Preparation and Properties of Glass-Ceramics Containing Ferroelectric Crystals

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For the purpose of showing the general principles upon which the preparation of high dielectric constant ceramics via crystallization of glasses should be based, our works on the two systems of $BaO \cdot TiO_2$-Al_2O_3-SiO_2 and PbO-TiO_2-Al_2O_3-SiO_2 have been reviewed. A particular attention has been paid to the glass-forming composition region, crystallization process of the glasses, microstructure of the crystallized glasses and their dielectric properties.

I. INTRODUCTION

Ceramics with high dielectric constant, for example, $BaTiO_3$ ceramics, are used extensively as components of electronic devices and are usually produced by sintering of crystalline powders. If such ceramics are produced by crystallization of glass (glass-ceramic process), the following advantages should be expected;

(1) Ceramics of shapes difficult to form by sintering such as thin sheet, fiber and tube are easily prepared because of good formability of glass.

(2) Glass-ceramics thus obtained are easily sealed together with each other, or with the other ceramics or metals at relatively low temperatures because of low softening temperature of glass.

(3) Wide spectrum of dielectric properties can be obtained by controlling the microstructure.

(4) High electrical resistivity and high dielectric strength may result from pore-free structure.

(5) Ceramics with little aging and low temperature coefficient of dielectric constant are easily obtained by controlling particle size.

(6) Transparent ceramics may be obtained by controlling particle size.

With all these advantages, however, there are two problems in the glass-ceramic process; one is the dilution of ferroelectric crystals by glass-forming components and the other is complex effect of microstructure on the dielectric properties. To obtain glass network-forming oxides such as SiO_2, B_2O_3 and Al_2O_3 have to be added to the ferro-electric-crystal components, since the latter alone cannot be vitrified by conventional melting. This necessarily results in the dilution of the ferroelectric crystals by non-ferroelectric components, and the problem arises as to how the amount of precipitated ferroelectric crystals is increased within the given composition range. However, the dielectric constant may not be the function of the amount of the ferroelectric crystals alone, but the microstructure of the crystallized glass may be important, too. This

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requires us to study the effect of microstructure on dielectric constant and to find the way of controlling it.

So far, many works have been published on glass-ceramics of this kind. The subjects covered were preparation of glass, crystallization process of glass, dielectric properties, electro-optic effects and transparency of the crystallized glass *etc*.[1-16] A review paper has been published by Herczog.[17] However, few studies have dealt systematically with the fundamental problems in producing high dielectric constant glass-ceramics. The present paper is the summary of the author's investigations[6,11,14,16,25] conducted as to glass-ceramics with high dielectric constant and aims at finding the principles underlying their preparation.

II. PREPARATION OF GLASS

To obtain glass-ceramics in which a large amount of ferroelectric crystals is precipitated, it is necessary, first of all, for the parent glass to contain ferroelectric-crystal components as much as possible.   In other words, the content of network-form-ing oxides to be added to form glass should be as little as possible.   The minimum content of network-forming oxides which is required to form glass is much influenced by the kind of network-forming oxide and cooling rate of the melt during forming process. These effects were examined with glasses in the system $BaO \cdot TiO_2 - Al_2O_3 - SiO_2$.   It should be born in mind that this system is formally considered the pseudo-binary system $BaO \cdot TiO_2 - SiO_2$ to which Al_2O_3 was added.

II. 1. Effect of Kind of Network-Former

About 50 g of the batch mixtures of various compositions in the system $BaO \cdot TiO_2 - Al_2O_3 - SiO_2$ were melted in a platinum crucible at 1450°C for 1 hour in an electric furnace. The melts were poured on a steel plate and pressed into plates approximately
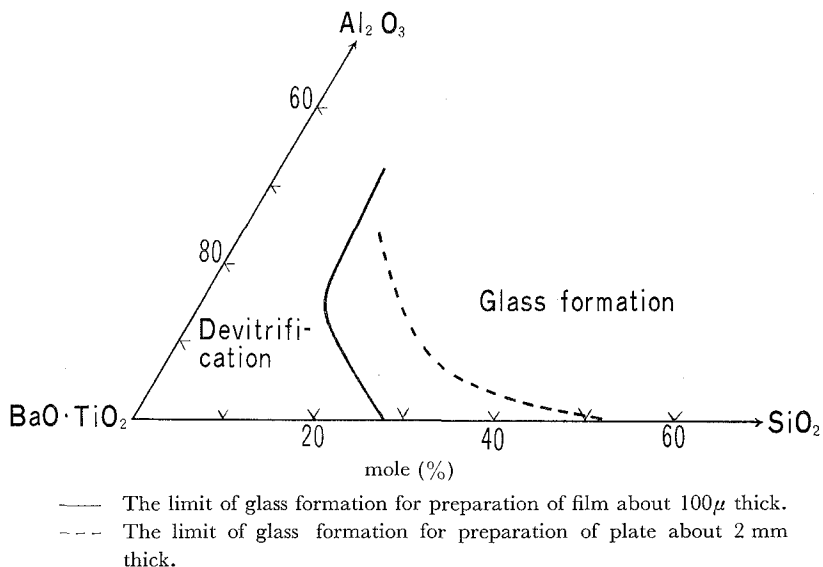

The limit of glass formation for preparation of film about 100μ thick.
The limit of glass formation for preparation of plate about 2 mm thick.

Fig. 1. Glass formation area in the system $BaO \cdot TiO_2 - Al_2O_3 - SiO_2$.

2 mm thick. The composition region in which transparent glasses were obtained by this procedure is shown by dotted line in Fig. 1.[5] It is seen from the figure that the addition of Al_2O_3 to the pseudo-binary system $BaO \cdot TiO_2$-SiO_2 extends the glass formation region and makes it possible to obtain glasses containing the high concentration of the BaO and TiO_2 components compared with the system without addition of Al_2O_3. This effect of Al_2O_3 will be explained as follows. In glasses in the system $BaO \cdot TiO_2$-SiO_2 the Ba^{2+} ions behave as network-modifier ions, breaking the glass network and increases the tendency of the glass to devitrify. However, when such modifier ions are introduced into glasses together with Al_2O_3, nonbridging O^{2-} ions are not produced. Hence, the resulting aluminosilicate glass has a higher symmetry in bond strength than a $BaO \cdot TiO_2$-SiO_2 glass.[18] This has an effect of stabilizing the glassy state and would be lead to the spread of the glass formation region.

II. 2. Effect of Cooling Rate

As is well known, glass formation region varies with the cooling rate of the melt. To examine this, the following method of rapid quenching was tried.

The crucible containing a molten glass was turned over upside down in the hot furnace kept at 1550°C and the molten glass flowing downward was passed through between two cold drams of solid cast iron, which were situated under the furnace and rotated in mutual contact. By this procedure pieces having the form of leaf about 50 to 100 μ thick were obtained. The glass formation determined with this quenching method is shown by a solid line in Fig. 1.[11] It can be seen from the figure that the glass formation region is extended much further toward the higher concentration of the BaO and TiO_2 components by the rapid cooling compared with the case described in paragraph **II.1.** Incidentally, Ulrich et al.[7] obtained pure $BaTiO_3$ glass in minute particles by quenching the melt in water.

It is concluded from these experiments that rapid quenching of the melt gives the parent glasses containing much amounts of components of given ferroelectric crystals and, with a cooling rate limited, the appropriate combination of network-forming oxides is also important in determining the amount of the necessary components which can be incorporated into glass.

III. CRYSTALLIZATION OF GLASS

Detailed study of the crystallization upon heat treatment was examined on two glasses of the compositions $BaO \cdot TiO_2$ 60, Al_2O_3 14, SiO_2 26 mole % and PbO 40, TiO_2 25, Al_2O_3 10, SiO_2 25 mole %.

