

Some Physical Properties of Glass-Ceramics and Their Relation to Microstructure

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The effects of microstructure on physical properties of glass-ceramics, especially the effects of extraordinary fineness of their constituent crystallites on their mechanical strength, transparency and dielectric property were investigated.

Glass-ceramics of a photosensitive opal type consisting mainly of lithium disilicate and quartz crystal grains with various diameters ranging from 0.85μ to 2.3μ were prepared from glasses of the composition, SiO_2 81, Li_2O 12.5, K_2O 2.5, Al_2O_3 4, CeO_2 0.03 and Au 0.027 percent by weight by exposing them to the ultraviolet ray for various periods followed by heating up to 900°C . The Rowan expression, $\sigma = \text{const} \cdot d^{-1/2}$, where σ is the modulus of rupture and d is the average diameter of the crystallites separated out in the specimens, was found to be valid for these specimens.

From the glass of the same composition as described above a glass-ceramic having good transparency was obtained by exposing it to the U. V. ray for the most appropriate period followed by heating up to 620°C . The grain size of lithium metasilicate crystallites separated out in this specimen was estimated to be about $70\text{ m}\mu$ in diameter from its optical absorption data.

Dielectric loss at 1 Mc frequency of glass-ceramics was found to be dependent not on the grain size of the constituent crystallites but mainly on the intrinsic value of dielectric loss of the constituent crystallites; the specimens containing β -spodumene crystallites showed the low value of dielectric loss whereas those containing β -eucryptite crystallites showed the high value.

INTRODUCTION

Since Stookey's invention on 'glass-ceramics', a great number of papers on these new materials have been published. They cover various subjects from fundamental to applied, such as mechanism of nucleation and crystallization in glass, new kinds of nucleating agent, chemical compositions of the base glass suitable for each of the nucleating agents, and physical and chemical properties of the glass-ceramics mostly of practical use. A little unexpectedly, however, systematic and fundamental studies on the properties of the glass-ceramics, especially ones made in relation to their microstructure are still very few in numbers, in spite of their importance for the further improvement in qualities of the glass-ceramics.

The following description is a summary of the authors' three articles published in the *Journal of the Ceramic Association, Japan* (*J. Ceram. Assoc. Japan*,

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67, 263 (1959); 68, 158 (1960); 69, 393 (1961)). Their subjects are mechanical strength, optical transparency, and dielectric loss of various glass-ceramics, which were investigated mainly in relation to their microstructure.

Unusually small and uniform size of the constituent crystallites in glass-ceramics, ordinarily ranging from 1 to 0.01 microns, is one of the main causes which endow the glass-ceramics with many special characteristics. Therefore, special emphasis was laid on clarification of the relation of the size of crystallites with the properties of this material.

MECHANICAL STRENGTH

Some glass-ceramics have an extraordinarily high mechanical strength mounting up to, for instance, 6,000 kg/cm² (modulus of rupture), when their chemical compositions and the process for crystallization were properly adjusted. The cause of this high value in strength is not simple; many factors such as intrinsic strengths of constituent crystallites and glassy matrix, their adhesion strength at the interfaces, their difference in thermal expansion, their proportion in amount in the body, the size of crystallites, etc., may affect the mechanical strength of glass-ceramics in various ways as in the case of ordinary ceramic materials. Among these factors, in the present study, the authors have investigated especially the effect of the size of crystallites because its extraordinary smallness is a striking contrast to the ordinary ceramics consisting of crystallites of, ordinarily, 5~50 microns.

In order to single out this effect and to keep the other factors constant, glass-ceramics of the photosensitive type, the crystal size of which can be arbitrarily varied by changing the time of exposure to the ultraviolet ray, were chosen as the test specimens.

Experimental

The glass of the composition, SiO₂ 81, Li₂O 12.5, K₂O 2.5, Al₂O₃ 4, CeO₂ 0.03, Au 0.027 percent by weight¹⁾, was melted in an amount of 100 grams in a platinum crucible, poured on an iron plate, pressed into a plate of 5 mm in thickness, and cut into bars of the size 2.5×5×50 mm. These bars were exposed to ultraviolet light by placing them at a distance of 10 cm from a 500 watt high pressure mercury lamp for 2 to 1000 minutes. After the exposure they were heated at three steps, first at 510°C for 30 minutes to cause formation of gold nuclei, then at 620°C for 60 minutes to cause precipitation of lithium metasilicate crystals, i. e., to cause partial crystallization of the base glass, and finally at 900°C for 60 minutes to convert the base glass to almost completely crystalline body consisting of lithium disilicate and quartz crystallites. An optical-microscopic observation of the polished thin cross-section of the specimens heated up to 900°C showed that the grain size of crystallites is uniform, varying with the U. V. exposure time as noted in Table 1. The mean diameter of the crystal grains decreases with increasing the exposure time up to 180 minutes and then increases. The results of determination of the modulus

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Table 1. Relation between exposure time and diameter of crystallites in specimens, modulus of rupture and Vickers hardness.

