Microstructure and Strength of Crystallized Glass of Photoceram-Type

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1. Introduction
In the previous works1,2, it was reported that the strength of metastably phase-separated glasses was dependent on the size of glassy particles dispersed in the glassy matrix and that it decreased with increasing particle size. The present study is concerned with the strength of glass-ceramics in which crystalline particles are dispersed in a glassy matrix, in contrast to the phase-separated glasses in which dispersed particles are glassy. In order to investigate the effect of crystal grain size on the strength, particularly, a photo-sensitive glass which could be converted to glass-ceramics having crystal grains of various sizes by changing the irradiation time was used in the present study.

Tashiro and Sakka3 already studied the strength-grain size relationship for the same glass-ceramic as used in the present study and found that the strength of the samples in which lithium disilicate and quartz crystals were precipitated was dependent on their grain size. In their study no consideration was made on the structure of the surface of the sample which was exposed to the ambient atmosphere during heat treatment. Recently, however, it was reported that, in general, the surface of glass-ceramics have a microstructure different from that of the bulk4,5 and may greatly influence their strength behavior6. In view of this, it was considered necessary to make research on the strength with a particular attention to the effect of the original surface of samples. In the present study it was attempted to make strength measurements after removing the original surface layer by etching with hydrofluoric acid solution.

So far many studies have been published on the strength of glass-crystal composite systems7, which were prepared by hot-pressing powder mixtures, but relatively few studies have been made on the strength of glass-ceramics.

2. Experimental methods
2.1 Preparation of glasses
A glass of the composition SiO2 81, Li2O 12.5, K2O 2.5, Al2O3 4, CeO2 0.03, Au 0.027% in weight was used in the experiment. All the chemicals used for the preparation of the glass were of reagent grade except for the SiO2 which was a high purity quartz sand used for manufacture of optical glasses. In order to prevent spontaneous precipitation of gold during cooling of the melt, a portion of K2O (1% out of 2.5%) was added to the batch as potassium nitrate, which had oxidizing power, and the rest as potassium carbonate. A mixture of raw materials was melted in a Pt–10% Rh crucible in a silicon carbide electric furnace for 4 hours at 1,450°C. Rods of about 4 mm diameter were drawn from the melt and used for the experiment.

2.2 Gamma-irradiation
It is known that U.V. irradiation promotes precipitation of crystals in the glass used in the present study and their size can be changed by changing the U.V. exposure time8. The U.V. ray has a disadvantage that its penetration distance is relatively short. In the present experiment, therefore, the glass was irradiated by γ-ray, which was reported to be effective in nucleating gold colloids, similar to U.V. ray9. Total γ-ray dose was varied by changing the time of irradiation from none to 217 hours with a constant dose rate of 1.75×104 r/hr.

2.3 Heat treatment
The samples which had been irradiated by γ-ray were heated on a schedule shown in Fig. 1; they were heated up at a rate of 5°C/min and held at 510°C for 1 hour, at 620°C for 2 hours and at 900°C for 4 hours. After cooling, the sample was etched with hydrofluoric acid solution to remove the surface layer.

[Fig. 1 Schedule of heat treatment for crystallizing the glass]
°C for 2 hours, for the formation of gold colloid, lithium metasilicate and lithium disilicate, and lithium disilicate and quartz, respectively. A series of samples (series 1) were heated up to 620°C (not subjected to the heat treatment at 900°C) and the other series (series 2) heated up to 900°C.

2.4 X-ray diffraction

Crystalline species found in the samples was identified by X-ray diffraction analysis. Powder diffraction patterns were obtained on the surface of the sample of plate form as well as on the powder obtained by crushing the plate samples.

2.5 Electron microscopy

Electron microscopic observation was made by the replica technique on the original surface and the interior of the crystallized samples. To observe microstructure of the interior of the samples, their original surface was ground away by about 2 mm and polished, and the resultant new surface was etched with 1% hydrofluoric acid solution for 15 seconds and replicated. A two step replica method using acetyl cellulose and carbon films shadowed with chromium was used.