III. 1. $BaO \cdot TiO_2$-Al_2O_3-SiO_2 Glass

Glass samples of rectangular shape, $10 \times 10 \times 2$ mm, were heated to various temperatures at a rate of 5°C/min, and allowed to cool immediately from the respective temperatures. With the heat-treated samples x-ray diffraction analysis was made on the surface before and after grinding to a depth of 700 μ. The intensities of the strongest diffraction lines from the crystalline species found in the samples are plotted as functions of temperature of heat treatment (maximum heating temperature) in Fig. 2.[16] In Fig. 3 are given photographs of the cross-sections of the samples, which
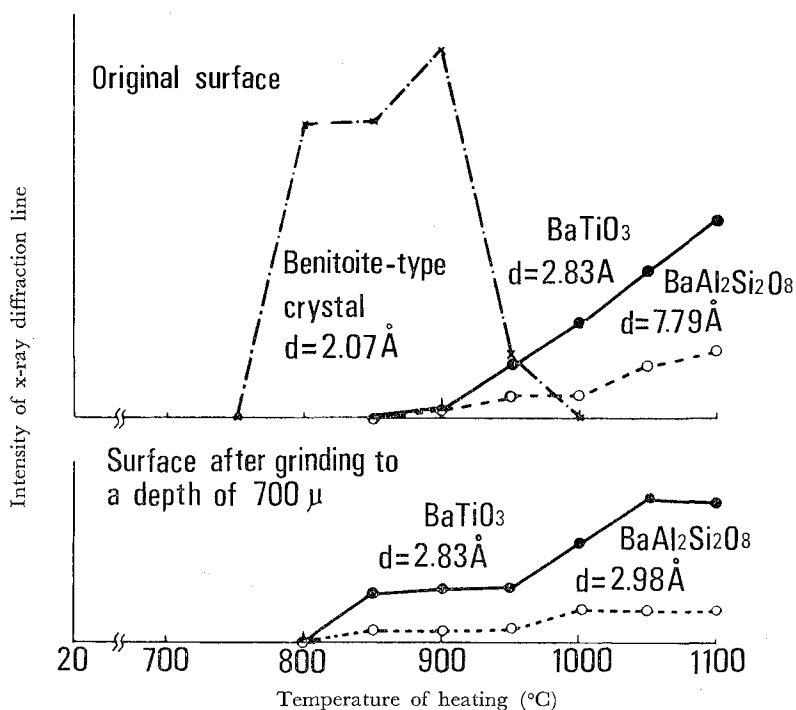
Original surface

BaTiO₃
d=2.83Å

Benitoite-type
crystal
d=2.07Å

BaAl₂Si₂O₈
d=7.79Å

Intensity of x-ray diffraction line

Surface after grinding to
a depth of 700 μ

BaTiO₃
d=2.83Å

BaAl₂Si₂O₈
d=2.98Å

20   700   800   900   1000   1100

Temperature of heating (°C)

Fig. 2.   Change in intensities of x-ray diffraction lines obtained for the
BaO·TiO₂-Al₂O₃-SiO₂ glass heated to various temperatures.

were taken under a transmission microscope with crossed nicols.

As shown in these figures crystallization behavior at the original surface of the sample is different from the interior.   At the surface, needle-like benitoite-type crystals, which are assumed to have the similar composition with parent glass,[16] start first to precipitate at 750°C in oriented fashion, and then tiny perovskite-type BaTiO₃ and hexacelsian (BaAl₂Si₂O₈) crystals start to precipitate at 850°C at the expense of the benitoite-type crystals.   At higher temperatures the latter crystlas increase in amount with increasing temperature.   On the other hand, in the interior the benitoite-type crystals do not precipitate but the tiny BaTiO₃ and hexacelsian crystals start to precipitate at the temperature as low as 800°C and their growth proceeds up to 1100°C without any transformation.

III. 2.   PbO-TiO₂-Al₂O₃-SiO₂ Glass

X-ray diffraction analysis was made also for the PbO-TiO₂-Al₂O₃-SiO₂ glass heated to various temperatures by the similar schedule as in the preceding paragraph.   The original surface and the surface appearing after grinding to a depth of 500 μ were examined.   The intensities of the strongest diffraction lines from the respective crystalline species and the axial ratio (c/a) of the perovskite-type PbTiO₃ crystals are shown in Fig. 4[14] as functions of temperature of heat treatment.   The electronmicroscopic photographs showing the structure of the interior of the heat-treated glasses are shown in Fig. 5.[14]

Combination of the observations shown in Fig. 4 and 5 makes it possible to follow

(1) 800°C

(2) 900°C

(4) 1000°C

(3) 950°C

(5) 1100°C
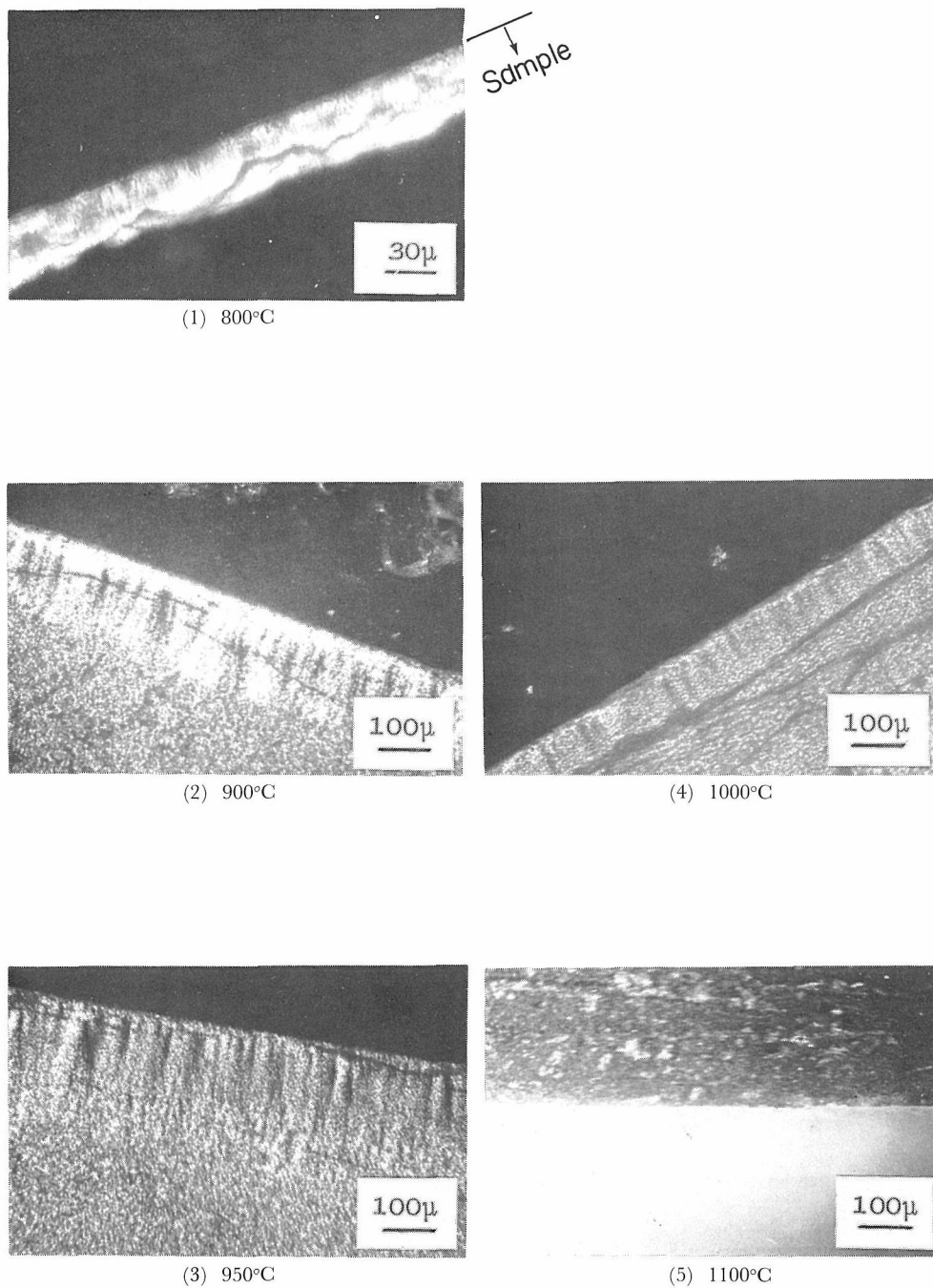
Fig. 3. Cross-sections of the BaO·TiO₂-Al₂O₃-SiO₂ glass heated to various temperatures. Observation was made by transmission optical microscope with crossed nicols.