Time of exposure to U. V. light (minutes)	Diameter of crystallites (μ)	Modulus of rupture (kg/cm ²)	Vickers hardness (kg/mm ²)
0	2.3	1750	639
2	1.4	2180	685
30	1.1	2330	729
180	0.85	2610	785
600	1.3	2450	739
1000	1.4	2350	664

of rupture and the Vickers hardness for these specimens are also given in the same table. The modulus of rupture was measured by the method of three point loading with a Shimadzu strength test machine, Model RS-2; the span of two anvils supporting a specimen was 30 mm, and a rate of applying a load in the center of the specimen was 2.5 mm/min. The Vickers hardness was measured with a Leitz micro-indentation hardness tester, DURIMET; a diamond pyramid indenter was pressed into the surface of specimens with a load of 200 grams.

X-ray diffraction analysis revealed that the species of crystalline phases in these specimens were lithium disilicate and quartz, and the amount of the two crystals was constant respectively irrespective of the difference in U. V. exposure time.

Discussion

The existence of an optimum U. V. exposure time, i. e., 180 minutes (Table 1), can be explained as follows. The decrease of the size of crystal grains with increasing the exposure time up to 180 minutes is simply due to the increase in number of gold metal colloids which act later as a nucleating agent for the crystallization of the lithium silicates. When the exposure time exceeds 180 minutes, however, the gold particles would become so small in size as to become ineffective as nucleating agents²⁾, because the total amount of gold introduced into the glass is limited (0.027 %) and the size of each of gold particles decreases as their number increases. More detailed discussion will be made in the next section.

The relation between the modulus of rupture and the average diameter of crystallites given in Table 1 is shown graphically in Fig. 1. The abscissa represents the diameter and the ordinate the modulus of rupture both in logarithmic scale. A straight line in the same figure is a representation of the following equation derived theoretically by Orowan³⁾ for the polycrystalline aggregates.

$$\sigma = \text{const} \cdot d^{-1/2} \quad (1)$$

where σ is the modulus of rupture of the aggregate and d the diameter of the constituent crystal grains. This equation is based on Griffith's flaw theory on fracture and also on the following assumption: When a tensile force is applied,

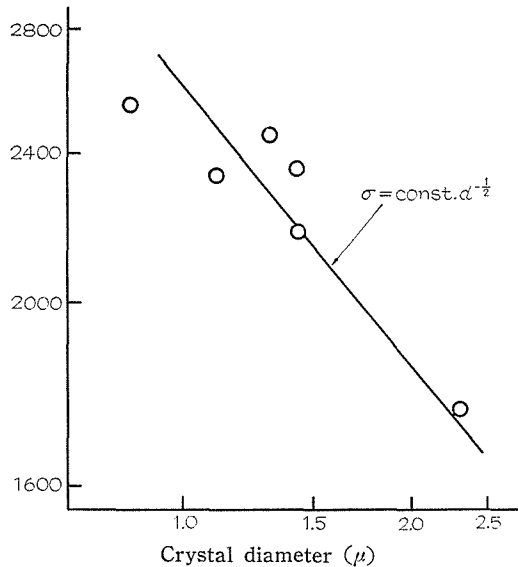


Fig. 1. Relation between modulus of rupture and grain size.

a microcrack having the length nearly equal to the diameter of a crystal grain is first produced along a cleavage of its crystal and then this crack penetrates into the neighboring grain across their boundaries as a result of the concentration of stress at the crack tip, and finally propagates to entire fracture.

Previous experiments, for example, the ones made by Knudsen¹⁾, have shown that the equation (1) holds for some of polycrystalline materials such as chromium carbide and thoria. The material so far investigated are, however, composed of crystal grains whose diameter is in the range from 10μ to 1000μ ¹⁾. In Fig. 1 the circles representing the measured values for our specimens are seen near the line representing the equation (1). This fact has a meaning that the equation (1) holds also for the crystalline aggregates whose constituent crystal grains have the diameter much smaller than 10μ .

It should be noted here, however, that the validity of the equation (1) for the present experiment does not necessarily mean that the fracture of our specimens was caused by the penetration of the crack into the inside of the constituent crystal grains; it might have been caused by the crack penetrating along crystal grain boundaries, because the equation also holds for this case²⁾. The analysis of the result of our measurement on Vickers hardness given in Table 1 will assist to solve whether the fracture mechanism is transcrystalline or intercrystalline.

Fig. 2 is a graphical representation of Vickers hardness and the average diameter of crystallites, both plotted on a log basis.

