Microstructure and Properties of Fused-Cast NaNbO₃-BaTiO₃ Ceramics

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A fusion cast method was applied to fabricating dense polycrystalline ferroelectric NaNbO₃-BaTiO₃ ceramics which are difficult to densify by the conventional sintering method. By casting the melt of the composition $0.7\text{NaNbO}_3 \cdot 0.3\text{BaTiO}_3$ previously heated at 1500°C into a cylindrical graphite mold held at 500°C and subsequently cooling it in a laboratory atmosphere, a dense ceramic composed mainly of columnar crystals except for near the center of the mold was obtained. The crystals precipitated were the perovskite-type NaNbO₃-BaTiO₃ solid solution and their (111) or (211) planes were orientated parallel to the inner surface of the mold. Porosity and dielectric constant of the fused-cast ceramic were 3.6% and 2900, whereas those of the sintered ceramic of the same composition were 24.7% and 2200, respectively. Addition of the SiO₂ in amount of 0.03 mol ratio to the base composition of the fused-cast ceramic was found to be strongly effective in decreasing its porosity to 1.0%, without producing the appreciable detrimental effect on its dielectric constant.

I. INTRODUCTION

The conventional method for fabricating ferroelectric ceramics is to sinter cold–pressed powder compacts of their raw materials in an ambient atmosphere. To obtain highly densified ceramics, some other methods such as hot-pressing,[1] atmosphere sintering[2] or glass-ceramics[3] methods are used. These improved methods are especially useful for the powder compacts which are difficult to sinter. The hot-pressing or atmosphere sintering method, however, necessitates the use of costly apparatuses and/or the strictly controlled fabricating conditions. For the glass–ceramics method, addition of glass-forming oxides such as SiO₂ and Al₂O₃ in fairly large amount to the ferroelectric base materials is usually necessary, which is detrimental for obtaining the ceramics with high dielectric constant.

The present article describes an attempt to fabricate densified polycrystalline ferroelectric ceramics by a fusion cast method; *i.e.* the method of direct solidification of melts in a mold. The ceramics of the system NaNbO₃-BaTiO₃ ,which are difficult to sinter by the conventional sintering method,[4] have been chosen as the test material. The fusion cast method has already widely been applied to fabrication of many metals and some refractory ceramics such as Al₂O₃-MgO[5] and Al₂O₃-ZrO₂[5] *etc.*, but not to that of ferroelectric polycrystalline materials with fine microstructure.

II. EXPERIMENTAL

1. Phase Diagram

The phase diagram of the system NaNbO₃-BaTiO₃, which is represented by the

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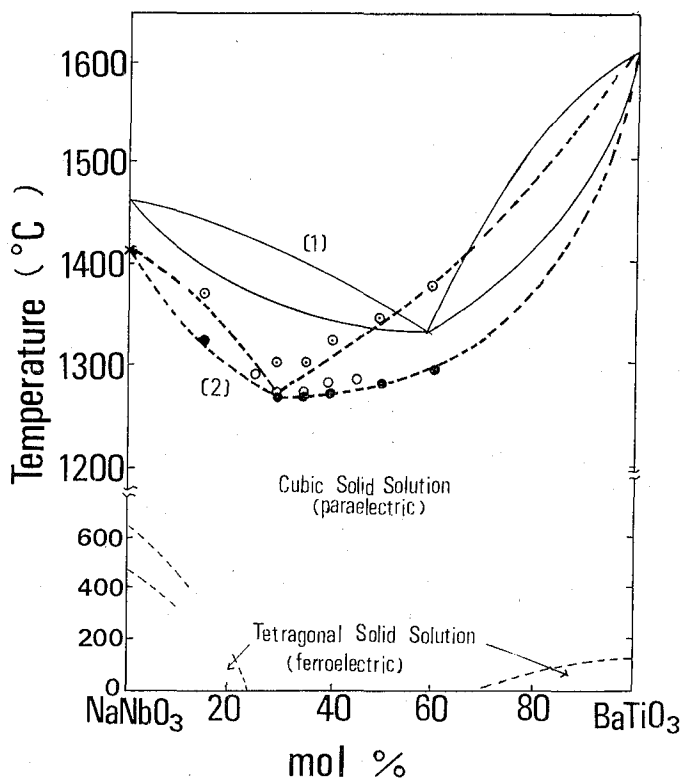
Fig. 1. Phase diagram of the system NaNbO₃-BaTiO₃.
  (1): after Roy *et al.* (1953)
  (2): present experiment
      ⊙: liquidus temperature determined by DTA
      ●: solidus temperature determined by DTA
      ○: solidus temperature determined by high temperature
         optical microscope
      ×: after Roy *et al.* (1959)

curves (1) in Fig. 1, was early reported by Roy *et al.*[6] In this system a continuous series of perovskite-type solid solutions is present over the entire composition range. The temperature of transition from a paraelectric phase to a ferroelectric phase varies with varying compositions.