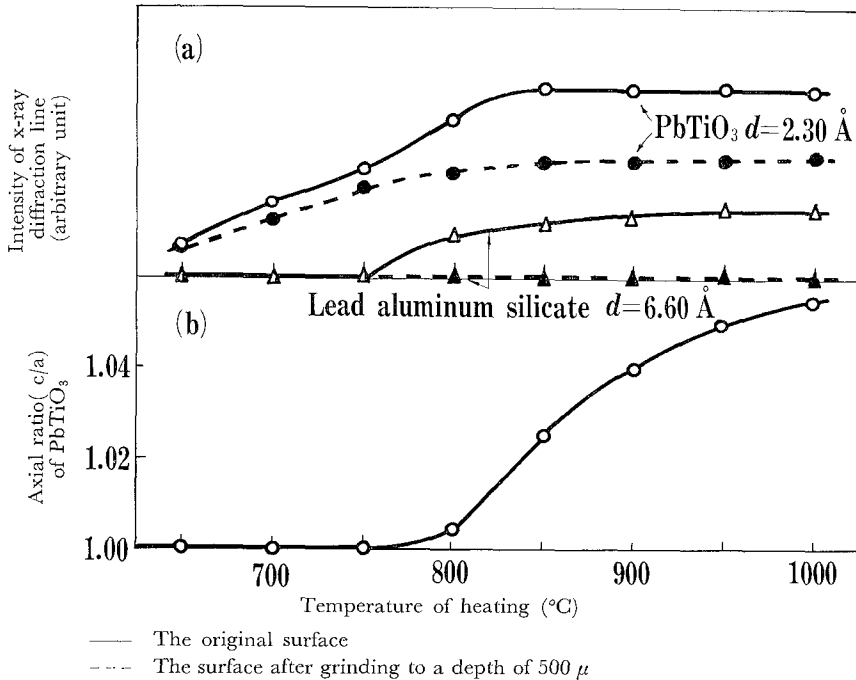Fig. 4. Dependence of crystal content and axial ratio of $PbTiO_3$ in the PbO–TiO_2-Al_2O_3-SiO_2 glass-ceramic upon temperature of heat treatment.

the change caused in glass by heat treatment. It is seen, first of all, that the glass is already separated into two glassy phases before heat treatment. With heat treatment the separated phase grow, and the perovskite-type $PbTiO_3$ crystals start to precipitate at about 650°C throughout the sample. Their amount increases with increasing temperature of heating. Above 850°C recrystallization of the $PbTiO_3$ crystals occurs without further increase in their amount, forming aggregates of $PbTiO_3$ crystals. The aggregates grow in size and at the same time spread throughout the sample. The diameter of the individual $PbTiO_3$ crystals, on the other hand, continues to increase up to 1000°C, which is accompanied by an increase of their axial ratio. Besides these, the precipitation of needle-like lead aluminum silicate crystals[19] begins at about 800°C at the surface of the sample. The crystallization process mentioned above is summarized schematically in Fig. 6.

Briefly, as the temperature of heat treatment is raised, the amount of the ferroelectric crystal precipitated in the glass increases and other structural changes such as precipitation and transformation of non-ferroelectric crystals, which are especially pronounced at the surface, grain growth and change of continuity of the ferroelectric crystals also take place. So, it is possible to obtain various microstructures by changing the temperature of heat treatment. To determine an optimum way of heat treatment, information on effects of the amount of ferroelectric crystals and microstructure on the properties of crystallized glass are required.
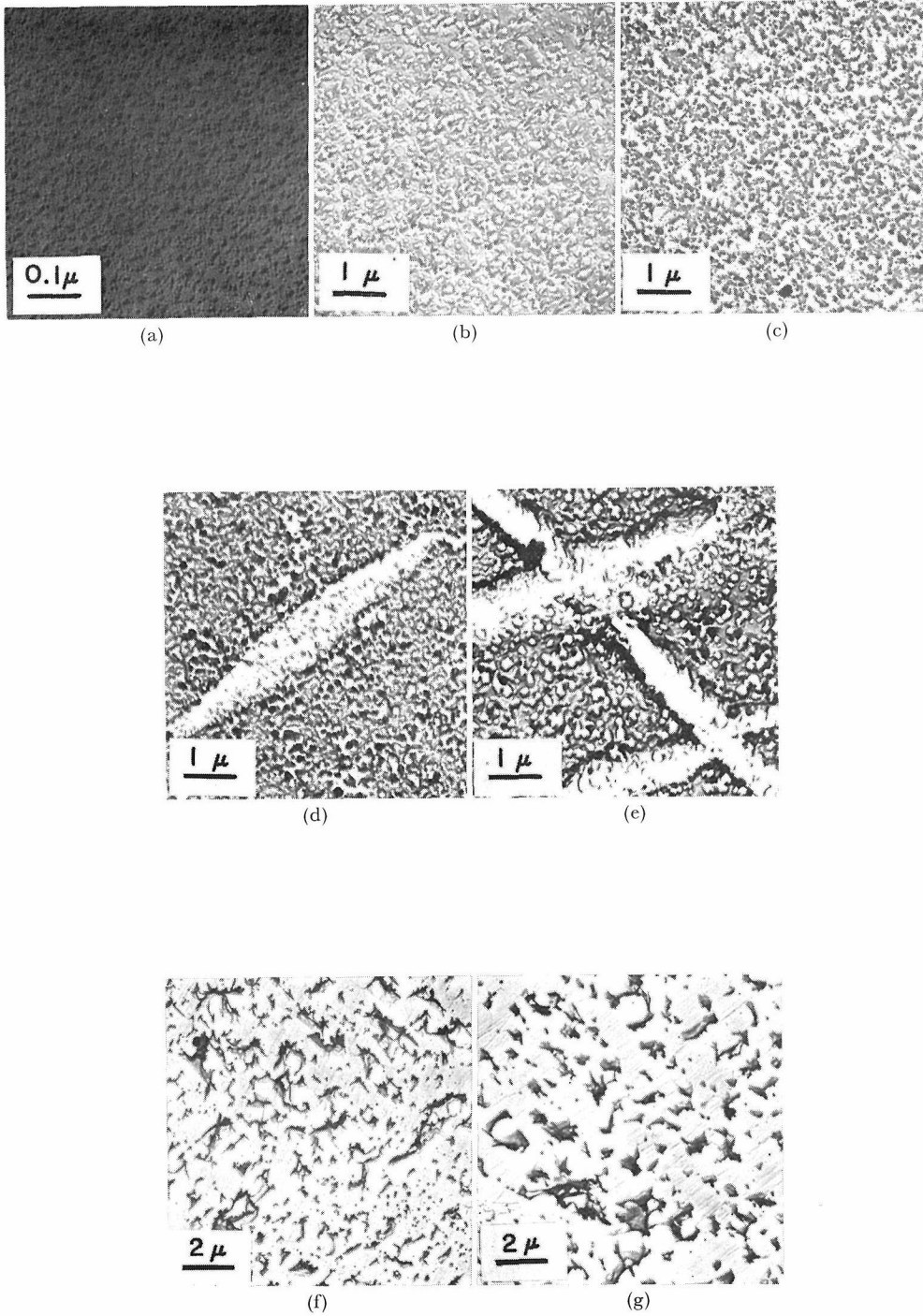
Fig. 5. Electronmicrographs of the PbO-TiO$_2$-Al$_2$O$_3$-SiO$_2$ glass before heating (a) and reheated up to 630°C (b), 800°C (c), 850°C (d), 900°C (e), 950°C (f) and 1000°C (g).

