PbTiO₃–PbO–B₂O₃ Glass-Ceramic Thin Films by a Sol-Gel Process

Kunio SAEGUSA

Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd., 6, Kitahara, Tsukuba-shi, Ibaraki 300-32

ゾル-ゲル法による PbTiO₃–PbO–B₂O₃ ガラスセラミックス薄膜の作製

三枝邦夫

住友化学工業(株)筑波研究所, 300-32 つくば市北原 6

PbTiO₃ (PT)–PbO–B₂O₃ ferroelectric glass-ceramic thin films were produced by a sol-gel process. A pin-hole free thin film was obtained when it was prepared in a way that small PT crystals developed in a glass matrix using the RTA technique. The achievement of high PT content (>50 mol%) at levels unattainable by the conventional glass-ceramics preparation methods was semiquantitatively shown. PT crystallized at a temperature below 500°C. The dielectric properties of the 0.6PT–0.4(PbO·B₂O₃) film fired at 600°C were $\epsilon=143$, and $\tan \delta=0.04$.

[Received April 9, 1996; Accepted July 17, 1996]

Key-words : Glass-ceramics, Sol-gel, PbTiO₃, Thin film

1. Introduction

Ferroelectric thin films have been widely investigated for their potential application in capacitor and LSI technology. The sol-gel method is a well-known technique for preparing these thin films.^{1)–9)} These films, however, often have defects that cause short-circuits,^{8),9)} making some applications difficult. Glass-ceramic material may be used to solve this problem because of its vitreous and pore-free nature. Numerous ferroelectric glass-ceramic studies in bulk materials have appeared regarding the production and properties of these materials.^{10)–19)} The ferroelectric crystalline phase in studied materials have included PZT,¹⁰⁾ PbTiO₃,^{11)–17)} BaTiO₃,^{18),19)} for example. Although a high crystalline phase content is desirable for the higher dielectric constant, this content is quite limited using the conventional glass-ceramic technique employed in previous reports. The efficiency of TiO₂ and ZrO₂ in promoting nucleation leads to devitrification when the ferroelectric phase exceeds a small fraction (Fig. 1), a fraction too small for practical applications. Forming a thin film by glass-ceramics has also been difficult.

The purpose of high temperature melting in the conventional process is to achieve a homogeneous amorphous mixture of components. An alternative method for achieving such a molecular level mixture without high temperature melting could allow glass-ceramic production while suppressing devitrification. Furthermore, the range of glass-

ceramic compositions, currently limited by the difficulty of glass-formation, would be expanded. This paper describes a technique for preparing such a mixture and converting it to a PbTiO₃ glass-ceramic thin film. Starting materials were mixed to form a homogeneous solution, which was spin-cast on a substrate, then dried to a gel film. This gel film was further converted to a glass-ceramic thin film by heating at a temperature adequate for crystallization. Using this approach initially for the preparation of PT–PbO–B₂O₃ glass-ceramic thin film, it has been possible to achieve a pin-hole free, high dielectric constant thin film.

2. Experimental procedure

2.1 Preparation of the solution

The PT precursor stock solution was prepared basically according to standard methods.¹⁶⁾ One mol of lead (II) acetate trihydrate (99.9%, Wako Pure Chemicals Ind. Co., Osaka, Japan) was dissolved into 8 mol of 2-methoxyethanol (GR grade, Wako Pure Chemicals Ind. Co.) in a four-necked flask under an N₂ atmosphere and then distilled at 150°C for 2h. This distillation was repeated three times, and the lead concentration was adjusted to 1 mol/kg (Pb stock solution). One mole of titanium tetraisopropoxide (Wako Pure Chemicals Ind. Co.) was distilled with 2-methoxyethanol in a similar manner as the Pb stock solution, and the Ti concentration was adjusted to 1.5 mol/kg (Ti stock solution). Two moles of boric acid was distilled with 2-methoxyethanol in a similar manner as the Pb stock solution, and the B concentration was adjusted to 4 mol/kg (B stock solution). The Pb stock solution (0.45 mol) was mixed with an equimolar amount of Ti precursor stock solution, and the mixture was distilled until no distillate was observed. The concentration of this solution was adjusted to 1 mol/kg with respect to Pb (PT stock solution).

To achieve partial hydrolysis, H₂O was added with nitric acid to the PT stock solution, which was stirred at 80°C with an [H₂O]/[Ti] ratio of 1.3. After maturing, the solution was adjusted to 0.65 M with respect to Pb by reduced-pressure distillation at 80°C. The Pb and B stock solutions were mixed at 80°C for 2h to prepare the Pb–B solution (PbO·B₂O₃, 2PbO·B₂O₃, 7PbO·B₂O₃). This Pb–B solution was mixed with the PT stock solution in the proportion shown in Table 1 to form the PbO–TiO₂–B₂O₃ solution.