The accuracy of measurement of the liquidus and solidus temperatures shown by the curves (1) is, however, dubious, since the melting temperature of the $NaNbO_3$ reported afterwards[7] by the same authors differed appreciably from that reported earlier. The present authors, therefore, reexamined the liquidus and solidus temperatures by differential thermal analyses and also by the observation with a high temperature optical microscope.

Batch mixtures yielding composition of various $NaNbO_3$-$BaTiO_3$ mol ratios were prepared from reagent grade chemicals of Na_2CO_3, Nb_2O_5, $BaCO_3$, and TiO_2. About 10 g of the batches were pressed into a disc 40 mm in diameter under 2000 Kg/cm², heated in a SiC furnace at 1100°C for 90 min, crushed to −150 mesh, pressed again into the disc under the same pressure and reheated at 1200°C for 90 min, for

completion of the solid state reaction of the batches. A small portion of the resultant specimen was crushed to −150 mesh and subjected to the DTA. The DTA was made at a heating rate of 2°C/min. Powdered α-Al$_2$O$_3$ was used as a reference. The temperatures at the start and the end of an endothermal peak were taken as the solidus and liquidus temperatures, respectively. To confirm the solidus temperature, the other small portions of the specimens were observed under the high temperature optical microscope during heating and the temperature at which any liquid phase began to appear was determined. The liquidus and solidus temperatures thus determined are plotted in Fig. 1. The dotted lines (2) are respectively the liquidus and solidus lines estimated from these data.

2. Fusion Casting

Batch mixtures yielding composition with various NaNbO$_3$/BaTiO$_3$ mol ratios

Table I. Composition of Melt (mol ratio)

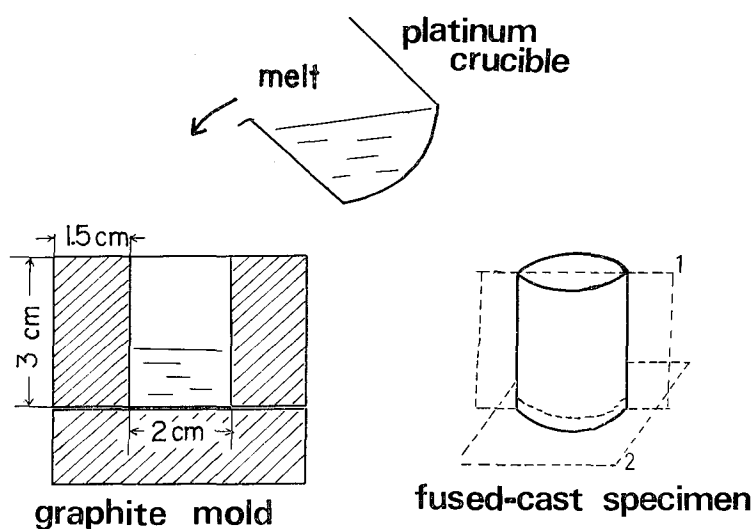| No.	NaNbO$_3$	BaTiO$_3$	SiO$_2$	AlO$_{1.5}$	BO$_{1.5}$
1	1.00				
2	0.85	0.15			
3	0.70	0.30			
4	0.60	0.40			
5	0.50	0.50			
6	0.40	0.60			
7	0.30	0.70			
8	0.70	0.30	0.03		
9	0.70	0.30		0.03	
10	0.70	0.30			0.03
11	0.70	0.30	0.06		

Fig. 2. Graphite mold used and fused-cast specimen.

and those with some additives were prepared from reagent grade chemicals of Na_2CO_3, Nb_2O_5, $BaCO_3$, TiO_2, SiO_2, $Al(OH)_3$, and B_2O_3. Their oxide compositions are given in Table I. About 40 g of the batches were melted in a 50 ml platinum crucible in a SiC furnace at 1400°–1500°C for 30 min. The melts were poured into a graphite mold in a form of a cylinder shown in Fig. 2. The fused-cast bodies were cut perpendicularly to the base of the cylindrical specimens at the center of the base or parallel to the base at a distance of 2 mm from the base, as shown in Fig. 2. Their exposed faces, after polished, were observed with the naked eye and an optical microscope. The kind of crystalline phases precipitated in the fused-cast bodies and their orientation were analyzed by the X-ray diffraction method.