2.6 Strength

The three-point loading method was used to determine the modulus of rupture, the rod being supported on two knife edges and a load was applied at the center at a constant loading rate. The strength (modulus of rupture) was calculated by

$$\sigma = \frac{8PL}{\pi d^3}$$  (1)

where \(P\) is the load at rupture, \(L\) is the distance between the two supporting knife edges (30 mm in the present experiment) and \(d\) is the diameter of the glass rod. Six measurements were made on each type of sample.

3. Experimental results

3.1 Results on crystallized glasses obtained by heating up to 620°C (series 1)

3.1.1 X-ray diffraction

X-ray diffraction patterns of the powders obtained by crushing the crystallized samples are shown in Fig. 2 (a), (b) and (c). The sample which had not been exposed to \(\gamma\)-ray showed the peaks of lithium metasilicate and lithium disilicate crystals, while only lithium metasilicate crystals were detected in the samples which had been irradiated by \(\gamma\)-ray. The latter fact indicates that only lithium metasilicate crystals are precipitated in the interior. Fig. 2 (d), (e) and (f) show the X-ray diffraction patterns taken from the original surfaces of the plate samples. In these cases both lithium metasilicate and disilicate were found in all the samples. It was also noted that the (002) peak of lithium disilicate was abnormally high, indicating that this crystal is oriented at the original surface. The relative degree of orientation was the highest for the sample which had not been subjected to \(\gamma\)-irradiation before heating.

For all the samples irradiated by \(\gamma\)-ray, X-ray diffraction pattern of the original surface showed the presence of both lithium metasilicate and lithium disilicate, but that of the interior 20 \(\mu\) deep from the surface showed only metasilicate crystals. It can be said, therefore, that the surface layer of at least 20 \(\mu\) thick should be removed to investigate the relationship between the strength and the bulk structure without being influenced by the original surface.

3.1.2 Electron microscopic observation

Photographs in Fig. 3 are electron micrographs showing the microstructure of the interior of the crystallized samples. A few dendritic crystals were distributed irregularly in the sample not subjected to \(\gamma\)-irradiation, whereas thin, long crystals were precipitated uniformly in the irradiated samples. The size of crystals decreased with increasing \(\gamma\)-ray dose and it was the smallest at a total dose of 35\(\times 10^4\) \(\gamma\). The size of crystals increased, then, with further increase of \(\gamma\)-ray dose. It has been shown by the X-ray diffraction analysis (Fig. 2) that these crystals were lithium metasilicate.

Fig. 4 gives electron micrographs showing the surface structure of the samples which had been irradiated by \(\gamma\)-rays before heat treatment. There
are pretty large glassy spots about 1 μ in size, where no crystals are found, in the sample γ-rayed by 35×10^4 r.

3.1.3 Bending strength Fig. 5 shows the change of the strength with the gradual removal of the surface layer by etching with 10% hydrofluoric acid. As shown in the figure, the strength is in the range of 40~50 kg/mm² before etching, independent of the γ-ray dose. As the etching is continued, the strength decreases pronouncedly for the sample which was not irradiated and it more or less increases for the samples which were irradiated.

In Fig. 6 the strength obtained after removing the surface layer of 40 μ is plotted as a function of γ-ray dose. The strength is the lowest for the sample which was not irradiated. With increasing γ-ray dose it increases, reaching a maximum at a dose of 35×10^4 r. Further irradiation, however, results in reduction in the strength. The plot of the strength versus the grain size of the crystals precipitated in the sample is shown in Fig. 7.
The length of the longer axis of the crystals was taken as the grain size, which was determined approximately using Fig. 3. It can be seen from Fig. 7 that the strength increases as the grain size decreases. The data is not plotted for zero dose (no irradiation) because the two kinds of crystals were found in the sample which had not been irradiated, in contrast to the irradiated samples in which only one crystalline species (lithium disilicate) was found.

3.2 Results on crystallized glasses obtained by heating up to 900°C (series 2)

3.2.1 X-ray diffraction In Fig. 8 are shown the X-ray diffraction pattern taken from the powder (top pattern) and those taken from the plate samples without crushing to powder (lower four patterns).