In general, Vickers hardness, H , of a substance is related to its yield strength, Y , by

$$H = 2.68Y \quad (2)^{6)}$$

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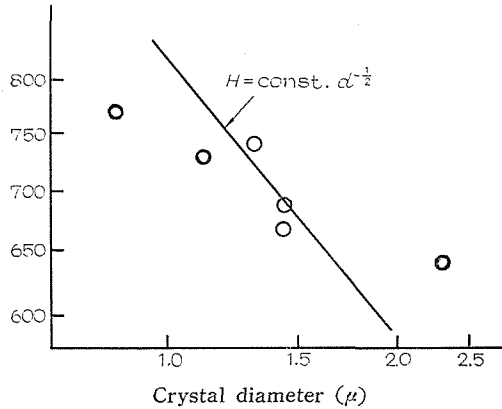


Fig. 2. Relation between Vickers hardness and grain size.

The yield strength of polycrystalline materials is also related to the average diameter (d) of their constituent crystal grains by

$$Y \propto d^{-1/2} \quad (3)$$

or

$$Y \propto d^{+1} \quad (4).$$

Equation (3) is derived theoretically if one assume that deformation in a polycrystalline aggregate is caused by a slip within grains⁷⁾. If a slip occurs at grain boundaries, however, it should be revised to equation (4) because in this case the tendency for slipping increases in proportion to the total area of the grain boundaries⁸⁾. Combining equation (2) with equation (3) or (4), we have

$$H = \text{const} \cdot d^{-1/2} \quad (3)'$$

$$H = \text{const} \cdot d^{+1} \quad (4)'$$

Fig. 2 indicates that the measured values are near the straight line represented by the equation (3)', which would probably mean that the fracture mechanism for our specimens be transcrySTALLINE.

TRANSPARENCY

Although opaque glass-ceramics are being used widely as kitchen wares, the production of transparent glass-ceramics in commercial scale has not yet been started. An aim of the present experiment is to obtain a fundamental knowledge on the relationship between optical transparency and the grain size of the glass-ceramics.

Experimental

In the course of the experiment described in the previous section, the writers have found that the glass specimen used in that experiment could be converted to a transparent red glass-ceramic when it was heated at 620°C for 60 minutes after subjected to the U. V. exposure for 180 minutes. As described above, 180 minutes was the optimum U. V. exposure time to make the size of



Exposure time 0 1 2 10 30 180 600 1000
(minutes)

Fig. 3. Photograph showing the effect of U. V. exposure time on transparency of the glass heated at 620°C for 60 minutes.

crystal grain of the resulting opaque glass-ceramics the smallest. The transparency could not be obtained when the U. V. exposure time was made longer or shorter than 180 minutes. Fig. 3 shows photographs of the specimens subjected to these heat treatments. Their thickness was 2.0 mm. The condition of heat treatment was the same for all the specimens, i. e., first at 510°C for 30 minutes for formation of gold colloids and then at 620°C for 60 minutes for formation of lithium metasilicate crystallites. The specimens in Fig. 3 are placed on a sheet of paper marked with letters 'A' so that qualitative measurement of the degree of their transparency could be made. The specimen not exposed to U. V. ray (the exposure time, 0) is colorless and transparent because it contains neither gold colloids nor lithium metasilicate. With increasing U. V. exposure time opacity of the specimen increases because the lithium metasilicate crystallites nucleated by gold colloids are separated out from the glass phase. When the U. V. exposure time exceeds 10 minutes, opacity begins to decrease, reaching a minimum at the 180 minutes' exposure time. The specimen exposed to U. V. ray for 180 minutes is very transparent though its color is deep red due to precipitation of gold colloids. When the exposure time exceeds 180 minutes opacity again increases with increasing exposure time.

Fig. 4 shows light transmission curves of the specimens shown in Fig. 3.

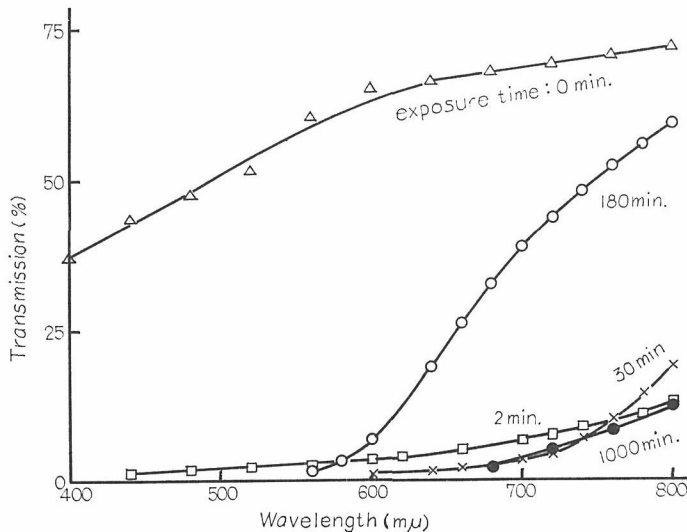


Fig. 4. Transmission curves for the glass subjected to the U. V. exposure and the heat treatment. Lithium metasilicate crystallites are precipitated within the glass. (Specimen thickness : 2.0 mm).