2.1. Microstructure of Fused-Cast Ceramics

2.1.1. Effects of Mold Temperature

The melt with the composition of $0.7NaNbO_3 \cdot 0.3BaTiO_3$ (No. 3) obtained by heating at 1500°C for 30 min were poured into two molds, one held at room temperature and another at 500°C, and then the both molds were allowed to cool in a laboratory atmosphere. The photographs of their cross sections both perpendicular to their bases are shown in Fig. 3. As can be seen from the photographs, the specimen cast into the mold previously heated at 500°C has a fairly dense structure except for its central region constituting of large pores; columnar crystals about 200 μ in diameter grew perpendicular to the inner surface of the mold densely and regularly. On the other hand, the specimen cast into the mold previously held at room temperature has a rather porous structure.
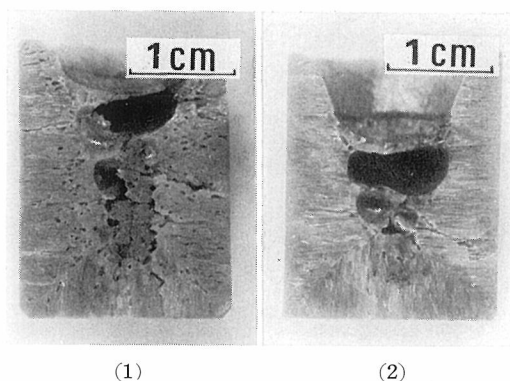

Fig. 3. Effect of temperature of mold.
(Composition: $0.7NaNbO_3 \cdot 0.3BaTiO_3$
Melting temperature: 1500°C)
(1): mold temperature 20°C
(2): mold temperature 500°C

2.1.2. Effects of Melting Temperature

Melts No. 3 heated at 1400°C and 1500°C, respectively, for 30 min were poured into the mold previously held at 500°C and then allowed to cool in a laboratory atmosphere. The photographs of the cross sections perpendicular to the bases of the

cylindrical specimens are shown in Fig. 4 for the two specimens. As can be seen from the photographs, the specimen cast from 1500°C has, except for its central region, a much more dense and regular texture than that cast from 1400°C.
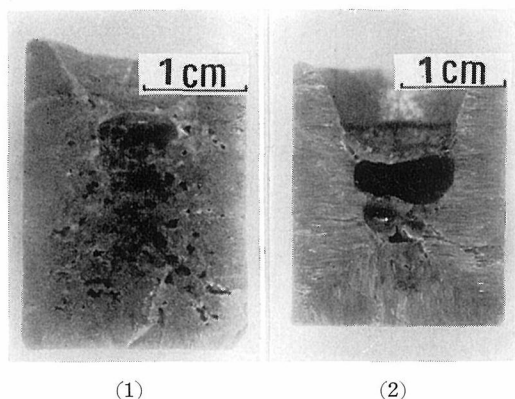

(1)   (2)

Fig. 4.   Effect of temperature of melt.
(Composition: 0.7NaNbO$_3$·0.3BaTiO$_3$.
Mold temperature: 500°C)
(1): melting temperature 1400°C
(2): melting temperature 1500°C

2.1.3. Effects of NaNbO$_3$/BaTiO$_3$ Mol Ratio

Batch mixtures yielding compositions 1 to 7 given in Table I were melted at 1500°C for 30 min, poured into the mold heated at 500°C and then cooled in a laboratory atmosphere.   The photographs of the cross sections perpendicular to the bases of the cylindrical specimens are shown in Fig. 5.   Figure 6 shows microphotographs of the cross sections parallel to the bases of the specimens.   As can be seen from these photographs the fused-cast specimens with NaNbO$_3$/BaTiO$_3$ mol ratios larger than 7/3, the congruently melting composition, have fairly dense textures composed mainly of unidirectionally oriented columnar crystals, whereas those with NaNbO$_3$/BaTiO$_3$ mol ratios less than 6/4 have rather porous textures.

