14. Preparation of Thin Films of BaTiO₃ Glass-Ceramics and Their Dielectric Properties

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1. Introduction

Methods for preparing BaTiO₃ glass-ceramics in the form of plate thicker than one mm or of minute sphere have already been reported by various workers¹⁾. The present article deals with a method for preparing the same glass-ceramics but in the form of film thinner than 100 μ . Dielectric properties and micro-structure of such films are also described.

2. Experimental Data

2.1 Method for Forming Glass into Film

Glasses melted were of the composition corresponding to $(100-x-y)$ BaTiO₃· x Al₂O₃· y SiO₂ in mole percent. The same glasses were already melted by the authors for preparing BaTiO₃ glass-ceramic plates about 2 mm thick¹⁾. The glasses of this series, especially those rich in BaO and TiO₂, are extremely fluid above their liquidus temperatures, and as a result the thickness of glass is likely to become as thin as 1 to 10 μ , if the film is formed by ordinary hand blowing. The films obtained by this method were too fragile for ordinary handling after crystallized.

The most suitable method found by the authors for the efficient preparation of films having enough mechanical strength was to allow the molten glass to pass through between a pair of rotating cast iron drums being in contact with each other. An apparatus used is schematically shown in Fig. 1

(a). About 50 g of the mixed batch was melted in a platinum-10% rhodium crucible placed in an electric furnace with silicon carbide heating elements. As shown in detail in Fig. 1 (b), the crucible was hung on two side-walls of an alumina refractory container by two platinum arms (sign 11) protruding from the outer surface of the crucible. After the glass batch was melted, the crucible was inclined by pulling a platinum wire (sign 12) welded at its end to the bottom of the crucible. The molten glass was thus poured down drop by drop through a hole made in the bottom of the furnace, passed through between the two drums, 180 mm in diameter, which rotate in mutual contact at a speed of 200 rpm, and finally issued in pieces in the form of leaf, about 50 mm² in area and about 50 to 100 μ in thickness. No film less than 50 μ thick was obtained. Although the homogeneity in thickness of each piece of film was found to be much affected by the smoothness of the drum surface, it was not difficult technically to keep the variation of its thickness within $\pm 1 \mu$.

2.2 Crystallization of Glass Films

The glass films thus prepared were laid on a square piece of platinum sheet and heated in the electric furnace with silicon carbide heating elements up to 1100°C at a rate of 5°C per min, then held at 1100°C for one hour followed by natural cooling in the furnace. The crystallized films were strong enough to withstand fairly rough handling.

2.3 Glass Formation Region

Various glasses of the composition corresponding to $(100-x-y)$ BaTiO₃· x Al₂O₃· y SiO₂ in mole per cent were melted at 1550°C and formed into pieces of film by the method described above. The batch materials used were cp-grade barium carbonate, titanium oxide and aluminum hydroxide, and high-grade quartz powder usually used in the manufacture of optical glasses. It was found that some kinds of the films issued from the drums devitrified partially or almost entirely. A solid line in Fig. 2 represents a boundary between two regions, i.e. glass formation and devitrification regions. Such a boundary was already determined by the authors¹⁾ for the compositions of the same

1. Furnace, 2~4. Shutter, 5. Thermocouple, 6. Container for crucible, 7. Platinum-10% rhodium crucible, 8. Drum, 9. Motor, 10. Platinum wire, 11. Platinum arm, 12. Platinum wire

Fig. 1. Apparatus for preparing thin glass films.

Fig. 2. Glass formation area in the system $\text{BaO} \cdot \text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$.

series but in the form of plates about 2 mm thick, which is given by a dotted line in Fig. 2 for comparison. The glass formation region was much broader for the case when the melts were formed into films than formed into thick plates because of higher rate of quenching in the former case.

2.4 Dielectric Properties

2.4.1 Dependence of Dielectric Properties upon Heat-Treatment The glass films about 100 μ thick of the composition, No. 7 in Table 1, were subjected to various heat-treatments. Some of them were heated up to 900°, 1000°, 1100° and 1200°C respectively, at a rate of 5°C/min and after reached to their maximum temperature, allowed to cool outside of the furnace. The others were all heated up to 1100°C at a rate of 5°C/min, maintained at 1100°C for 0, 1, 3, 5 and 20 hrs respectively, and then subjected to natural cooling.