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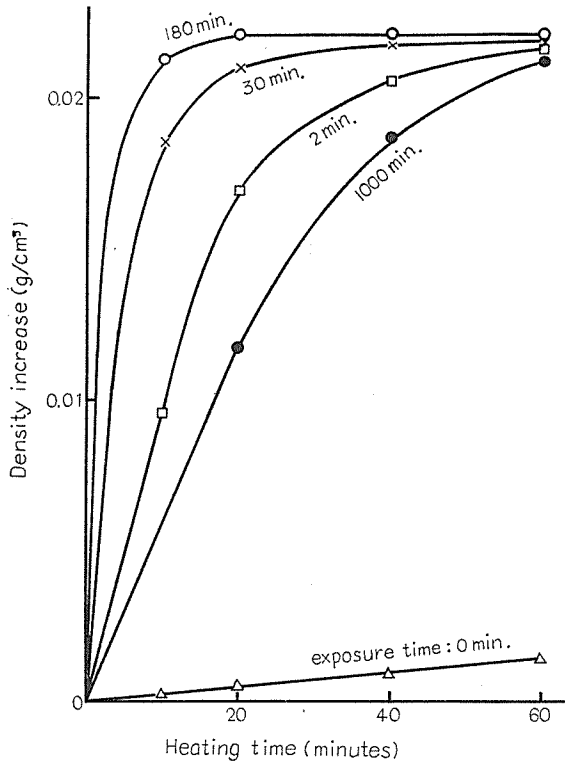


Fig. 5. Increase in density of the glass by heating at 620°C.

The measurements was made with a Beckmann Type DU photoelectric spectrophotometer.

Fig. 5 shows the results of measurement on density of the same specimens.

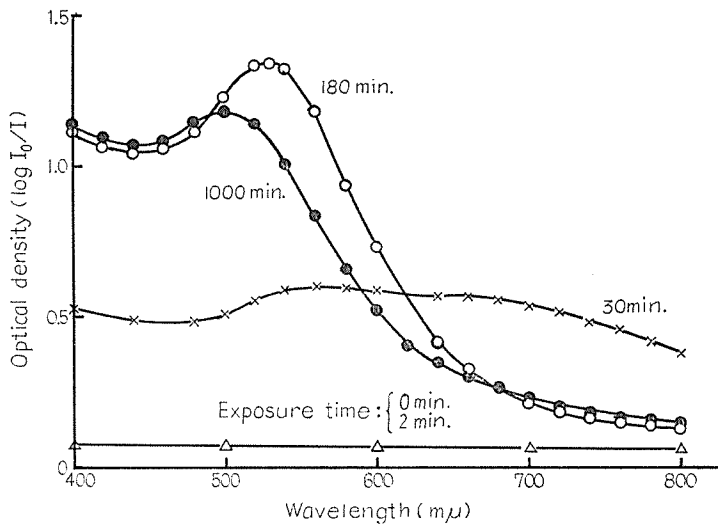


Fig. 6. Comparison of absorption spectra for the glass subjected to the U. V. exposure and the heat treatment (510°C, 30 minutes).

Gold colloids are precipitated in the glass.

For this measurements a sink float method was used. Except for a specimen not subjected to the U. V. exposure all of the specimens have the same density (after 60 minutes' heating at 620°C).

As described above, the specimens above used contain both gold colloids and lithium metasilicate crystallites except for a specimen not subjected to U. V. exposure. For the estimation of the grain size of the lithium metasilicate crystallites, which will be discussed later, light transmittance was measured on another series of specimens containing only gold colloids, which were prepared by heating pieces of glass only up to 510°C after exposed to U. V. ray; heating at 620°C was not made in order to avoid the crystallization of lithium metasilicate.

The chemical composition of glass, and the procedures for U. V. exposure and heating at 510°C were all the same as for the specimens used above. Fig. 6 shows the light transmission curves measured for these specimens.

Discussion

For the specimens with the U. V. exposure time of 30 and 180 minutes the grain size of lithium metasilicate separated out in the glass phase was so small that an ordinary optical microscope could not be used for its determination. Therefore, its estimation was made on the basis of the theory of light scattering of a material containing small particles, using the spectrophotometric data shown in Fig. 4 and 6.