Before reheating.
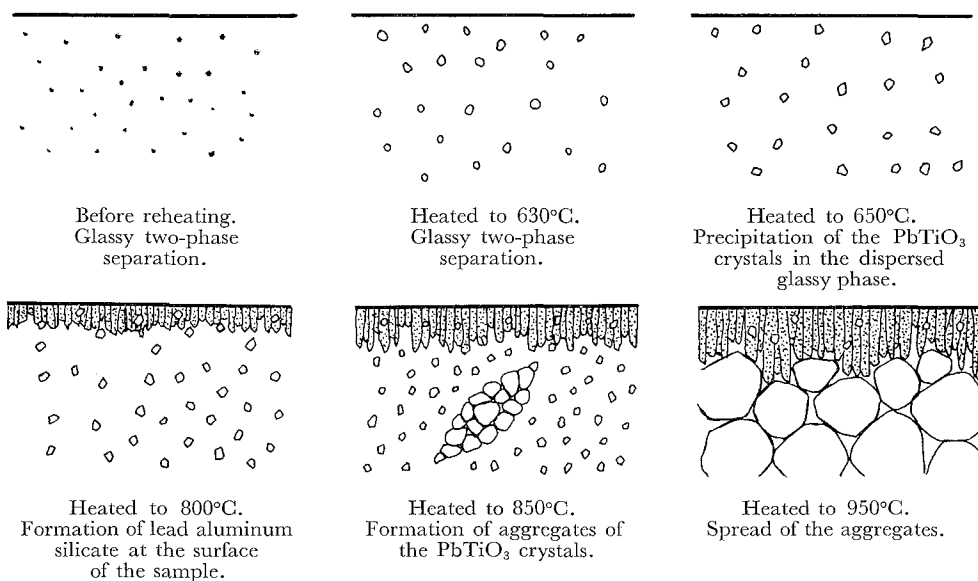Glassy two-phase
separation.

Heated to 630°C.
Glassy two-phase
separation.

Heated to 650°C.
Precipitation of the PbTiO$_3$
crystals in the dispersed
glassy phase.

Heated to 800°C.
Formation of lead aluminum
silicate at the surface
of the sample.

Heated to 850°C.
Formation of aggregates of
the PbTiO$_3$ crystals.

Heated to 950°C.
Spread of the aggregates.

Fig. 6. Schematic representation of crystallization process of the
PbO-TiO$_2$-Al$_2$O$_3$-SiO$_2$ glass.

IV. DIELECTRIC CONSTANT IN RELATION TO MICROSTRUCTURE

The dielectric constat of the crystallized glass depend not only on the amount of the ferroelectric crystals precipitated but also on the microstructure of the sample.

IV. 1. Effect of the Amount of Ferroelectric Crystal

The rectangular pieces, $10 \times 10 \times 1$ mm, of seven glasses in the system BaO·TiO$_2$–Al$_2$O$_3$-SiO$_2$, whose compositions are shown by seven points in Fig. 16, were heated from room temperature to 1100°C at a rate of 5°C/min, held there for 1 hour and then cooled in the furnace. Resultant crystallized glasses contained, besides BaTiO$_3$ crystals, various silicate crystals such as hexacelsian and BaTiSiO$_5$, depending on the glass composition. In Fig. 7,[6] the room temperature dielectric constant at 1 Mc/s of the crystallized glass is plotted as a function of the amount of the BaTiO$_3$ crystals precipitated.   The amount of the BaTiO$_3$ crystals was determined from x-ray diffraction data and density measurement.   It is seen from the figure that the dielectric constant of the crystallized glass substantially depends on the volume fraction of ferroelectric crystal, irrespective of the kind of coexisting silicate crystals.

IV. 2. Effect of Grain Size and Continuity of Ferroelectric Crystal

In Fig. 8 the dielectric properties (at room temperature and 1 Mc/s) of the PbO-TiO$_2$-Al$_2$O$_3$-SiO$_2$ glass described in paragraph **III. 2** are shown[14] as functions of temperature of heat treatment.   As can be seen, the dielectric constant of the crystallized glass varies with temperature of heat treatment in a complex way.

The increase in dielectric constant with increasing the heating temperature from 650° to 750°C would be due simply to the increase in the amount of the PbTiO$_3$ crystal in the sample, since in this temperature range no noticeable change in microstructure

of the sample and size of the crystals is observed.

In the temperature range from 750° to 850°C the dielectric constant goes through a maximum and then decreases, inspite of continued increase in the amount of $PbTiO_3$ crystal. It may appear at first sight that the formation of lead aluminum silicate[19] at the surface of the sample is responsible for this behavior. This possibility is denied, however, since the removal of the surface layer did not affect the variation of the dielectric constant. At present it is most likely that the grain size and axial ratio of the $PbTiO_3$ crystals related to the change of dielectric constant with temperature of heating mentioned above. In this temperature range the grain size and axial ratio of the $PbTiO_3$ crystals undergo great changes, as seen in Fig. 4 and 5. According to Herczog[3], the dielectric constant of the polycrystalline $BaTiO_3$ varies with the crystal grain size especially in the range from 0.1 to 10 μ, causing a maximum of the dielectric constant at about 1 μ. At the grain size much larger than 1 μ, no stress is produced in the crystal grains during their ferroelectric transition because of stress relaxation by domain wall motion. As the grain size becomes smaller and approaches 1 μ, formation and motion of domain walls become energetically unfavorable, and great stresses are induced in the grains, resulting in the increase in dielectric constant of the materials.[20] When the grain size becomes still smaller, the effect of a depolarized layer,[21] which exists at surfaces of the crystal particles and acts to lower the dielectric constant, becomes remarkable. These two effects make a maximum peak to appear at about 1 μ of grain size in the curve illustrating the dielectric constant-grain size relationship. Although the reasoning mentioned above should be discussed further,[22] the variation in dielectric constant with grain size itself has been experimentally confirmed for the polycrystalline $BaTiO_3$. For the polycrystalline $PbTiO_3$, such a relationship has not been established experimentally. Theoretically, however, it is highly probable that such a relation holds for the polycrystalline $PbTiO_3$ as well. If so, the complex change of dielectric constant in the temperature range from 750° to 850°C (Fig. 8) can be explained in the following way. Due to the continued increase in the amount of the $PbTiO_3$ crystals, the dielectric constant increases in the range from 750° to 800°C. As the temperature increases, however, the crystal grain grow gradually, which has effect of decreasing the dielectric constant of the crystal due to the relaxation of the stresses in the grains. Since this effect becomes predominant at about 800°C, the dielectric constant of the sample actually begins to decrease. It should be noted that the change in the axial ratio of the $PbTiO_3$ crystal beginning at about 800°C (Fig. 4) is also attributed to the stress relaxation mentioned above.

The dielectric constant increases again at the temperatures over 850°C. This is attributed to connection of the fine-grained $PbTiO_3$ crystals, that is, formation of large crystal aggregates (Fig. 5). It is known that dielectric constant of a mixture consisting of crystals with high dielectric constant and a glass matrix with low dielectric constant is low when the crystals are isolated by the glass matrix, whereas it is high when the crystals are connected with each other from one face to another face of the sample.

It is noticed from these experiments that the grain size and continuity of ferro-electric crystals greatly affects the dielectric constant of the crystallized glass.