Results of measurements on dielectric properties of the resultant crystallized glasses are shown in Fig. 3 and 4. Measurements of the dielectric constant and loss tangent were made by using a Q-

Fig. 3. Dependence of dielectric properties (at 1 Mc and at room temperature) of glass-ceramics 100 μ thick on heating temperature. Specimen composition; $\text{BaO} \cdot \text{TiO}_2$ 60, Al_2O_3 14, SiO_2 26 mole%

Fig. 4. Dependence of the dielectric properties (at 1 Mc and at room temperature) of glass-ceramics 100 μ thick on heating time at 1100°C. Specimen composition; $\text{BaO} \cdot \text{TiO}_2$ 60, Al_2O_3 14, SiO_2 26 mole%

meter (Type GM-102, Yokogawa Electric Works, Ltd.) at 1 Mc at room temperature. As electrodes, silver paint was applied on the film specimens and dried at 180° to 200°C.

2.4.2 Dependence of Dielectric Properties upon Composition The glass films of the various compositions given in Table 1 were heated up to 1100°C at a rate of 5°C/min, maintained at 1100°C for 5 hrs and then allowed to cool naturally in the furnace. The dielectric properties of the

Table 1. Glass composition.

Specimen No.	Composition (mole%)		
	$\text{BaO} \cdot \text{TiO}_2$	SiO_2	Al_2O_3
1	70.0	15.0	15.0
2	70.0	19.5	10.5
3	70.0	24.0	6.0
4	70.0	30.0	0.0
5	60.0	14.0	26.0
6	60.0	20.0	20.0
7	60.0	26.0	14.0
8	60.0	32.0	8.0
9	60.0	40.0	0.0

Fig. 5. Dielectric properties (at 1 Mc and at room temperature) of glass-ceramics about 100 μ thick in the system $\text{BeO} \cdot \text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$. Heat treatment; Room temp. $\xrightarrow{5^\circ\text{C/min}}$ 1000°C (5 hrs) $\xrightarrow{\text{in furnace}}$ room temp.

films thus crystallized are shown in the compositional triangle of Fig. 5. From the figure it can be seen that the dielectric constant increases with increasing $\text{BaO} \cdot \text{TiO}_2$ content for the specimens with the same mole per cent ratio of Al_2O_3 to SiO_2 , and also it shows the maximum when the mole per cent ratio of Al_2O_3 to SiO_2 is about 35/65 for the specimens with the same $\text{BaO} \cdot \text{TiO}_2$ content.

2.4.3 Dependence of Dielectric Properties on Thickness of Specimens It was already reported by the authors¹⁾ that the crystallized glass of the composition $\text{BaO} \cdot \text{TiO}_2$ 60, Al_2O_3 14 and SiO_2 26 by mole per cent, when formed into the plate about 1 mm thick, shows a dielectric constant of about 500. This value is about twice of that (270) obtained for the same composition (No. 7 in Table 1) in the form of the film 100 μ thick. In order to investigate this discrepancy the relation between the dielectric constant and the thickness of the specimens was examined in more detail for the specimens having the same composition ($\text{BaO} \cdot \text{TiO}_2$ 60, Al_2O_3 14, SiO_2 26 mole%) but of various thickness. For the preparation of the specimens thicker than 100 μ the glass melts were poured on a steel plate and pressed with another piece of steel plate. For the preparation of those thinner than 100 μ the method of squeezing molten glass between two iron drums described above was used. The thickness of the specimens could be varied by changing the rate of rotation of the drums in the range between 20 and 300 rpm. The heat treatment applied was the same as described in the paragraph 2.2.

The results are shown in Fig. 6. It should be noted that the dielectric constant changes abruptly at the thickness of the specimens of about 200 μ .

2.5 Microstructure near the Surface

For reasoning the difference in dielectric constant between thin and thick specimens, microstructure of the two crystallized specimens (No. 7 in Table 1) having the thickness of 100 μ and

Fig. 6. Dielectric properties of glass-ceramics with various thickness.