The solution was then spin-coated on Pt(500 nm)/Ti(50 nm)/SiO₂(400 nm)/Si(100) wafer substrate at 2000 rpm and baked at 300–500°C. This procedure was repeated

Fig. 1. Composition studied in PbO–TiO₂–B₂O₃ system. Previous work (□ Glass, ■ Devitrification), this work (○).

Table 1. Crystallization Behavior of Various PbO-TiO₂-B₂O₃ Compositions

Sample Number	PbO /mol%	B ₂ O ₃ /mol%	TiO ₂ /mol%	PT Designed Content /vol%	PT Content* /%	TG-DTA Peak /°C	Crystallinity (I/I ₀)** /%	Glass Forming Component Composition (Designed)
00	50	0	50	100	100	493	100	None
21	50	10	40	74	99	484	100	PbO·B ₂ O ₃ 20 mol%
41	54.5	9.1	36.4	66	80	458	100	2PbO·B ₂ O ₃ 20 mol%
22	50	23.1	26.9	46	38	477	37	PbO·B ₂ O ₃ 46 mol%
42	59.4	18.8	21.9	36	62	450	79	2PbO·B ₂ O ₃ 46 mol%
72	60	20	20	32	46	411	59	2PbO·B ₂ O ₃ 50 mol%
73	50	20	30	52	40	470	46	PbO·B ₂ O ₃ 40 mol%
74	65	5	30	51	82	455	115	7PbO·B ₂ O ₃ 14 mol%

*Semi-quantitative PbTiO₃ content was calculated by the relative (101) peak area of PbTiO₃ in PbO-TiO₂-B₂O₃ powders

fired at 700°C (The (101) peak area of pure PbTiO₃ powder fired at 800°C = 100).

**Crystallinity is expressed by the relative (101) peak intensity to that of pure PbTiO₃ powder fired at 800°C.

several times to obtain the desired thickness. Then the sample was fired at 500–900°C with different ramp rates from 10 to 600°C/min in the RTA infra-red heating furnace (RTA-145, ULVAC, Yokohama). When a ramp rate higher than 20°C/min was employed, the sample was baked at 400–500°C to eliminate organic substance before firing.

This glass-ceramic component solutions (PbO-TiO₂-B₂O₃) were allowed to gel, and the gels were dried at 130°C in air for the TGA-DTA measurements. Powders were prepared for XRD and SEM measurements by calcining the dried gels.

2.2 Characterization

Dielectric constant and $\tan \delta$ were measured by a precision LCR meter (HP-4284A, Hewlett Packard). The microstructure of the thin film was observed by scanning electron micrograph (SEM; JSM-5200, JEOL, Tokyo, Japan) and FE-SEM (S-800, Hitachi, Japan). The crystallization behavior of the powder was observed by XRD (RAD-2c, Rigaku-Denki Inc., Tokyo, Japan) and TG-DTA (2000, MAC Science, Tokyo, Japan).

Gold was evaporated through a mask to form top electrodes (0.3 mm in diameter) for the electrical measurement. The unshort-circuit percent was calculated by the number of unshort-circuited electrodes out of 40 top electrodes per sample. The film thickness was measured by an etching technique. A part of the thin film was masked by a polymer coating, followed by the etching with HF-H₂O₂ solution and the etched step height was measured by a surface profilometer.

3. Results and discussions

3.1 Design rationale for component levels

The component levels within the glass-ceramics were chosen to maximize the crystal phase content. The composition of the glass-ceramics was designed to have the chemical potential of the individual components equal both in the crystal and the glass phase so that the constituents of the crystal phase do not move into the glass phase. For example, the chemical potential of Pb in PT crystals should be equal to that in the glass phase at the calcination temperature when both phases are in equilibrium. Given the difficulty of accurately calculating the chemical potential of Pb in the glass phase, its potential was assumed to be equal to that in the crystal phase of the same chemical composition. The chemical potential diagram ($\log(a_{\text{Pb}}/a_{\text{B}})$ vs. $\log(a_{\text{Pb}}/a_{\text{Ti}})$) at 773 K with $P_{\text{O}_2}=0.2$ was drawn using a thermodynamic data base (MALT)²⁰ and the PbO·B₂O₃ was found to be in equilibrium with PbTiO₃. Thus the designed