The X-ray diffraction analyses revealed that the fused-cast specimens with NaNbO$_3$/BaTiO$_3$ mol ratios larger than 7/3 precipitated only one kind of perovskite-type crystals with lattice constants almost the same with those of the crystals obtained by sintering the corresponding compositions at 1225°C.   Whereas those with NaNbO$_3$/BaTiO$_3$ mol ratios less than 6/4 precipitated two kinds of perovskite-type crystals, which could not be obtained by sintering the corresponding compositions.   Furthermore, the X-ray diffraction analyses revealed that the columnar crystals precipitated from the melts with NaNbO$_3$/BaTiO$_3$ mol ratios larger than 7/3 grew regularly so that their (111) or (211) planes were oriented parallel to the surface of the mold.

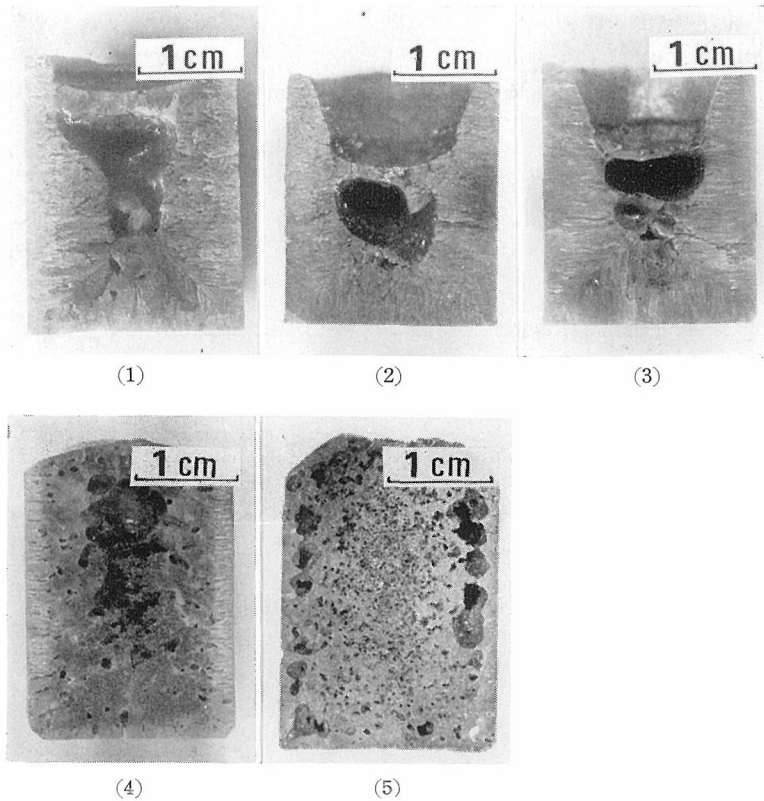Fig. 5 Effect of composition of melt.
(1): NaNbO$_3$ (2): 0.85NaNbO$_3\cdot$0.15BaTiO$_3$ (3): 0.70NaNbO$_3\cdot$0.30BaTiO$_3$
(4): 0.60NaNbO$_3\cdot$0.40BaTiO$_3$ (5): 0.40NaNbO$_3\cdot$0.60BaTiO$_3$

2.1.4. Effects of Additives

Batch mixtures yielding compositions of 0.7NaNbO$_3\cdot$0.3BaTiO$_3$ (No. 3) with addition of SiO$_2$, AlO$_{1.5}$, or BO$_{1.5}$ in 0.03 mol ratio were melted at 1500°C for 30 min, poured into the mold previously heated at 500°C, and then cooled in a laboratory atmosphere. The cross sections of the specimens cut perpendicular to their bases are shown in Fig. 7. Addition of the SiO$_2$ gave a more dense texture to the cast bodies especially at their outer region whereas addition of the AlO$_{1.5}$ or BO$_{1.5}$ gave textures with many cracks or pores. When the amount of the SiO$_2$ added was increased up to 0.06 mol ratio, the texture of the fused-cast specimens varied as seen in Figs. 8 and 9; the former shows photographs of the cross sections perpendicular to their bases and the latter shows the microphotographs of the cross sections parallel to their bases. It can be seen from these photographs that both the total volume of the pores at the grain boundaries and the size of the crystal grains decrease with increasing SiO$_2$.