Specimen composition; $\text{BaO} \cdot \text{TiO}_2$ 60, Al_2O_3 14, SiO_2 26 mole% Heat treatment; Room temp. $\xrightarrow{5^\circ\text{C/min}}$ 1100°C (1 hr) $\xrightarrow{\text{in furnace}}$ room temp.

1500 μ was investigated. For convenience in the following description the thinner specimen will be referred to as the "film" and the thicker one the "plate".

2.5.1 X-Ray Diffraction Analysis First, the "film" and the "plate" were powdered and subjected to X-ray diffraction analysis. In both specimens tetragonal barium titanate (BaTiO_3) and hexacelsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$) were identified. No differences in the position and intensity of their diffraction lines were observed between the both specimens.

Secondly, in order to investigate the microstructure near the surface, the "plate" was successively abraded off in various thickness with Al_2O_3 abrasive powder and, instead of powder form, the specimen was mounted on a holder of X-ray diffractometer. The results of the X-ray analysis made of the surfaces abraded off in various thickness are plotted in Fig. 7. The figure shows that the intensities of the (101), (200) and (111) reflections of barium titanate and also of the (101) and (102) reflections of hexacelsian are almost the same for all of the abraded surfaces irrespective of their depth from the original surface. In marked contrast to these, the intensities of the (001) and (004) reflections of hexacelsian show great changes with the depth of the abraded surface: They are markedly big for the surfaces from the original surface to the depth of 100 μ , but reach to the respective constant values over about 200 μ .

The relative intensity among the three lines for barium titanate and also among the four lines for hexacelsian, for the abraded surface deeper than 200 μ , was found to be the same, respectively, as those determined for the powdered "plate" specimens described above.

Changes in intensities of the X-ray diffraction lines with the depth were not investigated for the

Fig. 7. Changes in intensities of X-ray diffraction line obtained for the planes of various depth from the original surface of the specimen.

Specimen composition; $\text{BaO} \cdot \text{TiO}_2$ 60, Al_2O_3 14, SiO_2 26 mole%

"film" specimens because of the technical difficulty of their successive abrasion, but the X-ray diffraction chart obtained only for the original surface of the "film" was the same as that of the "plate".

2.5.2 Observation with Metalurgical Microscope

Fig. 8 is a micrograph taken with a reflected light of a polished cross-section of a piece of "plate". A rim of about 200μ in width appears to have a different texture from that of the interior. Such a rim, however, was not always observed on all of the cross-sections, even when the presence of a rim with peculiar structure was indicated by the X-ray diffraction analysis described above. This means that the observation with the metalurgical microscope is not a sure means to confirm the presence of a special microstructure near the surface of the "plate", but a simple and useful method for the morphological investigation of the microstructure, if it could be observed under the microscope.

Fig. 8. Cross section of glass-ceramics (BaO·TiO₂ 60, Al₂O₃ 14, SiO₂ 26 mole%).

2.5.3 Observation with Electron Microscope

Electron microscopic examination was made of the original surfaces of the "plate" and the "film" and also the surface of the former abraded off by 40μ and 400μ in depth from their original surfaces. All of the surfaces were etched by immersing in 5% NaOH at 50°C for 75 min and their chromium-shadowed carbon replicas were prepared.

Fig. 9 (a) through 9 (d) are the electronmicrographs of their respective surfaces. No difference is found in appearance between Fig. 9 (a) and Fig. 9 (b). The photographs are, however, both obscure, probably as a result of the mask of their surface with a thin glass layer which is frequently observed on the original surface of usual glass-ceramics. In Fig. 9 (c) two kinds of crystal particles, i.e. spherical particles of 0.2 to 0.7μ in diameter and acicular particles of 0.05 to 0.5μ in width and 0.5 to 3μ in length, are observed. From their crystal habits majority of the spherical ones appears to be barium titanate and the acicular ones hexacelsian with an orientation parallel to the surface of the specimen. No essential difference is found in appearance between Fig. 9 (c) and

- (a) The original surface of the plate 1.5 mm thick.
- (b) The original surface of the film 100μ thick.
- (c) The surface of the plate abraded off by 40μ from the original surface.
- (d) The surface of the plate abraded off by 400μ from the original surface.