IV. 3. Effect of Arrangement of Non-Ferroelectric Crystal

The above discussions on dielectric properties are concerned with the plate samples
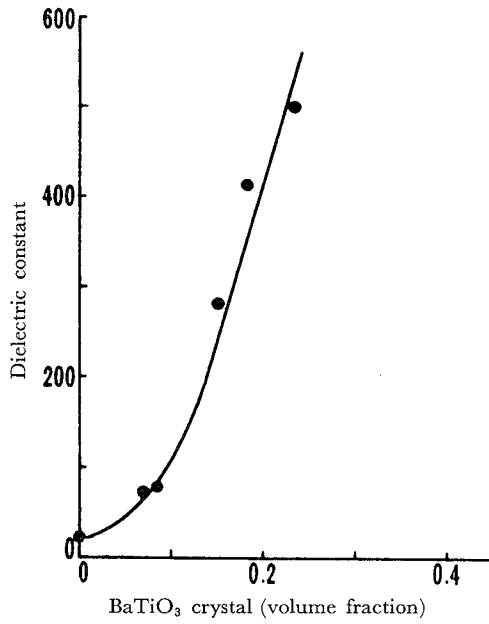
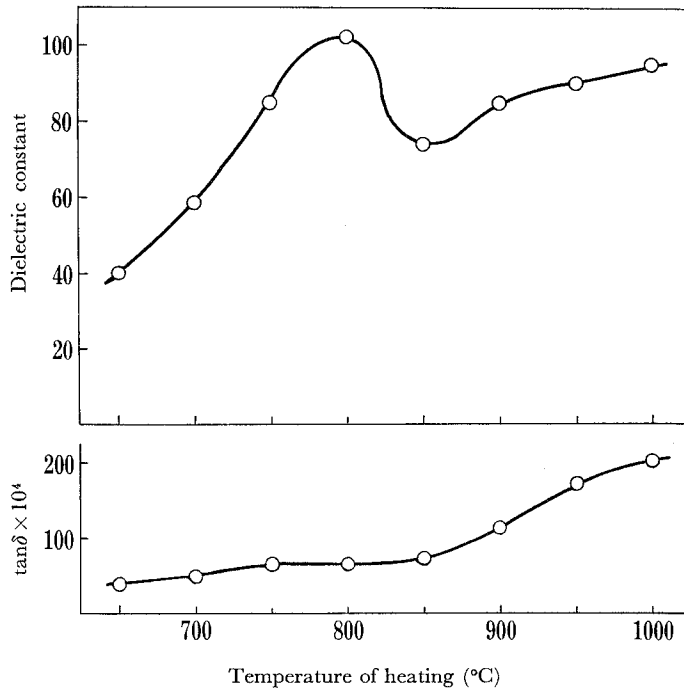Fig. 7. Dielectric constant of the BaO·TiO$_2$-Al$_2$O$_3$-SiO$_2$ glass-ceramics *vs.* content of BaTiO$_3$ crystal.

Fig. 8. Dependence of dielectric properties of the PbO-TiO$_2$-Al$_2$O$_3$-SiO$_2$ glass-ceramic upon temperature of heat treatment.
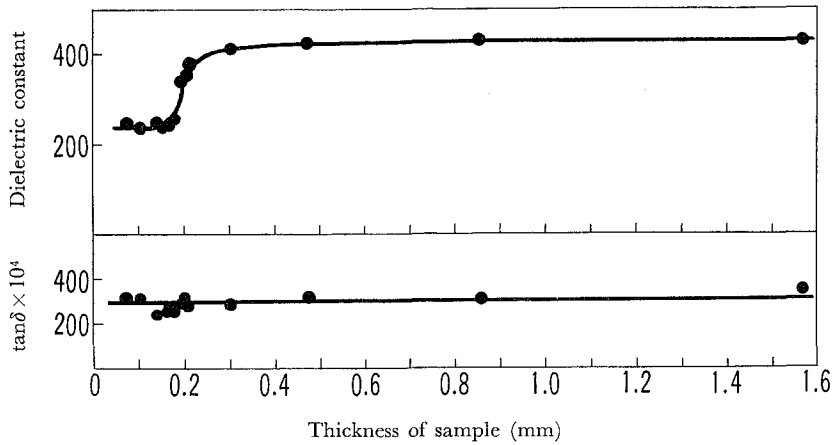
Fig. 9. Variation of dielectric properties of the BaO·TiO$_2$-Al$_2$O$_3$-SiO$_2$ glass-ceramic with thickness of the sample.

1 to 2 mm thick. In this paragraph the thinner crystallized glass sheets are discussed. Sheets of the BaO·TiO$_2$-Al$_2$O$_3$-SiO$_2$ glass (the composition was given in paragraph **III.**) with various thicknesses in the range of 50 μ to 1.6 mm were crystallized by the same heat treatment as in paragraph **IV. 1.** and their dielectric properties at 1 Mc/s were measured at room temperature. The results are shown in Fig. 9.[11] It is seen that the dielectric constant is strongly dependent on the sample thickness. More particularly, it changes remarkably at a critical thickness region of 0.2–0.4 mm below which it is low and above which it shows a higher value.
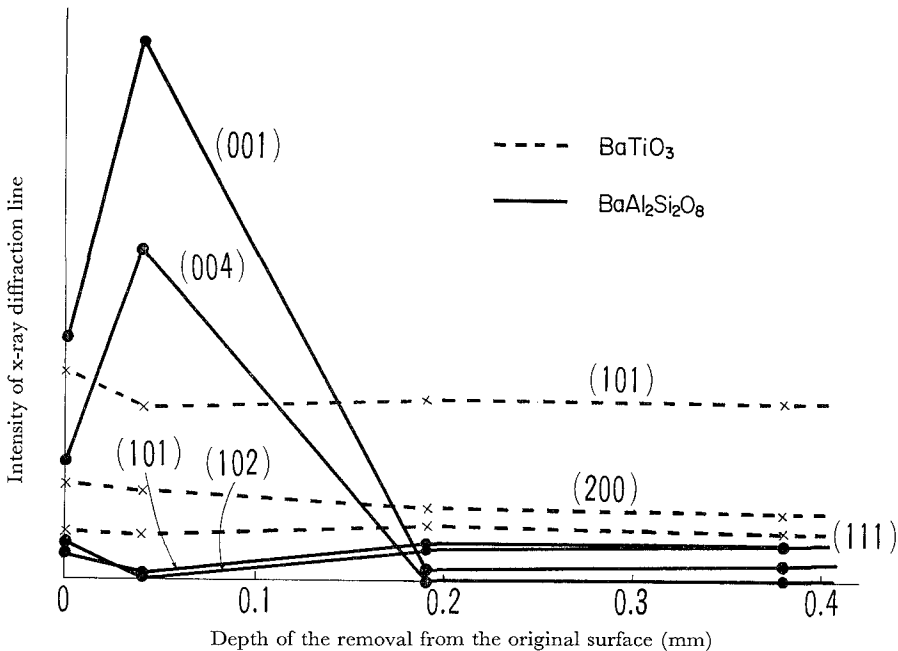
Fig. 10. Intensities of x-ray diffraction lines for the surfaces of the BaO·TiO$_2$-Al$_2$O$_3$-SiO$_2$ glass-ceramic ground to varying depths.

Fig. 11. Arrangement of the hexacelsian in the BaO·TiO$_2$-Al$_2$O$_3$-SiO$_2$ glass-ceramics.

The results of the x-ray diffraction analysis for the powdered samples indicated that there is no difference in the kinds of crystals precipitated (perovskite-type BaTiO$_3$ and hexacelsian) and their amounts between the thin and thick samples. In addition, no difference was detected in the grain size and continuity of the BaTiO$_3$ crystals by electronmicroscopic observation. When the thick samples were subjected to the x-ray diffraction anslysis after their original surfaces were successively ground off to varying depths, intensities of the diffraction lines of the hexacelsian crystal varied remarkably with depth removed, although those of the BaTiO$_3$ crystal remained nearly constant (Fig. 10).[11] More specifically, marked increases in intensities of the (001) and (004) reflections, and a slight decreases in those of the (101) and (102) reflections of hexacelsian was observed as the original surface layer was removed up to about 200 μ. This can be interpreted to show presence of preferred orientation of the hexacelsian crystallites. Generally, hexacelsians are likely to be precipitated as lath-like crystals with cleavage parallel to their (001) plane.[23] Therefore, it is expected that at near the surface of the samples hexacelsian crystals probably appear in such a manner that their cleavage planes are parallel to the surface of the sample. On the other hand, in the interior of the samples, i.e. in the portion deeper than 200 μ from the original surface, hexacelsian would be distributed rather at random without preferred orientation. This is demonstrated by the relative intensities of the x-ray diffraction lines of hexacelsian being similar to those of the powdered sample. The arrangement of the hexacelsian crystallites are shown schematically in Fig. 11.