Fig. 2. (a) TG-DTA plots of precursor gels of designed composition of 0.8PT·0.2(2PbO·B₂O₃) and (b) DTA plots of 600°C calcined gels of 0.8PT·0.2(2PbO·B₂O₃).

glass phase forming composition was determined to be PbO·B₂O₃. The composition of 2PbO·B₂O₃ was also studied due to its quasi-stable crystal phase composition on the phase diagram.²¹⁾

3.2 Crystallization behavior

TGA-DTA plots of the dried gels indicate the crystallization temperatures of PT to be 458°C for 0.8PT·0.2(2PbO·B₂O₃) and 484°C for 0.8PT·0.2(PbO·B₂O₃) (Fig. 2(a), Table 1). Thus, the higher PbO to B₂O₃ ratio of the glass-forming component yielded the lower crystallization temperature. Both crystallization temperatures were lower than for the pure PT gel (493°C in Table 1).

The perovskite phase of PT was observed in trace amounts at 450°C, becoming more prominent at temperatures above 500°C, until only this phase could be observed at 600°C using pure PT (Fig. 3). In the glass-ceramics, the pyrochlore phase predominated in PT-PbO·B₂O₃ system at 500°C, whereas the perovskite phase predominated even at 480°C in PT-2PbO·B₂O₃ system (Fig. 4). This crystallization behavior observed by XRD agrees well with the TGA-DTA results.

Both the solid and the liquid phases must have existed at around 500°C in this glass-ceramic sample because there was the endothermic peak upon heating in a DTA plot (Fig. 2(b)) corresponding a liquid phase and there were PT peaks in the XRD results (Fig. 4) corresponding a crystal phase.

3.3 Crystal phase content

The designed volume fraction of the crystal phase was calculated assuming that every Ti atom was consumed along with an equimolar amount of PbO to form PT, and that the

remaining PbO and B₂O₃ formed the glass phase. The densities of the components are 7.96 kg/cm³ for PT, 5.5 kg/cm³ for PbO·B₂O₃, and 6.5 kg/cm³ for 2PbO·B₂O₃.²²⁾ Letting V_0 represent the volume fraction, W_0 the weight fraction, m_0 the molar fraction, M_0 the molecular weight and d_0 the density of the crystal phase, and V_1 , W_1 , m_1 , M_1 and d_1 the corresponding parameters for the glass phase, V_0 can be ex-

pressed as follows:

$$V_0 = M_0 m_0 / d_0 (M_0 m_0 / d_0 + M_1 m_1 / d_1)$$

The PT content was semi-quantitatively calculated using the relative XRD(101)-peak area of PT in the glass-ceramic powder. The (101)-peak area of the pure PT powder calcined at 800°C for 30 min was taken as the reference (area=100). Because the calibration on the known amounts of PT and the glass had not been done, the obtained PT contents were semiquantitative. The designed PT volume fractions and the obtained PT contents (fired at 700°C for 30 min) are summarized in Table 1.

The PT contents became roughly close to the designed PT volume fractions and seemed rather unaffected by the composition of the glass-forming component when the

Fig. 3. XRD patterns of PT calcined at (a) 450°C, (b) 500°C, (c) 550°C and (d) 600°C (perovskite (○)).

Fig. 4. XRD patterns of 0.8PT·0.2(2PbO·B₂O₃) calcined at (a) 480°C, (b) 500°C and (c) 600°C (pyrochlore (●), perovskite (○)).

Fig. 5. SEM photographs of 0.54PT·0.46(2PbO·B₂O₃) thin films fired at (a) 500°C×5h, (b) 600°C×2h, (c) 700°C×0.5h, (d) 700°C×1 min, (e) 800°C×1 min and (f) 800°C×1 min (perspective view).

Fig. 6. SEM photographs of $x\text{PbO}-y\text{TiO}_2-z\text{B}_2\text{O}_3$ thin films fired at 700°C for 1 min (baked at 400°C for 30 min). (a) $x/y/z=50/23/27$ ($0.54\text{PT}\cdot 0.46(\text{PbO}\cdot\text{B}_2\text{O}_3)$), (b) $x/y/z=60/22/19$ ($0.54\text{PT}\cdot 0.46(2\text{PbO}\cdot\text{B}_2\text{O}_3)$), (c) $x/y/z=50/30/20$ ($0.6\text{PT}\cdot 0.4(\text{PbO}\cdot\text{B}_2\text{O}_3)$) and (d) $x/y/z=65/30/5$ ($0.86\text{PT}\cdot 0.14(7\text{PbO}\cdot\text{B}_2\text{O}_3)$).

glass-ceramics were fired at 700°C . This indicates that the chemical potential of Pb in the glass phase was close to that in the PT crystal phase in this experiment. However, the measured PT contents were generally higher than the expected contents probably because of the following two reasons. First, the estimation of background noise in the XRD data could bring the area variation of 5–10%. Second, the absolute value of the content has not been calibrated.