When light is transmitted through a material containing spheric small particles, its change is given by

$$I = I_0 e^{-Ft} \quad (5)$$

where I_0 is the initial intensity, I is the transmitted intensity, t is the optical pass length, and F is the scattering factor. When $\rho < \lambda/2\pi$, where ρ is the radius of spheric particles and λ is the wave length of the incident light, F is given by

$$F = \frac{24\pi^3 n_0^4}{\lambda^4} \cdot V \cdot NV \cdot \left(\frac{n^2 - n_0^2}{n^2 + 2n_0^2} \right)^2 \quad (6)^9$$

where V is the volume of a particle, i. e., $V = 4/3 \cdot \pi \rho^3$, N is the number of particles contained in unit volume of the material, n_0 is the refractive index of the medium, and n is the refractive index of particles.

From the density measurement (Fig. 5) it has been confirmed that its value was almost the same for all the specimens exposed to U. V. for over 2 minutes. This fact can be explained if we assume that the total amount of the lithium metasilicate crystallites precipitated (NV in equation (6)) be the same for all the specimens; i. e., the change occurring with increase in U. V. exposure time is not in the total amount of lithium metasilicate crystallites but in their number. If we further assume that the whole of Li_2O introduced in our specimens be consumed as a component of lithium metasilicate crystallites, the value of NV is calculated to be 0.35. If we insert this value, and also 1.51 (measured) for n_0 and 1.59¹⁾ for n , into equation (6), we have

$$F = 1.45\rho^3/\lambda^4 \quad (7)$$

We measured the light transmission of the two series of specimens, the one containing only gold colloids and the other both gold colloids and lithium metasilicate crystallites (see Fig. 4 and 6). If we assume that the change of light absorption due to the crystal growth of gold colloid is negligibly small in the temperature range from 510° to 620°C, we can have the light absorption due to only the formation of lithium metasilicate crystallites from the data shown in Fig. 4 and 6; i. e., by subtracting the light absorption of the specimen heated at 510°C from that of the specimen heated up to 620°C. This is shown

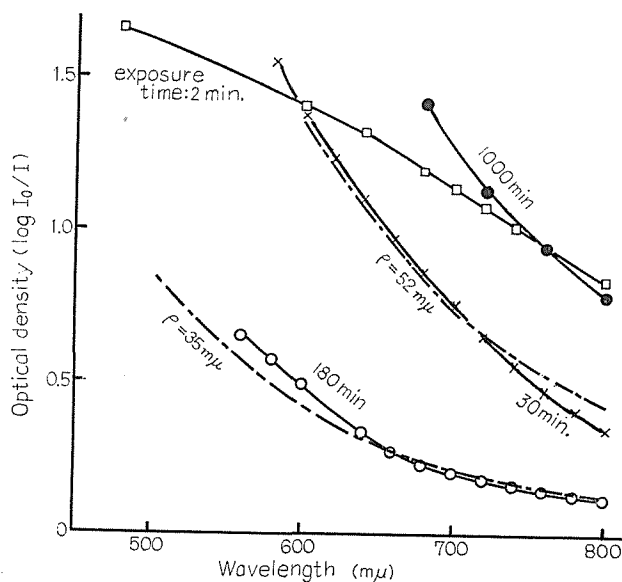


Fig. 7. Increase in absorption of the glass due to precipitation of lithium metasilicate crystallites.

by the solid lines in Fig. 7. The dotted lines in the same figure represent the calculated values using equation (7). The curves calculated by assuming $\rho = 35 \text{ m}\mu$ and $\rho = 52 \text{ m}\mu$ are seen to be in good agreement with those observed for the specimens with exposure time of 180 minutes and 30 minutes. For the specimens with the exposure time of too short (2 minutes) or of too long (1000 minutes), no agreement was obtained with the values calculated by equation (7) whatever the grain size was assumed. This would mean that the grain size of the crystallites formed in these specimens are so big that equation (7) can not be applied. Actually the determination by an ordinary optical microscope showed that the grain size is much greater than the order of the wave length of visible rays as shown in Table 2. In the table, the values for the specimens with the exposure time of 30 and 180 minutes are those estimated from the spectrophotometer data as described above. From Table 2, it can be concluded that the transparent glass-ceramics may be obtained if the size of lithium metasilicate crystallites formed in it be made nearly $70 \text{ m}\mu$ in diameter by exposing them to U. V. ray for the most appropriate time, say

Table 2. Relation between exposure time and diameter of precipitated lithium metasilicate crystallites.

Exposure time (minutes)	Color and wave length of absorption peaks of glass after precipitation of gold particles	Color and opaqueness after precipitation of lithium metasilicate crystals	Diameter of lithium metasilicate crystals (μ)
0	No color	No color, transparent	
1	"	White, strongly opaque	
2	"	White, strongly opaque	1.0*
10	Blue, 560 and 660 $m\mu$	Whitish blue, opaque	
30	" "	Whitish blue, a little transparent	0.104**
180	Red, 530 $m\mu$	Red, transparent	0.070**
600	Red, 510 $m\mu$	Pink, opaque	0.5*
1000	Red, 500 $m\mu$	Pink, opaque	1.0*

* Observed under optical microscope.