The dielectric constant of hexacelsian itself would be much lower than that of the mixture of BaTiO$_3$ crystal and their surrounding glass matrix. Thus the portion near the original surface of the sample is considered to have a structure in which high capacity elements consisting of the BaTiO$_3$ crystal and the glass matrix, and low capacity elements of hexacelsian crystals with preferred orientation are connected in series. Consequently, the dielectric constant of the surface layer would be much lower than that of the interior in which the hexacelsian crystals are precipitated without preferred orientation.[24] When the thickness of the sample is large, the effect of the surface layer with low capacity is insignificant in determining the apparent dielectric constant of the whole sample. With decreasing the thickness, however, the effect would become larger gradually, and at about 200 μ, it would be strong enough to cause a sudden decrease in dielectric constant of the sample.

It should be remembered that the dielectric constant of the crystallized glasses is greatly affected by the arrangement of the non-ferroelectric crystals.

IV. 4. Effect of Microcracks

In this paragraph the thick-film dielectrics which are formed by firing glass powder
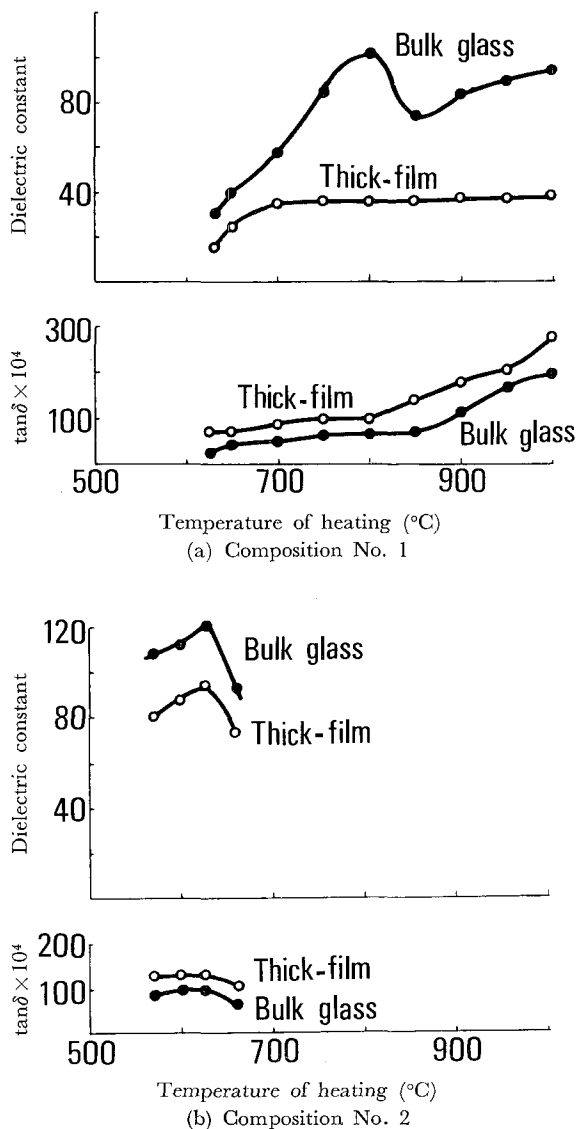
Fig. 12. Dielectric properties of thick-film dielectrics and glass-ceramic
plate as functions of temperature of heat treatment

printed on Al_2O_3 ceramic substrate are discussed.   The powder glasses with the
compositions PbO 40, TiO_2 25, Al_2O_3 10, SiO_2 25 mole % (No. 1), which is the same
in composition as the glass in paragraph **III. 2,** and PbO 45, TiO_2 25, Al_2O_3 10, SiO_2
12, B_2O_3 8 mole % (No. 2) were mixed with alkyd varnish, printed in the form of disc
about 12 mm in diameter and 100 μ thick, over the palladium conductor previously
printed on the Al_2O_3 substrate, fired by heating from room temperature to various tem-
peratures at a rate of 5°C/min and cooled immediately in the air.   The dielectric
properties at 1 Mc/s measured at room temperature for the thick-film dielectrics thus
obtained are shown as functions of the temperature of heat treatment (maximum

heating temperature) in Fig. 12.[25]   For comparison, the data for the plate glass–ceramics, 2 mm thick, having the same composition and subjected to the same heat treatment are shown.   For the composition No. 1 the dielectric constant of thick-film dielectrics is much lower than those of the bulk glass-ceramics irrespective of their temperatures of heat treatment, whereas for the composition No. 2 the values of dielectric constant of the thick-film are almost comparable to those of the bulk glass–ceramics.

The lower value for the thick-film dielectrics No. 1 can not be attributed to pores which might have been formed in the dielectrics in the course of sintering, since there was little difference in dielectric constant between the bulk glass-ceramics and glass-ceramics obtained by sintering glass powder without being applied on the substrate.   The kind, amount, axial ratio, grain size, and arrangement of the precipitated $PbTiO_3$ crystals do not appear to be important factors lowering the dielectric constant of the thick-film dielectrics, since the results of x-ray diffraction analysis did not reveal any significant difference between the bulk glass-ceramics and the thick-film dielectrics.   Reaction of the thick-film dielectrics with palladium bottom conductor can not be a cause of low dielectric constant of the thick-film dielectrics.   The x-ray diffraction analysis did not give any evidence of the presence of reaction products and further, the thin glass sheet, 100 μ thick, did not show any decrease in dielectric constant when it was crystallized with palladium paste applied.

Although both the thick-film dielectrics No. 1 and 2 seemed to have uniform continuous film to the naked eyes, many microcracks were observed on the surface of the thick-film dielectrics No. 1 under a metallurgical microscope (Fig. 13).[25]   When the thicker dielectric film, 0.6 mm thick, was applied on the substrate and fired, severer cracks were formed (Fig. 14).[25]   Detailed inspection of the thicker dielectric film lead us to assume that some of the cracks makes a laminar structure with dielectrics.   If so, the cracks will reduce the apparent dielectric constant of the thick-film   dielectrics
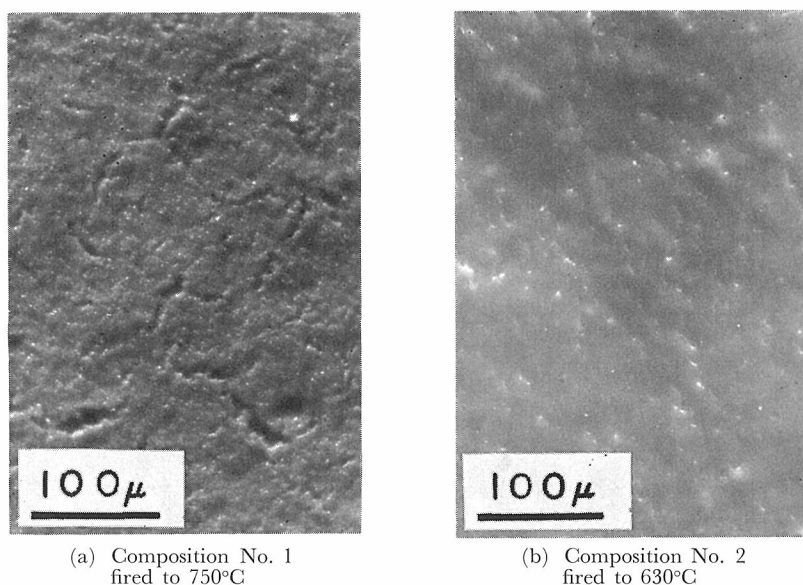

(a) Composition No. 1
fired to 750°C

(b) Composition No. 2
fired to 630°C

Fig. 13.   The surfaces of the thick-film dielectrics.