The X-ray diffraction pattern of the pulverized samples, which is considered to show crystalline phases precipitated in the bulk of a sample, was identical for all the samples regardless of the total X-ray dose and showed the formation of lithium disilicate and α-quartz crystals. The X-ray patterns of the plate samples also showed the presence of lithium disilicate and α-quartz crystals. The intensity relations for the peaks ascribed to lithium disilicate crystals, however, were much different from those observed on the pattern taken from the powder, indicating that there is orientation of the crystals at the original surface; intensities of the (002) reflection was abnormally high compared with those of the (130), (040) and (111) reflections. The ratio of the intensity of the (002) peak to that of (111) peak was 0.26 for the powder, while it was 35.8, 4.71, 0.83 and 0.50 for the surfaces of the plate samples which were subjected to X-rays of 0, 3.5×10⁴ r, 10.5×10⁴ r and 35×10⁴ r, respectively. The relative degree of the orientation as revealed from the X-ray patterns decreased with increasing X-ray dose but did not disappear completely at the largest X-ray dose used in the present experiment. The degree of the orientation decreased, however, as the original surface layer was removed progressively by grinding and no orientation was found any more after a 50 μ layer was removed, as shown by the fact that the X-ray diffraction pattern became identical to that taken from the pulverized sample. This result suggests that the samples whose original surface layers have been removed by about 50 μ or more have to be used in order to investigate the relationship between
the strength and the microstructure of the interior of the samples.

3.2.2 Electron microscopy Electron micrographs representing the microstructure of the interior of the samples are shown in Fig. 9. Hexagonal, columnar fine crystals are distributed randomly, but fairly uniformly, throughout the photographs. The width (shorter axis of the column) to length (longer axis) ratio is approximately in the range of 2~4 for most of the crystals. It can be seen that the size (width and length) of the crystals changes with γ-ray dose; first, it decreases with increasing γ-ray dose, reaches a minimum at a dose of $3.5 \times 10^4$ and then increases again. The mean sizes (width and length), determined on Fig. 9, are summarized in Table 1. The values cited are the average of the sizes obtained for about 100 particles.

Electron micrographs shown in Fig. 10 are those representing the surface structure of the samples. Hexagonal, columnar crystals are distributed rather randomly for the sample crystallized after irradiation (Fig. 10 (b), similar to the electron micrographs of the interior, in accord with X-ray results indicating less orientation. On the other hand, the surface structure is different from that of the interior for the sample crystallized without irradiation.

3.2.3 Bending strength Fig. 11 shows the bending strength plotted as a function of the depth of removal of the surface layer for the two representative samples, one crystallized without irradiation and the other crystallized after exposed to γ-ray of $3.5 \times 10^4$. For both the samples the strength first decreases with increasing depth of removal. After removal of a 10~20 μ layer, the strength continues to decrease, but with a much lower rate, and accordingly, it would be reasonable to consider that the strength after removal of the surface layer of, for example, 50 μ is representative of the strength not subjected to the effect of the microstructure of the original surface of the sample.

Table 1. Mean grain size of the crystals precipitated in the crystallized glasses obtained by heating up to 900°C (Series 2).

<table>
<thead>
<tr>
<th>γ-ray dose (roentgen)</th>
<th>Mean length (μm)</th>
</tr>
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<tbody>
<tr>
<td>(not irradiated)</td>
<td>2.8</td>
</tr>
<tr>
<td>1.75x10^4</td>
<td>2.1</td>
</tr>
<tr>
<td>3.50x10^4</td>
<td>1.5</td>
</tr>
<tr>
<td>10.50x10^4</td>
<td>1.1</td>
</tr>
<tr>
<td>35.00x10^4</td>
<td>0.7</td>
</tr>
<tr>
<td>120.00x10^4</td>
<td>1.4</td>
</tr>
<tr>
<td>180.00x10^4</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Fig. 12 shows a plot of the strength versus γ-
ray dose. In the figure the solid circles denote the strength measured after removing the surface layer by 50 μ and open circles the strength measured without etching the original surface away. It is seen that although the level of strength is somewhat different, the apparent relation between the strength and γ-ray dose is similar in both cases; the strength decreases with increasing γ-ray dose, reaches a maximum and thereafter decreases again. In this figure the strengths obtained by Tashiro and Sakka are also incorporated and expressed by cross marks. It is to be noted that the horizontal axis represents the time of exposure to U.V. ray in this case.