The X-ray diffraction analyses of these specimens revealed that the fused-cast specimens with addition of the SiO$_2$ precipitated only one kind of the perovskite–
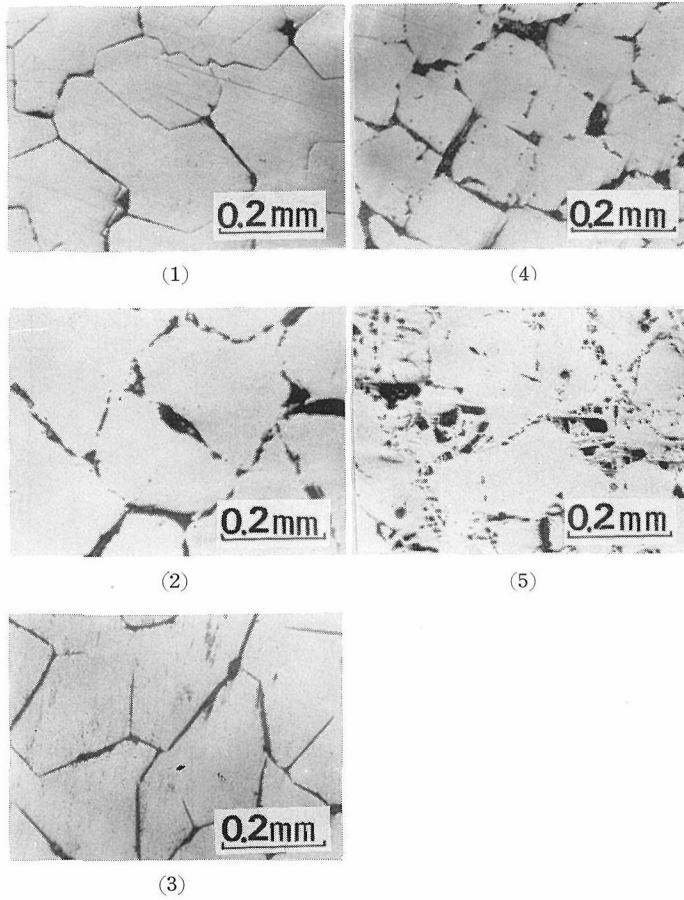
Fig. 6. Microphotographs of fused-cast specimens.
(1): NaNbO$_3$ (2): 0.85NaNbO$_3 \cdot$0.15BaTiO$_3$
(3): 0.70NaNbO$_3 \cdot$0.30BaTiO$_3$ (4): 0.60NaNbO$_3 \cdot$0.40BaTiO$_3$
(5): 0.40NaNbO$_3 \cdot$0.60BaTiO$_3$
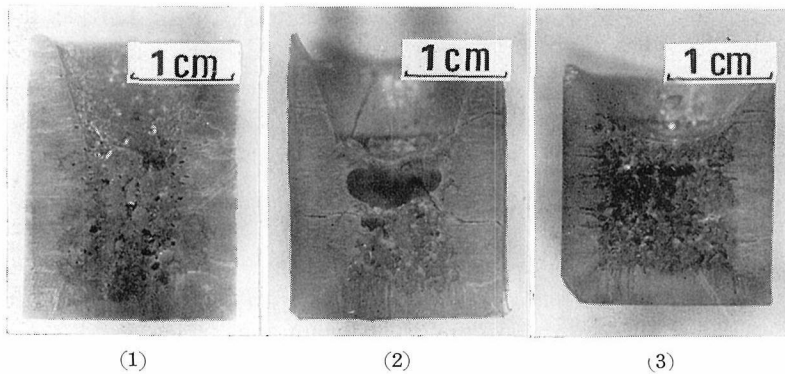

Fig. 7. Effect of addition of the third components.
(Base composition: 0.7NaNbO$_3 \cdot$0.3BaTiO$_3$)
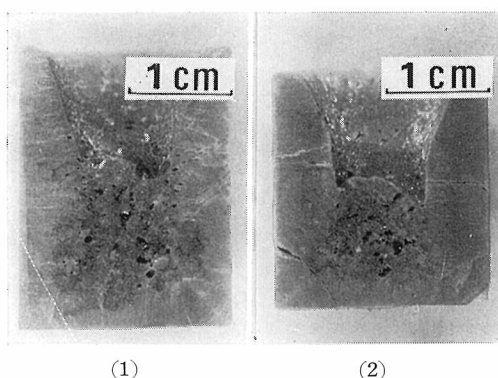(1): 0.03SiO$_2$ (2): 0.03AlO$_{1.5}$ (3): 0.03BO$_{1.5}$