| Firing temperature (°C) | No heat treatment | 590 | 610 | 650 | 1000 |

(a) Composition No. 1

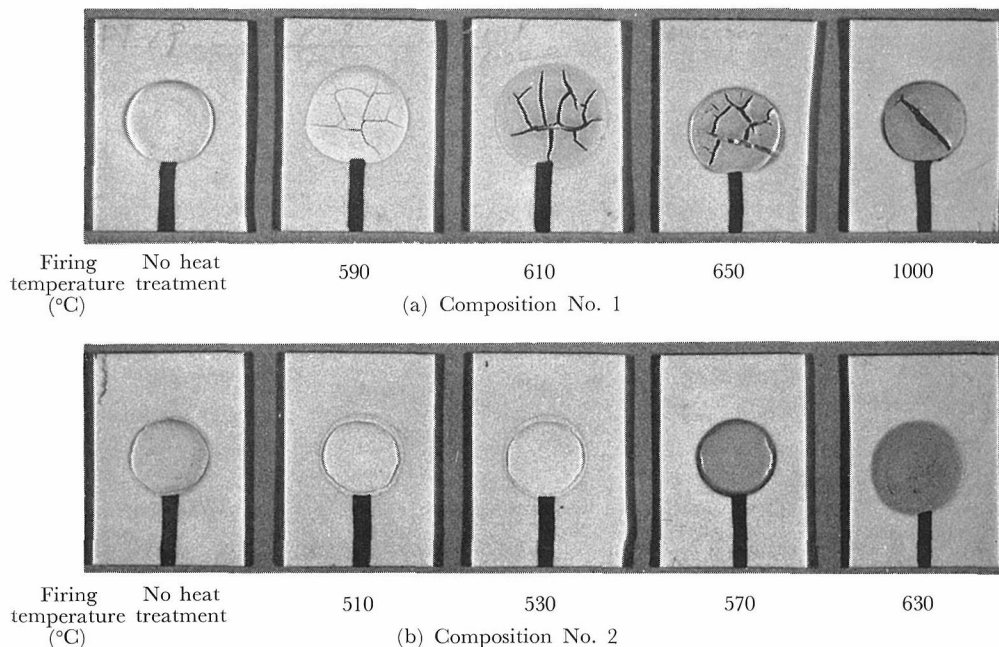| Firing temperature (°C) | No heat treatment | 510 | 530 | 570 | 630 |

(b) Composition No. 2

Fig. 14. Appearance of the thicker dielectrics produced by firing glass powder on alumina substrate

drastically, because the film of dielectrics is divided into a number of sheets between which there are thin voids.   No decrease in dielectric constant was observed when the glass No. 2 was used for making the thick-film dielectrics.   It should be noted that in this case no crack was detected both in the thinner film and thicker film (Fig. 13 and 14).
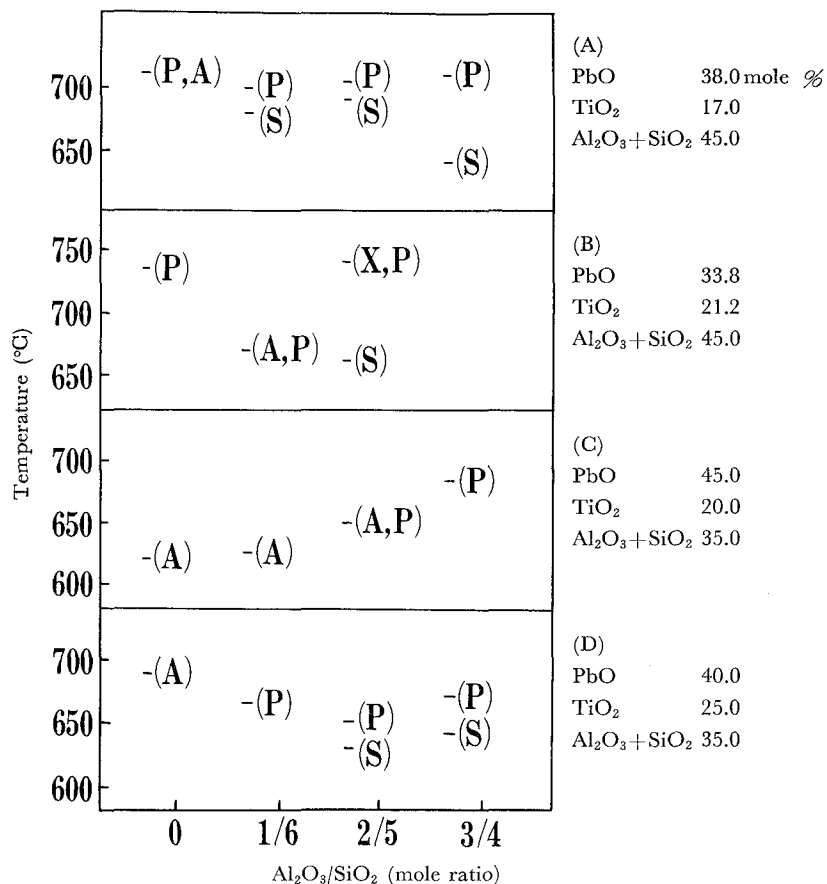
It has been shown in this paragraph that the dielectric constant of the crystallized glass is affected by microcracks, if any.

V. CONTROL OF MICROSTRUCTURE

V. 1. Kind and Amount of Crystal

The crystallization process of the PbO-TiO_2-Al_2O_3-SiO_2 glasses having various compositions were examined by differential thermal analysis and x-ray diffraction analysis.   The results are shown graphicaly in Fig. 15.[14]   It can be seen from the figure that with the replacement of the SiO_2 with Al_2O_3, the precipitation of the perovskite-type $PbTiO_3$, which has a high dielectric constant, via the glassy two-phase separation is promoted and the precipitation of the pyrochlore-type lead titanate[26] is suppressed, even though the content of PbO and TiO_2 are held constant.   Thus the kind of crystal to be precipitated in the glass can be controlled not only by the content of the ferro-electric-crystal component but also by the combination of the inert components.   It seems that the glassy two-phase separation promotes the precipitation of ferroelectric crystal.

Figure 16[6] shows the variation of volume fraction of the $BaTiO_3$ crystal precipitat-ed in the $BaO\cdot TiO_2$-Al_2O_3-SiO_2 crystallized glasses described in paragraph **IV. 1.** with

Temperature (°C)

700 -(P,A) -(P) -(P) -(P)
650   -(S) -(S)
                        -(S)

(A)
PbO   38.0 mole %
TiO$_2$ 17.0
Al$_2$O$_3$+SiO$_2$ 45.0

750 -(P)   -(X,P)
700
650   -(A,P) -(S)

(B)
PbO   33.8
TiO$_2$ 21.2
Al$_2$O$_3$+SiO$_2$ 45.0

700   -(P)
650   -(A,P)
600 -(A) -(A)

(C)
PbO   45.0
TiO$_2$ 20.0
Al$_2$O$_3$+SiO$_2$ 35.0

700 -(A)
650   -(P)   -(P) -(P)
                      -(S)
600   -(S)

(D)
PbO   40.0
TiO$_2$ 25.0
Al$_2$O$_3$+SiO$_2$ 35.0

0   1/6   2/5   3/4

Al$_2$O$_3$/SiO$_2$ (mole ratio)

P : Precipitation of perovskite-type PbTiO$_3$.
A : Precipitation of pyrochlore-type lead titanate.
X: Precipitation of unidentified crystal.
S : Separation into two glassy phases.

Fig. 15.   Crystallization process of the PbO-TiO$_2$-Al$_2$O$_3$-SiO$_2$ glasses.

the composition of parent glass.   It is seen from the figure that the content of the BaTiO$_3$ crystals precipitated varies with the Al$_2$O$_3$/SiO$_2$ mole ratio, even though the contents of BaO and TiO$_2$ components are held constant.

Herczog[3] successfully obtained the glass-ceramics containing large amounts of BaTiO$_3$ crystals from a series of compositions in the BaTiO$_3$-BaAl$_2$Si$_2$O$_8$ system.   This suggests that choosing a composition on a tie line between the components of a ferro-electric crystal and that of a non-ferroelectric crystal is a useful method for obtaining the glass-ceramics containing a large amount of ferroelectric crystal, because the consumption of the ferroelectric-crystal components by the precipitation of the third crystal may be prevented.