In Fig. 13 the bending strength, measured after removing the surface layer by 50 μ, is plotted as a function of crystal grain size (length), with both axes in logarithmic scale. The strength increases with decreasing grain size and is expressed approximately by

$$\sigma \propto d^{-1.8}$$

(2)

where $\sigma$ is the modulus of rupture and $d$ is the average grain size.

### 3.2.4 Fracture path

Fig. 14 is an electron micrograph showing fractures formed on the surface of the sample polished after the original surface layer of about 50 μ was ground away. The surface was indented with a 1 mm diameter steel ball to induce the fractures. According as where the fracture passes relative to the crystal grain, there are four modes, as shown schematically in Fig. 15; a fracture can pass the grain boundary in the direction parallel to the longer axis of the grain (longitudinal) (mode 1) or in the direction parallel to the shorter edge of the

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**Fig. 11.** Bending strength as a function of the depth of the surface layer removed for the crystallized glasses obtained by heating up to 900°C (series 2).

**Fig. 12.** Bending strength of the crystallized glasses obtained by heating up to 900°C (series 2) as a function of irradiation dose.

**Fig. 13.** Plot of bending strength after removal of a 50 μ layer versus grain size for the crystallized glasses obtained by heating up to 900°C (series 2).

**Fig. 14.** Electron micrographs showing the path of cracks in the crystallized glass obtained by heating up to 900°C.
hexagonal-shaped grain (transversal) (mode 2), or a fracture can pass through a grain along its longer axis (longitudinal) (mode 3) or along its shorter axis (transversal) (mode 4). Classification of the paths was made by counting the times of occurrence of the above modes for 108 particles. The result is shown by percentage occurrence in Table 2. It can be seen that the modes where the crack propagates longitudinally are much more than the modes where the fracture propagates transversally. Although this classification is based on the propagation path, it would not be unreasonable to extend the idea to the origin of fracture. That is, the fracture may be considered to start from the assumed cracks whose length is equal to the length of the grains. This may justify that the length of the grains was used as the particle size when the formula (2) was employed.

Table 2. Classification of the mode of fracture path relative to crystal grains.

<table>
<thead>
<tr>
<th>Path Type</th>
<th>Longitudinal</th>
<th>Transversal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundaries propagation</td>
<td>37%</td>
<td>18%</td>
</tr>
<tr>
<td>Intragranular propagation</td>
<td>27%</td>
<td>18%</td>
</tr>
</tbody>
</table>

4. Discussion

4.1 Microstructure of the crystallized samples

4.1.1 Grain size  As stated previously, the crystal grain size in the interior of the sample varied with γ-ray irradiation dose for the samples of both series 1 (heated up to 620°C) and series 2 (heated up to 900°C); it decreased with increasing total γ-ray dose till a minimum size, and then increased again. The reason for this was already discussed for the series 1 in the paper by Tashiro and Sakka. In their study they used U.V. ray instead of γ-ray which has been employed in the present study, but the effect of irradiation in nucleating gold colloids appears substantially the same.

Gamma-irradiation at room temperature produces nuclei for gold colloid and the number of gold colloids precipitated at 510°C increases with increasing γ-ray dose. Accordingly, the number of lithium metasilicate crystals, formed at 620°C as a result of nucleation by gold colloids, increases with increasing γ-ray dose. This results in decrease in the size of lithium metasilicate crystals precipitated in the glass is limited by the composition of the parent glass or more specifically, by the lithium content in the glass. As gold colloids increase in number, their size decreases since the gold content in glass is limited. It should be remembered here that the ability of gold colloids in nucleating lithium metasilicate crystals decreases, as the average size of gold colloids decreases. There is a critical size in the colloid particle below which the ability in nucleating the other crystalline species heterogeneously is lost. Therefore, two much irradiation causes the number of lithium metasilicate crystals to be reduced and their size to be increased. Thus the size of lithium metasilicate crystals is expected to become minimum at a certain γ-ray dose.

Also for the samples of series 2 which were produced by further heating the samples of series 1 at 900°C, a similar dependence of the grain size on γ-ray dose was observed. This would be explained as follows. In the samples of series 1 there are lithium metasilicate crystals (Li2O·SiO2) precipitated in a glassy matrix rich in silica. When lithium disilicate (Li2O·2SiO2) and quartz crystals are produced from such systems, it would be assumed that in a first approximation a metasilicate crystal produces a disilicate crystal by reacting with the surrounding silica-rich glass as the crystals are isolated by the silica-rich glassy phase. In turn, the silica-rich phase is separated by crystals. Thus the number and, accordingly, the size of newly formed crystals may be controlled by the number of crystals (lithium metasilicate) present originally in the sample.