Samples richer in PbO were more prone to crystallize probably because mass transfer was enhanced as a result of the low viscosity of the glass phase.

3.4 Microstructure

The SEM photographs of fired thin films are shown in Figs. 5–8. Small crystals have developed in a glass matrix in every thin film that was fired at 700°C (see for example, Figs. 6(a)–(d)). These crystals seemed to be the perovskite type PT from the XRD results. The grain growth was observed when the thin films were fired at 500°C then it became prominent at 600°C probably because the glass-forming components formed a liquid phase that enhanced

Fig. 7. An SEM of PT thin film fired at 700°C for 1 min.

Fig. 8. (a) FE-SEM and (b) EPMA of $0.6\text{PT}\cdot 0.4(\text{PbO}\cdot\text{B}_2\text{O}_3)$ single-coated thin film fired at 800°C for 1 min.

Table 2. Electrical Properties of PbO-*y*TiO₂-*z*B₂O₃ Thin Films

Sample No.	Film Thickness /nm	Baking Temp. /°C	Baking Time /min	Firing Temp. /°C	Firing Time /min	Unshort-Circuit Percent /%	Dielectric Constant /-	Dielectric Loss /-
00U	300			800	30	0		
00F	400	500	5	700	0.5	96	192	0.27
00Q	300	500	5	800	0.5	81	166	0.27
22A	340			500	300	0		
22C	340			700	120	0		
22E	520	400	30	700	1	88	181	0.053
42A	340			500	300	100	97	0.047
42B	340			600	120	0		
42C	340			700	30	0		
42F	516	400	30	800	1	100	140	0.22
72J	300	300	30	700	1	56	149	0.052
72L	300	400	30	700	1	100	154	0.059
72M	270	500	30	700	1	92	122	0.061
73I	375	400	30	700	1	96	125	0.031
73L	400	500	30	600	1	100	143	0.04
74K	420	500	30	600	1	100	128	0.052

the mass transfer. There was not a significant difference between the films fired at 700°C and 800°C (Figs. 5(d) and (e)).

Within the range of compositions tested in the present study, the glass-forming component of 2PbO·B₂O₃ showed the most enhanced crystal growth (Figs. 6(a)-(d)). Also, the larger the glass content was, the larger the crystallite size became (Figs. 6(a) and (b), (c) and (d)). They are probably due to the better mass transfer. Sometimes a film surface became so rough because of the enhanced grain growth that the unshort-circuit percent of the film became almost zero.

The microstructure of a glass-ceramic thin film fired by the RTA process was completely different from that of the pure PT thin film. There are a lot of pores among grains in the pure PT thin film (Fig. 7). The glass-ceramic thin films which were ordinarily fired have a similar structure (Figs. 5(a), (b) and (c)), however, the matrix-crystal structure is observed in the RTA processed thin films (Figs. 5(d), (e) and (f)). Thus, the RTA process seemed to be effective to improve the insulation (for example, 0 % (ordinarily fired sample (42D)) and 100% (RTA processed (42F)) shown in Table 2). The RTA technique also is expected to prevent PbO from evaporation due to its short processing time. When the RTA process was applied, organic substances were removed in advance, to avoid producing blow holes by an abrupt gas evolution. It was necessary to burn them out at temperatures higher than 400°C in view of the unshort-circuit percent (Table 2). This agreed well with the results of TG-DTA plots (Fig. 2).

The microstructure of the thin film also depended on the film thickness. The acicular TiO₂ crystals of several microns in length and the empty space where no dielectric thin film layer existed was observed in the case of single-coat thin films fired at 800°C (Fig. 8, the film thickness is around 100 nm). This is probably because PbO had disappeared by its high vapor pressure. The platinum electrode was completely covered with the dielectric layer in the case of triple-coat thin films (Figs. 5(f) and 6(c)). In order to obtain a homogeneous thin film, it is important to consider the film thickness and the compatibility between the liquid phase of the film and the substrate surface.