V. 2. Grain Size and Continuity

Figure 4 and 5 show that grain size and continuity of the PbTiO$_3$ crystals change with the temperature of heat treatment without variation of the amount of crystals.
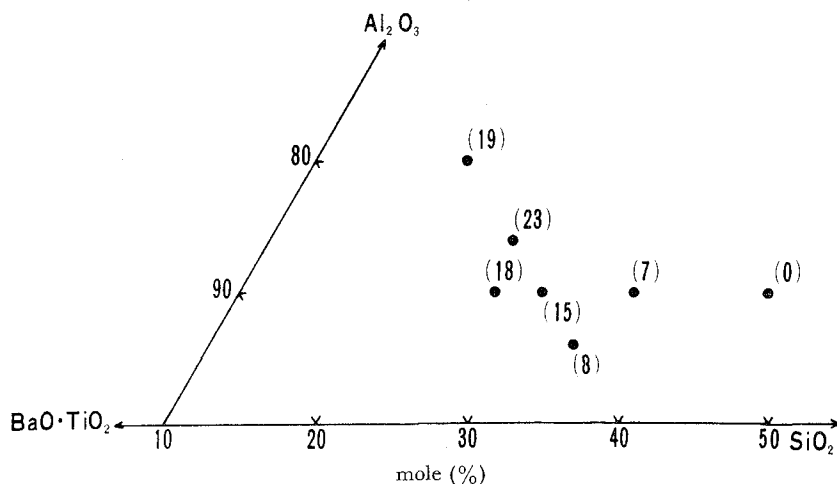
Fig. 16. Content (volume %) of $BaTiO_3$ crystal in the
$BaO \cdot TiO_2$-Al_2O_3-SiO_2 glass-ceramics.

In such a case the grain size or continuity of the ferroelectric crystals can be controlled by the condition of heat treatment.

On the other hand, Layton et al.[8] reported that grain size of the ferroelectric crystals is also controlled by the composition; for example, grain size of $NaNbO_3$ crystals is controlled by the content of SiO_2 in the system Na_2O-Nb_2O_5-SiO_2.

V. 3. Arrangement of Non-Ferroelectric Crystal

The cause of the preferred orientation of the hexacelsian crystals precipitated at near the original surface of the $BaO \cdot TiO_2$-Al_2O_3-SiO_2 glass-ceramics, as described in paragraph **IV. 3.** will be considered as follows. At near the surface of the glass sample, the $BaTiO_3$ and hexacelsian crystals are formed through the transformation of the metastable benitoite-type crystals (Fig. 2 and 3). The benitoite crystal has a layered structure,[27] in which layers consisting of Si_3O_9 rings are arranged parallel to (001) plane and barium and titanium ions exist between these layers. The metastable crystal found near the surface of the $BaO \cdot TiO_2$-Al_2O_3-SiO_2 glass-ceramics is considered to have a similar structure to benitoite crystal. Also hexacelsian has a layered structure,[23] in which layers having the composition $((Si, Al)O_2)_n$ are parallel to (001) plane and barium ions exist between these layers. Since both the benitoite-type crystal (metastable) and hexacelsian crystal have the layered structure characterized by silicate layers parallel to (001) plane, the hexacelsian crystals, when formed from the metastable benitoite-type crystals, will be oriented in the manner that the direction of its silicate layer will be the same as that of the silicate layer in the metastable crystal. On the other hand, x-ray reflection from (004) planes of the metastable benitoite-type crystal formed at the surface of the glass sample is extraordinarily stronger than the reflection for the powdered glass, indicating that the (001) plane of the metastable benitoite-type crystals is parallel to the surface of the glass sample. Thus the preferred orientation of the hexacelsian crystals near the surface of the glass sample could be attributed to the preferred orientation of the mother crystals of metastable benitoite-type from which the hexacelsian is formed.
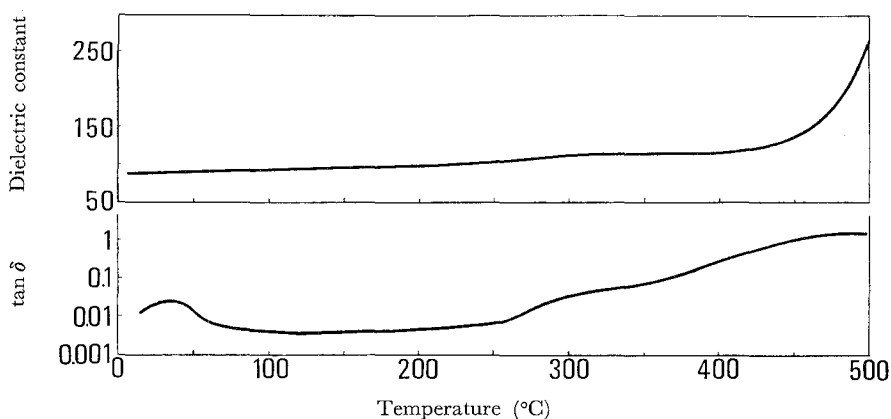
Fig. 17. Dependence of dielectric properties, at 1 Kc/s, of the PbO-TiO$_2$–
Al$_2$O$_3$-SiO$_2$-B$_2$O$_3$ thick-film capacitor upon temperature of measurement.

The reason why the metastable crystals of benitoite-type are formed only at near
the surface of the glass sample is unknown as yet.   By any means, in order to control
the arrangement of such non-ferroelectric crystals, surface treatment or choice of the
composition will be useful.

V. 4. Microcracks

Cracks in the thick-film dielectrics, described in paragraph **IV.4,** were found to be
formed in the firing process and not during cooling of the fired sample (Fig. 14).   Ac-
cordingly, the formation of the cracks is attributed to the shrinkage of a layer of glass
powder in firing process; the shrinkage of the layer of glass powder occurs due to the
tendency for the glass powder particles to adhere to each other in firing process.   The
glass powder also tends to adhere to the surface of the substrate which expands in firing
process.   Thus, cracks are formed in the layer of glass powder which is obviously weaker
than the alumina substrate.   The cracks once formed do not disappear on further firing
to higher temperatures since the glass powders begin to crystallize, preventing its
softening.   This is the case for the glass of the composition No. 1 shown in paragraph
IV.4.

The above discussion suggests, in turn, that formation of microcracks in the
thick-film dielectrics should be prevented by choosing the glass which soften before
crystallization in firing process.   This would be the case for the glass of composition
No. 2 shown in paragraph **IV.4,** in which no crack is formed.   By the way, thick-film
dielectrics No. 2 has such characteristics that it is formed by firing glass powder at the
temperature as low as 630°C and, in addition, it has a linear temperature dependence
of dielectric constant up to the temperature as high as 270°C, as shown in Fig. 17.[25]

VI. SUMMARY

To show the general principles required for the preparation of high dielectric
constant ceramics via crystallization of glasses, our works have been reviewed and the
following generalized informations have been obtained.

(1) Glasses rich in components of a given ferroelectric crystalline species can be prepared by rapid cooling of the melt or by appropriate combination of components of inert crystals.

(2) Upon reheating of the glass, the ferroelectric crystals are precipitated. In general, their amount increases as the temperature of heat treatment is raised.

(3) During heating of the glass, various structural changes, such as precipitation or transformation of non-ferroelectric crystals, grain growth and interconnection of the ferroelectric crystal, occur as functions of the temperature of heating. Orientation of crystallites may occur at near the surface of the sample.

(4) Dielectric constant of the crystallized glass is drastically influenced by arrangement (orientation) of non-ferroelectric crystals as well as content, grain size and continuity of the ferroelectric crystal. Cracks, if any, may also affect apparent dielectric constant.

(5) The microstructures as affecting the dielectric constant can be controlled to a great extent by the condition of heat treatment and composition of glass.

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