Fig. 9. Electronmicrographs of glass-ceramics (BaO·TiO₂ 60, Al₂O₃ 14, SiO₂ 26 mole%).

Fig. 9 (d), but the number of the crystals with acicular morphology appears to be larger for Fig. 9 (c) than Fig. 9 (d).

3. Discussion

Decrease in dielectric constant with decreasing thickness of the specimens is an adverse effect, especially when the BaTiO₃ glass-ceramics are used as capacitors in the electric circuit.

In general, the dielectric constant of the polyphase material containing ferroelectric material is determined by the kind, size, volume fraction and arrangement of the constituent phases. The results of the X-ray diffraction analysis made for the powdered specimens indicated that there is no difference in position and intensity of all the diffraction lines between the "film" and "plate". This means that in both specimens the kinds of crystals separated out and also their respective amounts are the same. No difference was indicated in the size of the crystals separated out by the electron microscopic examination between the original surfaces of the "plate" and "film".

The factor remained as the one affecting the dielectric constant of this polyphase material is therefore the arrangement of the constituent crystals. In relation to this a characteristic feature was confirmed by the X-ray diffraction analyses for the "plate" specimen: It is the marked increase in intensities of the (001) and (004) reflections, being accompanied with slight decrease in those of the (101) and (102) reflections, of hexacelsian precipitating near its original surface. This can be interpreted as a result of preferred

orientation of the hexacelsian. Generally, hexacelsians are likely to separate out as lath-like crystals with cleavage parallel to their (001) plane³⁾. Near the surface of the “plate” specimens hexacelsian probably appear in such a manner that their cleavage planes are parallel to the surface of the specimens. The crystals with the acicular morphology observed with electronmicroscope very near the original surface of the “plate” specimens (Fig. 9 (c)) would thus be the hexacelsian having such a preferred orientation. In the interior of the “plate” specimens, i.e. the portion deeper than 200 μ , hexacelsian would distribute rather at random without preferred orientation. This will be proved by the fact that the relative intensity of the X-ray diffraction lines of hexacelsian present in the portion deeper than 200 μ becomes equivalent to those of the powdered specimen. This is also supported by the difference in number of the acicular crystals between the two portions near and far apart from the original surface observed by the electronmicroscopic technique.

The dielectric constant of hexacelsian itself would be by far the lower than those of the mixture of barium titanate and their surrounding glass matrix. Thus the portion near the surface of the “plate” is considered to have a structure in which high capacitive elements consisting of barium titanate and the glass matrix, and low capacitive elements consisting of hexacelsian with a preferred orientation are connected in series. Consequently the dielectric constant of this surface layer would be much lower than that of the interior in which the hexacelsian are precipitated without preferred orientation³⁾.

When the thickness of the specimen is big, an effect of the surface layer with low capacity is insignificant on the apparent dielectric constant of the whole specimen, but with decreasing the thick-

ness, especially when it reaches to about 200 μ , the effect would be strong enough to cause a sudden decrease in dielectric constant of the specimen.

Orientation of the hexacelsian in the “film” specimens was unfortunately unable to be confirmed because of the experimental difficulties. It seems, however, to be natural to consider that the “film” specimen has the similar structure to that of portion near the original surface of the “plate” specimen having the hexacelsian with a preferred orientation.

The lower value in dielectric constant of the “film” than that of the “plate” would thus be explained.

4. Summary

1. Glass-ceramic films of 50 to 100 μ in thickness having dielectric constant of 500 and $\tan \delta$ of 0.03 (at 10⁶c/s) at the maximum conditions were prepared from glasses of the system BaO·TiO₂-Al₂O₃-SiO₂ by a method which comprises squeezing the glass melts by the two drums of solid cast iron rotating in mutual contact and subjecting the produced glass films to heat-treatments.

2. It was found that the dielectric constant of the glass-ceramics of this type is reduced to a half of that of their bulk when formed into a film thinner than about 200 μ . Its cause was attributed to a preferred orientation of hexacelsian precipitated near the surface of the specimens.