Fig. 8. Effect of SiO$_2$ addition.
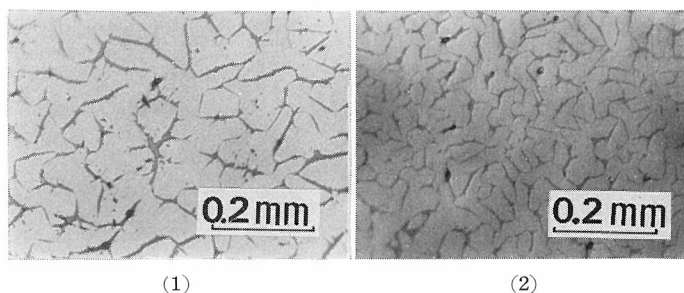(Base composition: 0.7NaNbO$_3$·0.3BaTiO$_3$)
(1): 0.03SiO$_2$ (2): 0.06SiO$_2$

Fig. 9. Microphotographs of fused-cast specimens added with SiO$_2$.
(Base composition: 0.7NaNbO$_3$·0.3BaTiO$_3$)
(1): 0.03SiO$_2$ (2): 0.06SiO$_2$

type crystals and their orientation was similar to that of the crystals precipitated from the base composition without the SiO$_2$.

2.2. Properties of Fused-Cast Ceramics

The fused-cast specimen with composition of 0.7NaNbO$_3$·0.3BaTiO$_3$ (No. 3) and that with addition of the SiO$_2$ in 0.03 mol ratio (No. 8) prepared by the methods described in **2.1.3** and **2.1.4** were cut parallel to their bases at the distances of 2 mm and 4 mm from their bases.   Porosity and dielectric properties of the disc specimens thus prepared were compared with those of the sintered specimens of the corresponding compositions.   The preparation of the sintered specimens was composed of cold–pressing the batch mixtures into discs 40 mm in diameter and 2 mm thick, under 2000 kg/cm^2, heating at 1100°C for 90 min, crushing to –150 mesh, pressing again into discs under the same condition, and reheating at 1225°C for 5 hr.   Their bulk densities were measured by the Archimedean technique.   Their porosities were obtained from their bulk densities and their true densities calculated from the lattice constants of the crystals determined by the X-ray diffraction.   In the calculation of their true densities, the SiO$_2$ added was assumed to be present as SiO$_2$ glass in the

fused-cast specimens, whereas as α-quartz crystal in the sintered specimens. Their values are listed in Table II. It can be seen from Table II that the porosities of the fused-cast specimens are appreciably lower than that of the sintered specimens and that even the small addition of the SiO_2 is strongly effective in lowering their porosities.

Table II. Porosity and Dielectric Properties of Fused-Cast and Sintered Ceramics

Composition (mol ratio)	True density (g/cm³)	Bulk density (g/cm³)	Porosity (%)	dielectric constant ε	tan δ
Fused ceramic					
0.7NaNbO₃·0.3BaTiO₃	4.90	4.73	3.6	2900	0.019
+0.03SiO₂	4.84	4.79	1.0	2800	0.013
+0.06SiO₂	4.79	4.75	0.8	2100	0.013
Sintered ceramics					
0.7NaNbO₃·0.3BaTiO₃	4.90	3.93	24.7	2200	0.010
+0.03SiO₂	4.86	4.34	12.9	2300	0.017
+0.06SiO₂	4.82	4.12	17.0	1900	0.020

The as-fused-cast disc specimens were blue-black and semiconductive. Annealing at 700°–1000°C for 5 hr was found to be effective in changing their color to white–yellow and in increasing their electric resistivities. In Table II are given dielectric properties of the annealed specimens measured at a frequency of 10^6 Hz at room temperature with a Q-meter. For these measurement silver paste was applied on both sides of the disc specimens. As can be seen from Table II the fused-cast specimens have higher dielectric constants than the sintered specimens of the corresponding compositions. Addition of the SiO_2 does not have any beneficial effect on their dielectric properties.

