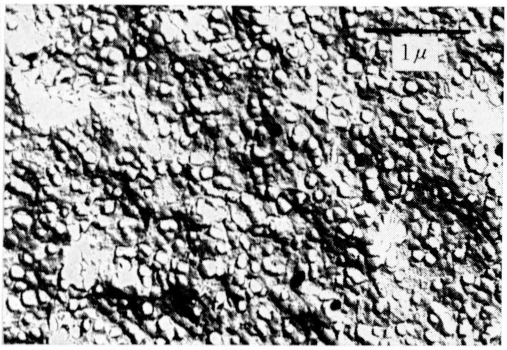

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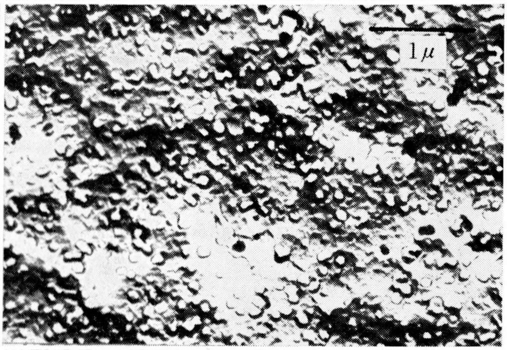

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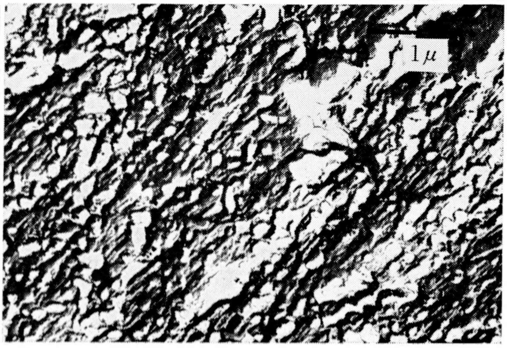
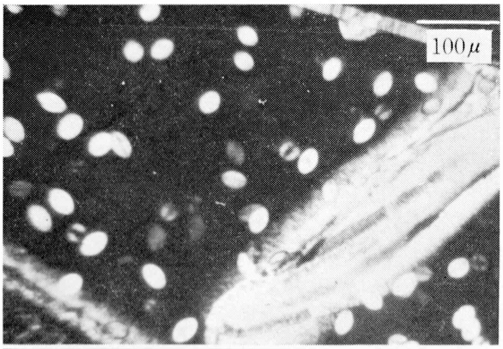


## EXPLANATION OF PLATE XX

Photomicrographs under the ordinary microscope.

1. Spherulites grown up in the glass with the composition of $Li_2O$: $SiO_2$ (1: 2) after heating at 580°C. (under crossed nicols)
5. Spherulite under parallel nicols.

2, 3, 4, 6, 7 and 8.
Various kinds of shapes and patterns of spherulites. (under crossed nicols)



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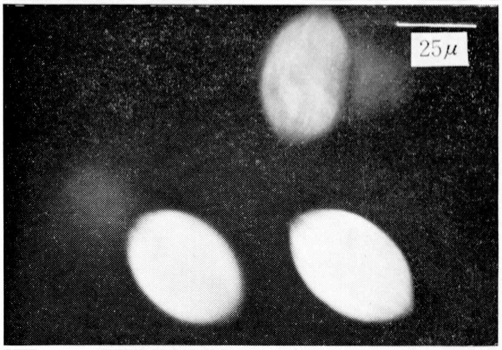

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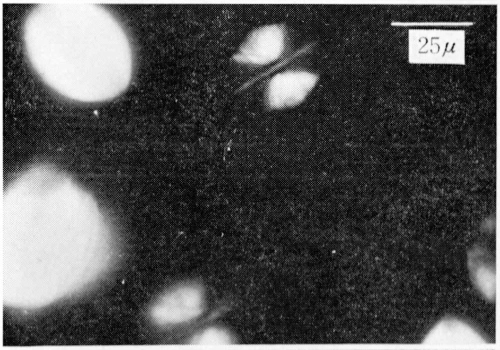

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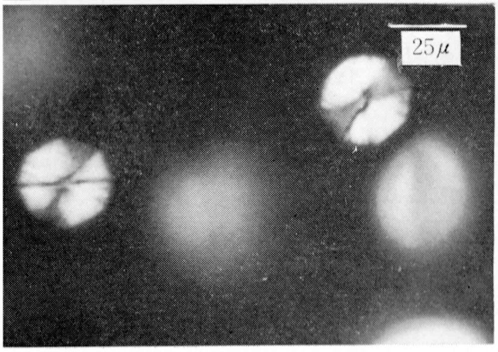

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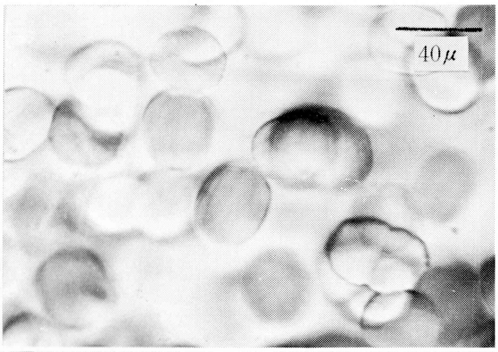