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チタン酸バリウムを含有する薄板状結晶化

ガラスの製造と、その誘電的性質

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薄板状の高誘電率材料を得ることを目的とした、BaO および TiO₂ を多量に含むガラスの結晶化に関する研究はすでに二、三報告されている。しかし、実際に薄板状の結晶化ガラスを作り、その誘電的性質について調べた結果はまだ報告されていない。本研究では、BaO·TiO₂-Al₂O₃-SiO₂ 系のガラスについて、厚さ 100 μ 以下の薄板状結晶化ガラスを作る方法を検討し、また得られた結

晶化ガラスの誘電的性質および微細構造などについて調べた。

得られた結果は次の通りである。

1. ガラス融液の入った坩堝を、底に穴をあけた炉内で逆転し、炉の下に流れ落ちる融液を相接する鉄製ローラーの間を通して成形することにより、50~100 μ 厚の薄板状ガラスを作ることができた。また同ガラスを再加

熱することにより、亀裂やしわのない、機械的にもかなり強い結晶化物を得ることができた。

2. 薄板状結晶化ガラスの誘電率はガラス組成中の $\text{BaO} \cdot \text{TiO}_2$ 含有量が多いほど大きく、また $\text{BaO} \cdot \text{TiO}_2$ 含有量が一定の時には、 Al_2O_3 と SiO_2 の比が約 35/65 (モル比) 付近で最大となった。この実験で誘電率の最高が 475, その $\tan \delta$ が 300×10^{-4} (周波数 1 Mc) の

ものが得られた。

3. これらの結晶化ガラスの誘電率は試料の厚さが薄くなるに従い小さくなり、特に約 200μ 以下の厚さの時には急に小さくなることを見出した。結晶化ガラスの微細構造を調べた結果、試料の厚さによる誘電率の変化は、試料表面付近のヘキサセルシアン配向が大きな原因となっていると考えられた。 (8/7/1967 受付)

ソーダ珪酸ガラス中の沃度の光反応*

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13. Photochemistry of NaI Doped Sodiumsilicate Glasses

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There have been very extensive studies on the photochemistry of transition elements in various glasses by many authors, but very few, of non-metallic anions dissolved in glasses. Therefore, the photochemistry of NaI containing sodiumsilicate glasses was investigated by the writers. The reason the writers took NaI as the reagent was that the photochemistry of iodine in some solvents and its electronic state had been fairly well known. The samples used in this study are shown in Table 1. The increases of absorption spectra after X- and UV irradiation, photo and thermal fading of their induced absorption were studied.

The increases of optical absorption in UV or X-ray irradiated glasses are shown in Fig. 1 and 2. Fig. 3 shows, how the induced absorption in the same glass after UV irradiation is affected by water.

Photo and thermal fading of these induced absorption bands are shown in Fig. 4~8.

As the result of examining of such absorption changes, it became clear that the induced absorption bands after X- or UV irradiation were $250 \sim 270 \text{ m}\mu$, $290 \text{ m}\mu$, $350 \text{ m}\mu$, $380 \text{ m}\mu$, and $715 \text{ m}\mu$ and in the case of dilute NaI containing glasses, moreover some weak end color centers of sodium silicate glasses in itself were overlapped on these induced bands, namely, iodine ion has a suppression effect on the growth of glass color centers by X-ray or UV irradiation.

Conversely $570 \text{ m}\mu$ band (electron trapping center in reduced $\text{Na}_2\text{O}-3\text{SiO}_2$ glass) was strengthened by photochemistry of NaI as shown in Fig. 12, but was very unstable.

Considering on the above results, the photochemistry of NaI containing glass is the photo-oxidation of I^- in the glass.

Assignments of induced bands after the irradiation are as follows; $250 \sim 270 \text{ m}\mu$ band depends on a electron trapping center in glass matrix, 290 , $350 \text{ m}\mu$ and 380 , $715 \text{ m}\mu$ depend upon I_3^- and I_2^- respectively.

The more basic is the glass, the absorptions of I_3^- and I_2^- are the more unstable, and moreover they causes thermal fading at the lower temperature. [Received Aug. 10, 1967]

1. 緒 言

ガラスを一種の固相溶媒と考えたとき、その中に溶解

された第三成分の光反応は、その物質が気相または、液体溶媒中で生ずる光反応機構とは著しく異なり、あるいは気、液相では予想し得ない生成系を生ずる場合がある。

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