** Calculated by the theory of light absorption.

180 minutes under the condition of the present experiment.

The decrease in grain size of lithium metasilicate crystallite with increasing the U. V. exposure time up to 180 minutes is a result of the increase in number of the gold nucleus as discussed in the previous section. However, this relation does not hold for the specimens with the U. V. exposure time longer than 180 minutes (see Table 2); i. e., the grain size of the crystallites increases with increasing the U. V. exposure time, and as a result the appearance of the specimen becomes opaque again (see Fig. 3). This fact can be explained if we assume a critical size of the gold particle being effective as a nucleus for the formation of lithium metasilicate crystals and also some spread of the distribution of particle size of gold particles present in each of the actual specimens. Fig. 8 shows this distribution schematically; the area under each of the distribution curve represents the total number of gold particles present in each of the specimens. Maurer¹⁰⁾ had already found for a kind of photosensitive glass that the number of gold particles increases with increasing the U. V.

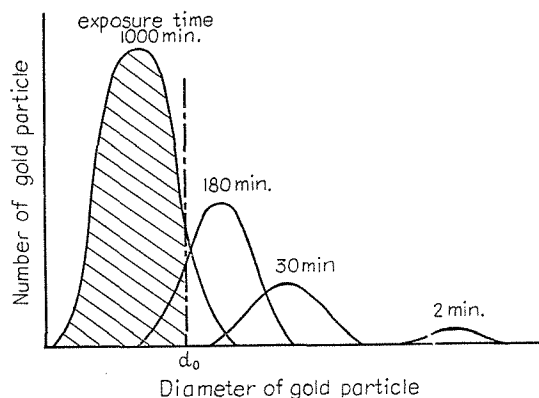


Fig. 8. Schematic representation of the relation between size and number of gold particle in the glass.

exposure time in proportion to the 3rd power of it. Now, if all of gold particles act as nucleating agents, the number of lithium metasilicate crystals formed on the gold nuclei will increase with increasing the U.V. exposure time. However, if there be a critical diameter d_0 (see Fig. 8), as noted above, for the gold nuclei, some parts of gold particles, whose number is represented by the hatched area in Fig. 8, do not act as nuclei, and consequently, we have a maximum number of gold particles for the specimen exposed to U.V. for the most appropriate period, say 180 minutes in the present experiment. For the specimens exposed to U.V. for longer period than this, the number of gold particles being effective as nuclei decreases with increasing the exposure time, and, as a result, the grain size of the lithium metasilicate crystals increases.

Regarding the critical size of an effective gold nucleus, Maurer²⁾ reported its existence in a photosensitive opal type glass and confirmed its size to be about $8\text{ m}\mu$ with an electron-microscope.

DIELECTRIC LOSS

According to Bunag and Koenig¹¹⁾, and Rigterink¹²⁾, dielectric loss of ordinary porcelains composed of fine crystalline particles and glassy matrix is mainly dependent on the four factors:

1. Kinds of crystalline phases,
2. Composition of glassy matrix,
3. Pores,
4. Grain size of crystals.

In the present section is described the effects of these factors investigated with glass-ceramics of various compositions.

Experimental

The effect of grain size of constituent crystallites was first investigated with the same specimens as prepared for the measurements of the modulus of rupture and transparency. Their composition, the conditions for U.V. exposure and heat treatment, the diameter of their constituent crystallites determined in

Table 3. Dependence of $\tan \delta$ upon diameter of crystallites in specimens.

Composition of glass: Li_2O 12.5, K_2O 2.5, Al_2O_3 4, SiO_2 81, CeO_2 0.03, Au 0.027 %
(by weight)

Time of U. V. exposure (minutes)	Specimens heated at 620°C^*		Specimens heated at 900°C^{**}	
	Diameter of crystallites (μ)	$\tan \delta$ at 1 Mc/sec ($\times 10^{-4}$)	Diameter of crystallites (μ)	$\tan \delta$ at 1 Mc/sec ($\times 10^{-4}$)
0	(glass)	(120)	2.3	32.7
2	1.0	51	1.4	33.9
30	0.104	41	1.1	33.3
180	0.07	51	0.85	34.6
600	0.5	42	1.3	36.4
1000	1.0	47	1.4	33.5

* Lithium metasilicate crystallites are precipitated.

** Lithium disilicate and quartz crystallites are precipitated.

the previous sections, and the results of determination of their loss tangent ($\tan \delta$) are listed in Table 3. The measurement of $\tan \delta$ was made at room temperature (15°~20°C) with a Yokogawa Electric Q meter (Type QM-102A) at a frequency of 1 Mc. The size of the specimens used was 20×20×3 mm. Silver paint was applied as electrodes on both sides of the specimens. The result shows that the value of $\tan \delta$ is constant irrespective of the size of constituent crystallites for both series of the specimens heated at 620° and 900°C, respectively; their changes are within experimental errors.