4.2.2 Structure of the original surface  In the samples of both series 2 the structure of the original surface was different from that of the interior; in the former lithium disilicate crystals, which were oriented, were formed at the surface in addition to metasilicates and in the latter the lithium disilicate crystals were oriented at the surface.

The composition of the glass used in the present study is situated within the lithium disilicate-silica region in the phase diagram, and it is natural to expect the formation of lithium disilicate instead of lithium metasilicates. Therefore, the formation of lithium metasilicate observed in the interior of the samples needs some explanation. Soga and Tashiro explained that gold colloids attract lithium ions around themselves and the lithium-rich area thus formed is converted to lithium metasilicate crystals. The present author is now doing more detailed study on this subject. Anyway, it can be said that in the samples heated at 620°C the gold colloids induce the formation of
lithium metasilicate crystals, and lithium disilicate crystals are formed if there is no gold colloid (this is the case for the glass not irradiated by γ-ray) or the effect of gold colloid is small for some reason (this occurs at the surface).

The lithium disilicate crystals are oriented at the surface of the samples heated up to 900°C. It should be noted that the lithium disilicate crystals formed at 620°C are also strongly oriented. Rindone¹, and Hayami, Ogura and Tanaka⁵ studied the crystallization of Li₂O·4 SiO₂ glass with or without platinum addition and reported that the disilicate crystals formed at the surface orient themselves pronouncedly in the platinum-free glass and slightly in the platinum-containing glass. It is assumed that the disilicate crystals nucleated by platinum particles are randomly distributed (not oriented), while the disilicate crystals produced at the surface without being affected by platinum orient themselves. In the glass used in the present study gold colloids appear to play a similar role as platinum particles in nucleating non-oriented crystals. The only difference is that gold colloids nucleate lithium metasilicate crystals and not disilicate crystals which are nucleated by platinum.

Lithium disilicate crystals preferentially orient themselves with the (002) plane parallel to the glass surface. The attempt to explain the reason for this was made by Booth and Rindone¹² and Weyl¹³.

4.2 Strength of the crystallized glasses

It is known that fine cracks (Griffith flaws) produced at the surface for various chemical and physical reasons play an important role when brittle materials are broken. In glass-crystal composite materials, it may be possible that the strength is determined by the surface cracks present in the glassy matrix, whose sizes are limited by the crystals embedded in the glass. This explains¹⁴ the grain size dependence of the strength of the composite materials for a given amount of crystals.

In the present study the original surface of the sample was removed by etching with hydrofluoric acid, that is, the surface cracks present in the original surface was removed. Nevertheless, the grain size dependence of the strength was observed for the samples heated up to 620°C as well as for those heated up to 900°C. Previously¹⁵, the grain size dependence was demonstrated for the metastably phase-separated glasses whose surface layer was removed. It was shown¹⁶ also that the cracks which might affect the strength could be formed within the dispersed particles, as well as at the boundaries between the particles and the matrix, or in the matrix between the particles, depending upon the conditions such as the difference in modulus of elasticity between the particles and the matrix.

Considering the fact that the amount of the matrix in the samples heated up to 900°C is relatively low (Fig. 9) and the grain size dependence of the strength is observed after the removal of the original surface, however, Orowan's theory derived from polycrystalline materials¹⁷ appears suitable to explain the present results on the samples of series 2. In other words, it seems that the grain size dependence of the strength does appear because the cleavage in the crystal grains or the grain boundaries act as a kind of crack. Generally, the relation between the strength σ and the grain size d for polycrystalline materials is expressed¹⁸ by

\[ \sigma = \text{const} \cdot d^{-n} \]

In Orowan's formula \( n = 1/2 \), but many polycrystalline materials¹⁹ have been found to obey the formula with \( n = 1/3 \). In the present study the \( n \) value was close to 1/3 (formula 2). The reason for \( n = 1/3 \) is not obvious at present.