III. DISCUSSION

1. Microstructure of Fused-Cast Ceramics

The experimental results described above indicated that the higher the temperature from which the melts were cast and the higher the temperature of the mold into which the melts were cast, the denser ceramics composed of columnar crystals could be obtained, whereas casting melts from lower temperatures into the mold of lower temperatures produced porous ceramics. The reason is interpreted as follows.

After a melt was cast into a mold, the melt is cooled near the mold wall faster than at the central part of the mold, since heat is removed mainly from the wall. Accordingly, crystal nucleation initiates from the mold wall. If the temperature at the central part of the mold is sufficiently high, the crystals grow gradually from the wall towards the central part during cooling, forming dense columnar crystals orientated regularly perpendicular to the inner surface of the mold. However, when the temperature of the central part of the mold is not so high, crystal nucleation and growth are likely to start from everywhere even near the central part of the mold, leaving many small pores distributed widely. Casting of the melt of higher

temperatures into the mold of higher temperatures keeps the temperature of the central part of the mold sufficiently high, to allow the columnar crystals to grow slowly from the surface of the mold, resulting in the formation of dense crystal aggregates.

The melts with lower $NaNbO_3/BaTiO_3$ mol ratio did not form dense ceramics, even when cast from higher temperature. This would be due to the extraordinary high nucleation rate of the metastable crystals whose precipitation was confirmed in the melts of the compositions, even at the fairly high temperature of the central part of the mold.

It should be noted that the melts with higher $NaNbO_3/BaTiO_3$ mol ratios produced dense ceramics composed of many crystals all having nearly equal lattice constants even when the melts had incongruently melting compositions. This is probably due to the two facts; small gaps between the liquidus and solidus temperatures of their compositions and fairly rapid cooling rates of their melts.

2. Dielectric Properties of Fused-Cast Ceramics

Generally, the dielectric constant of ceramics, in which spherical pores are dispersed in a continuous crystalline phase, is given by the formula[8]

$$1-\delta_1 = (\varepsilon_1-\varepsilon)(\varepsilon_2/\varepsilon)^{1/3}/(\varepsilon_1-\varepsilon_2)$$

where δ_1 is the volume fraction of the pores, and ε, ε_1, and ε_2 are the dielectric constants of the ceramic, pores ($=1$) and constituent crystals, respectively. If the data for the sintered specimen of the composition $0.7NaNbO_3 \cdot 0.3BaTiO_3$ given in Table II ($\varepsilon=2200$, $\delta_1=0.247$) are put in this formula one can estimate the dielectric constant of the constituent crystals in the sintered specimen, $\varepsilon_2=3250$. On the other hand, the volume fraction of the pore in the fused-cast specimen of the same composition was determined to be 0.036. If this value and the value of ε_2 estimated above are put into the above formula, one obtains $\varepsilon=3050$. This calculated value is nearly equal to the measured value of the dielectric constant of the fused-cast ceramic $\varepsilon=2900$, given in Table II. This agreement, although approximate, indicates that the higher dielectric constant of the fused-cast ceramic than that of the sintered one is mainly attributed to the extremely low value of porosity of the fused-cast ceramic. The small difference between the calculated and measured dielectric constants may be due to the difference in orientation between the crystals precipitated in the sintered and fused ceramics; in the former the constituent crystals were randomly orientated, whereas in the latter the crystals were preferentially orientated so that their (111) or (211) planes were parallel to the base of the cylindrical specimen, to which the electric field was applied perpendicular.

IV. SUMMARY

1. By casting the melt of the composition $0.7NaNbO_3 \cdot 0.3BaTiO_3$ previously heated up to 1500°C, into a graphite mold held at 500°C, and subsequent cooling the mold in a laboratory atmosphere, a dense ceramic mainly composed of columnar crystals

orientated perpendicular to the inner surface of the mold wall could be obtained.

2.   The fused-cast ceramic had a much lower porosity and higher dielectric constant than the sintered ceramic of the same composition; 3.6% and 2900 for the former whereas 24.7% and 2200 for the latter.

3.   Addition of the SiO$_2$ in an amount of 0.03 mol ratio to the base composition of the fused-cast ceramic was found to be strongly effective to decrease its porosity without producing appreciable detrimental effect on its dielectric constant.

ACKNOWLEDGMENT

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