The other factors affecting $\tan \delta$ were investigated with the glass-ceramics having more simple chemical compositions than specimens used above.

Their compositions are given in Table 4. Their major components are

Table 4. Major crystalline phases in glasses crystallized by heating up to different temperatures.

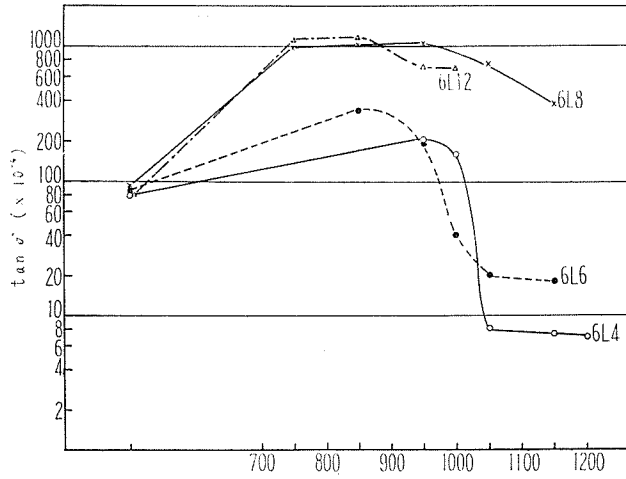
No.	Compositions (parts by weight)				Heating temperature (°C)						
	Li ₂ O	MgO	Al ₂ O ₃	SiO ₂	750	850	950	1000	1050	1150	1200
6L4	4	15	23	62			β -E*	β -E	β -S**	β -S	β -S
6L6	6	"	"	"		β -E	β -E	β -E	β -S	β -S	β -S
6L8	8	"	"	"		β -E	β -E	β -E		β -E	
6L12	12	"	"	"		β -E	β -E	β -E	β -E		
6L4Na	4	15	23	62	Na ₂ O 1.4		β -E		β -S	β -S	
6L4K	"	"	"	"	K ₂ O 2.1		β -E		β -E	β -S	
6L4Be	"	"	"	"	BeO 1.1		β -E		β -E, β -S	β -S	
6L4Ca	"	"	"	"	CaO 2.5		β -E, β -S		β -S	β -S	
6L4Sr	"	"	"	"	SrO 4.6		β -E		β -S	β -S	
6L4Ba	"	"	"	"	BaO 6.8		β -S, β -E		β -S	β -S	
6L4Zn	"	"	"	"	ZnO 3.6		β -E		β -S	β -S	
6L4Cd	"	"	"	"	CdO 5.4		β -S		β -S	β -S	
6L4Pb	"	"	"	"	PbO 10		β -E		β -S	S- β	

* β -E: β -Eucryptite, ** β -S: β -Spodumene.

Li₂O, MgO, Al₂O₃, and SiO₂. The amount of additional components, Na₂O, K₂O, BeO etc., represented, in Table 4, by parts by weight corresponds to a ratio of 0.045 mols of these additional components to 104 grams of the base composition. To each of these compositions platinum was added in an amount of 0.01% (by weight) as a nucleating agent. Each of the glass specimens was heated, for their crystallization, with a constant rate of 5°C per minutes up to various temperatures noted in Table 4, i.e., 750°, 850°, 950°, 1000°, 1050°, 1150°, and 1200°C, and kept there for 60 minutes respectively. Major crystalline phases separated out in these specimens, identified with a Shimadzu X-ray diffractometer, are also given in Table 4. Fig. 9 and 10 show the results of $\tan \delta$ measurement. The value of $\tan \delta$ measured with the original glass specimens before heat treatment are also shown in the same figures.

The glass-ceramic specimens mentioned above have of course no pores. In order to investigate the effect of pores on $\tan \delta$, a glass-ceramic specimen

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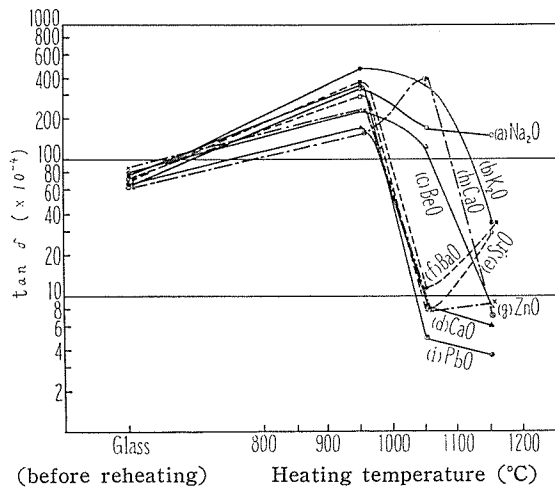


Glass (before reheating) Heating temperature °C

Fig. 9. Dependence of $\tan \delta$ at 1Mc/sec upon heating temperature for specimens crystallized by heating glasses in the system $\text{Li}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$.