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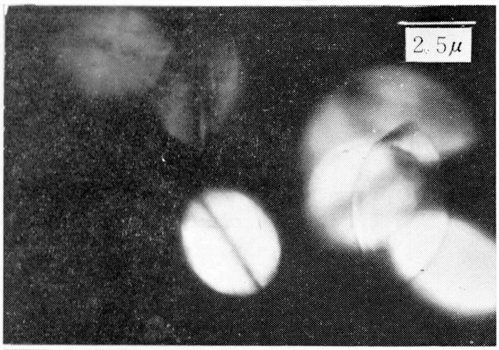

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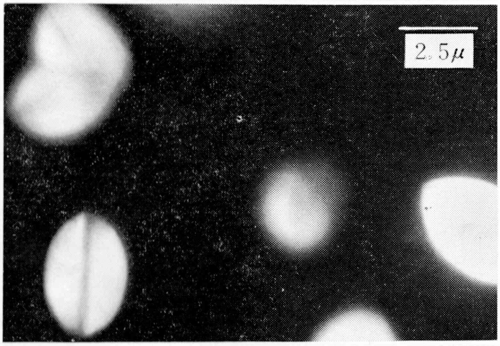

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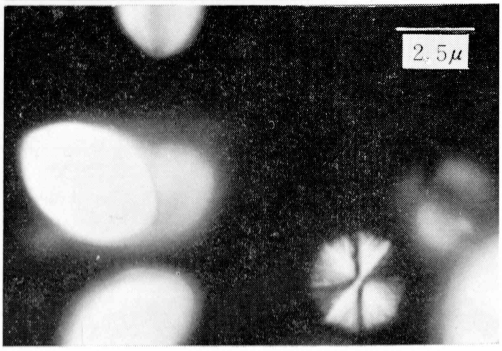

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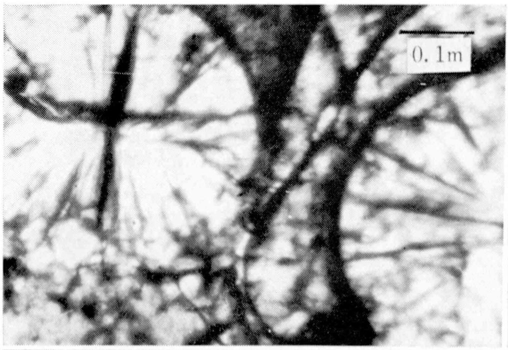
## EXPLANATION OF PLATE XXI

Photomicrographs under the ordinary microscope

1. Crystal aggregates grown up in the glass with the composition of $Li_2O:SiO_2$ (1:2) after heating at 600°C.
2. Those in the glass with the composition of $Li_2O:SiO_2$ (1:2) after heating at 650°C. (under parallel nicols)
3. Those in the glass with the composition of $Li_2O:SiO_2$ (1:3) after heating at 600°C. (under crossed nicols)
4. Those in the glass with the composition of $Li_2O:SiO_2$ (1: 3) after heating at 650°C. (under crossed nicols)
5. Glass rod with the composition of $Li_2O:SiO_2$ (1:2), just prepared. (under crossed nicols)
6. and 7.
   Glass rod with the composition of $Li_2O:SiO_2$ (1:2), obtained after about 2 months since preparation. (under parallel nicols)
8. Glass rod with the composition of $Li_2O:SiO_2$ (1:2), obtained after about 2 months since preparation. (under crossed nicols)

1



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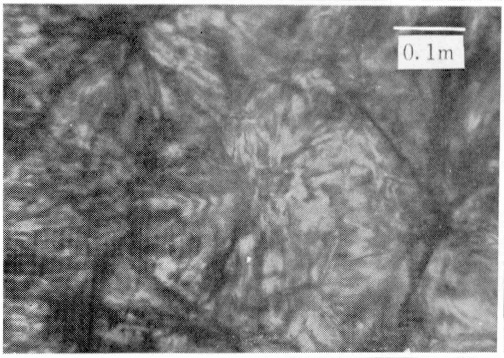

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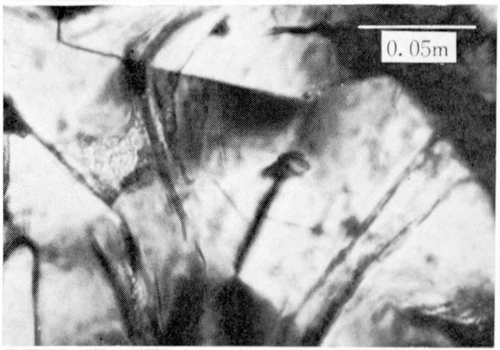

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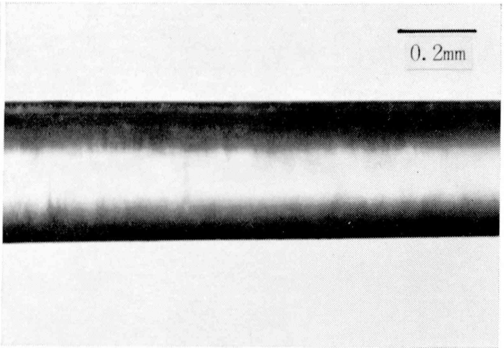
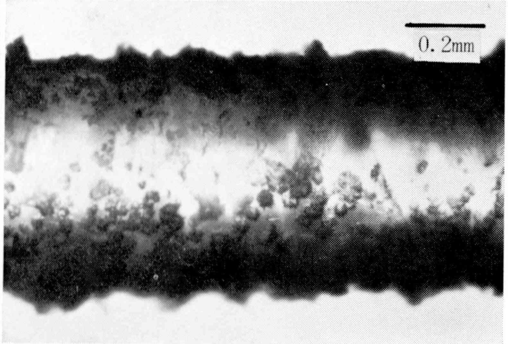


6

7



8