An apparent grain size dependence of the strength was also found before removal of the surface layer for the samples heated up to 900°C (Fig. 11). As the strength is much affected by the structure of the surface and this is different from that of the interior in the present case, the strength is not expected to have a relation with the structure of the interior (grain size). Therefore, the occurrence of the apparent relation seems to indicate that the surface structure changes parallelly with the grain size in the interior; actually, the length of the oriented crystallites decreased as the size of grains in the interior decreased. This might have resulted in the apparent relation between the strength measured on non-etched samples and the grain size in the bulk.

The values of the strength for the non-etched samples reported by Tashiro and Sakka³ are about one half of those reported in the present study, and the difference would be attributed mainly to the different shape of the test specimens used⁴⁰; they used rectangular pieces, whose edges may give additional weakness by a possible presence of notches, while the present authors tested on cylindrical rods.

For the samples heated up to 620°C (series 1) the strength before removal of the original surface was not dependent on the γ-ray dose (Fig. 5) and, accordingly, on the grain size in the interior. This would mean that the size of flaws present at the original surface is not changed so much with γ-ray dose. Actually, electron microscopic observation did not reveal any appreciable change in the surface structure due to γ-ray dose (grain
size and the distribution of glassy phases) for the samples irradiated by \( \gamma \)-ray. On the other hand, the crystals whose grain size depend on the \( \gamma \)-ray dose was precipitated in the interior of the sample as observed by an electron microscope. Therefore, for the sample whose surface layer was removed the grain size dependence of the strength would be expected and, actually, the strength increased with decreasing grain size. In the sample which was not irradiated by \( \gamma \)-ray, the newly exposed surface obtained after the removal of the surface showed a very rough appearance and this is believed to be the reason for the lowering of strength after the removal of the surface layer.

5. Summary

Microstructure and bending strength of a photo-ceram-type crystallized glass of the composition \( \text{SiO}_2 81, \text{Li}_2\text{O} 12.5, \text{K}_2\text{O} 2.5, \text{Al}_2\text{O}_3 4, \text{CeO}_2 0.03, \text{Au} 0.027 \% \) in weight were studied with a particular attention to its surface structure. The results are summarized as follows:

1) The surface of both the samples heated up to 620°C and up to 900°C had a structure different from the interior. In the former lithium disilicate crystals were precipitated at the surface of the sample in addition to lithium metasilicate which was the only crystalline phase found in the interior. The lithium disilicate crystals were oriented with the (002) plane parallel to the surface. In the latter the crystalline phases were lithium disilicate and \( \alpha \)-quartz throughout the sample, but the lithium disilicate crystals oriented themselves at the surface.

2) The bending strength of the crystallized glasses obtained by heating up to 620°C was independent of the size of crystals found in the interior, before removing the surface layer, while it increased with decreasing grain size after the original surface layer was removed.

3) The strength of the crystallized glasses obtained by heating up to 900°C was intimately related to the size of crystal grains precipitated in the interior both before and after removal of the original surface layer; the strength increased with decreasing grain size. Presence of the strength-grain size relationship for the samples before removal of the original surface layer was explained by the fact that the length of the oriented crystals at the surface decreased with the grain size in the interior. The strength-grain size relationship for the samples after removal of the surface layer was explained by Orowan’s theory on polycrystalline materials.

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Reference


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フォトセラム型結晶化ガラスの構造と強度

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金を含む感光ガラスをそれぞれ 620℃ および 920℃ まで加熱することによって得られた結晶化ガラスの微細構造と曲げ強度を調べた。いずれの場合も試料のもとの表面の構造は試料内部のそれと異なっていた。すなわち、試料表面では二珪酸リチウム結晶の配向が認められた。ただしこの程度は金コロイドを析出させるために使用したγ線照射の線量によって変化した。結晶化ガラスの曲げ強度は試料のもとの表面を除去すると結晶粒子の大きさによって変化し、粒径が減少するにつれて増大した。一方、もとの表面を除去しないで測定した曲げ強度は表面の微細構造によって変化した。すなわち、620℃ までの加熱によって得られた結晶化ガラスの強度はγ線線量によらなかったが、これは表面の結晶化が十分進まなかったためであろう。また 900℃ まで加熱することによって得られた結晶化ガラスの強度は、表面に存在する配向結晶の長さが減少するにつれて增大した。

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