Composition of glasses: (parts by weight)

	Li_2O	MgO	Al_2O_3	SiO_2
6L4	4	15	23	62
6L6	6	"	"	"
6L8	8	"	"	"
6L12	12	"	"	"



(before reheating) Heating temperature (°C)

Fig. 10. Dependence of $\tan \delta$ at 1Mc/sec upon heating temperature for specimens crystallized by heating the glasses containing various oxides.

Composition of the base glass: Li_2O 4, MgO 15, Al_2O_3 23, SiO_2 62 (parts by weight).

containing pores was prepared by sintering, at 1200°C , the pulverized glass of the same composition as that of the specimen No. 6L4 in Table 4. Its water absorption was determined to be 12% (by weight). In Table 5, its $\tan \delta$ is given together with that of the specimen No. 6L4 in Table 4, which was prepared by heating a piece of glass plate up to 1200°C .

Table 5. Dielectric losses of sintered specimen.

	Composition (parts by weight)				Firing temperature (°C)	Water absorption (%)	tan δ at 1Mc/sec
	Li ₂ O	MgO	Al ₂ O ₃	SiO ₂			
Specimen prepared by sintering pulverized glass	4	15	23	62	1200	12	40×10 ⁻⁴
Specimen prepared by crystallizing a glass plate (6L4)	4	15	23	62	1200	0	7×10 ⁻⁴

Table 6. Dielectric losses of pure polycrystalline bodies.

	Composition (parts by weight)			Firing temperature (C°)	Water absorption (%)	tan δ at 1Mc/sec
	Li ₂ O	Al ₂ O ₃	SiO ₂			
β -Eucryptite (Li ₂ O·Al ₂ O ₃ ·2SiO ₂)	11.9	40.5	47.6	1300	20	600×10 ⁻⁴
β -Spodumene (Li ₂ O·Al ₂ O ₃ ·4SiO ₂)	8.1	27.4	64.5	1300	20	60×10 ⁻⁴

X-ray diffraction analysis (see Table 4) showed that the crystal phases separated out in the glass-ceramic specimens were β -eucryptite and β -spodumene. In Table 6 are shown the values of tan δ for these pure crystals. The specimens used for this measurement were prepared by sintering mixtures of Li₂CO₃, Al₂O₃, and SiO₂ powders at 1300°C for 60 minutes.

Discussion

No relation was observed for the glass-ceramic specimens between the value of tan δ and the grain size of the constituent crystallites at least under the present experimental conditions, i.e., at a frequency of 1 Mc and within the narrow limits of grain size ranging only from 0.07 μ to 1.0 μ and 0.85 μ to 2.3 μ . However, if the measurement of tan δ be made at far lower frequency, say, at about 100 cycles/sec, and moreover with a set of specimens whose grain size has much wider limits, some relation might be expected to exist. Further investigations on this point are highly desirable.

As to the effect of existence of pores, the result given in Table 5 indicates clearly superiority of the non-porous glass-ceramic specimen to the glass-ceramic specimen with those pores as expressed by 12% water absorption; the value of tan δ for the former is only about one sixth of that for the latter.

The factor having the most strong effect on the value of tan δ is the crystal phase formed in the specimens. It can be seen from Fig. 9 that the change of tan δ with increasing the maximum heating temperature takes place in two steps; first the value of tan δ increases with increasing the heating temperature of each specimen, and then, after going through a maximum generally at about 950°C, it drops. The great drop in tan δ observed for the specimens of low Li₂O content (6L4 and 6L6 in Table 4) would have been caused by the formation of β -spodumene crystallite having a very low value of tan δ (see Table 6).

The formation of the β -spodumene crystallites at 950°C, being accompanied by disappearance of the β -eucryptite crystallites, was confirmed by the X-ray diffraction analysis for these specimens (see Table 4). The increase in $\tan \delta$ by the heat treatment up to 950°C would be due to the formation of β -eucryptite having a high value of $\tan \delta$ (see Table 6). A small drop in $\tan \delta$ at 950°C observed for the specimens of high Li_2O content (6L8 and 6L12) heated over 950°C can not be attributed to the formation of the β -spodumene crystallites because the X-ray diffraction analysis denied its formation. Its cause still remains unexplained, but is probably due to the partial dissolution of the β -eucryptite crystallites into the glassy matrix which might start above 950°C.

Among the components added to the base composition, PbO was found most effective in lowering the value of $\tan \delta$ of the glass-ceramic specimens. PbO would remain in the glassy matrix, lowering its value of $\tan \delta$. It is well known that glasses of high lead content have low values of $\tan \delta^{13)}$, and also the incorporation of PbO into porcelain bodies results in low values of $\tan \delta^{12)}$.

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