3.5 Electrical property

When the thickness is small (100–200 nm), the insulation of a film (unshort-circuit percent) was very low and many electrodes were short-circuited because of the reason discussed in the Section 3.2. When a film was as thick as about 300 nm and fired by the RTA technique, most of the high glass phase containing films showed high unshort-circuit percents. For example, the unshort-circuit percent was 88%, $\epsilon=181$, $\tan \delta=0.053$ (sample No. 22), and the unshort-circuit percent was 100%, $\epsilon=140$, $\tan \delta=0.22$ (sample No. 42) (Table 2). The dielectric constants are plotted with the theoretical curves based on the models of three different mixing modes (Fig. 9.)²³⁾ The dielectric constants obtained were extraordinarily high as glass-ceramics and were higher than the theoretical curves. This is partly because the high ferroelectric phase content attained by this sol-gel glass-ceramic technique, and partly because the crystals in the glass-ceramics grew almost as large as the film thickness, which made the glass-ceramic composite structure no longer be described by the random distribution model.

The quantity and the composition of the glass phase are

Fig. 9. Calculated dielectric constants of ferroelectric glass-ceramics based on different mixing models. A: mixture of platelike particles, B: mixture of spherical particles, C: porphyritic mixture containing platelike crystallites. ϵ (ferroelectric phase)=250, ϵ (glass phase)=8.

the most important factors in the present method. When glass phase content is small, crystal growth is not very much enhanced. On the other hand, too large glass content, which is favorable for the insulation, will lead to a smaller dielectric constant (Fig. 9). When the glass phase composition such as $\text{PbO-B}_2\text{O}_3$ is used, it enhances crystal growth too much and sometimes leads to poor insulation. The ideal glass phase composition may be the one which moderately enhances the crystal growth with a moderate liquid viscosity that allows glass to fill in the space in the thin films.

4. Conclusions

This study demonstrated the preparation of highly insulative, high dielectric constant glass-ceramic thin films that are composed of well developed crystals and glassy matrix by a sol-gel method. Preparing such materials by the conventional technique is difficult or impossible. Followings are the summary of this report.

(1) PT was found to crystallize at temperatures below 500°C in the sol-gel glass-ceramics system. A higher PbO to B_2O_3 ratio in the glass-forming component resulted in a lower crystallization temperature and higher PT crystalline content.

(2) The thin films that were fired at temperatures above 700°C by the RTA technique showed the structure in which crystals are embedded in a glass matrix.

(3) The thin films of a large glass phase content showed high unshort-circuit percent when they were thicker than 300 nm, and fired by the RTA technique. However, insulation of the thin film was sometimes suffered by the surface roughness that was caused by the overgrown grains.

(4) The dielectric constants of the glass-ceramic thin films were generally higher than the predicted values based on the random mixing model. For example, the unshort-circuit percent was 100%, $\epsilon=143$, and $\tan\delta=0.04$ for the $0.6\text{PT}\cdot 0.4(\text{PbO}\cdot\text{B}_2\text{O}_3)$ thin film.

Acknowledgment The author wish to acknowledge Mr. Y. Suzuki, Sumitomo Chemical Co., for his technical assistance in sample preparation, and Dr. R. F. Whittier, Mitsui Plant Biotechnology Research Institute, for his thoughtful suggestion.

(Presented at the Annual Meeting of the Ceramic Society of Japan, April, 1996)

References

- 1) K. D. Budd, S. K. Dey and D. A. Payne, *Brit. Ceram. Proc.*, **36**, 107-21 (1985).
- 2) Y. Hayashi and J. Blum, *J. Mater. Sci.*, **22**, 2655-60 (1987).
- 3) R. W. Vest and Jiejie Xu, *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, **35**, 711-17 (1988).
- 4) C. Chen and D. F. Ryder, Jr., *J. Am. Ceram. Soc.*, **72**, 1495-98 (1989).
- 5) S. L. Swartz, P. J. Melling and C. S. Grant, *Mater. Res. Soc. Symp. Proc.*, **152**, 227-32 (1989).
- 6) S. J. Milne and S. H. Pyke, *J. Am. Ceram. Soc.*, **74**, 1407-10 (1991).
- 7) N. Tohge, S. Takahashi and T. Minami, *J. Am. Ceram. Soc.*, **74**, 67-71 (1991).
- 8) S. S. Dana, K. F. Etzold and J. Clabes, *J. Appl. Phys.*, **69**, 4398-403 (1991).
- 9) L. E. Sanchez, D. T. Dion, S. Y. Wu and I. K. Naik, *Ferroelectrics*, **116**, 1-17 (1991).
- 10) W. Park and M. Yamane, *Glastech. Ber.*, **62**, 187-89 (1989).
- 11) Wu Mianxue and Zhu Peinan, *J. Non-Cryst. Solids*, **84**, 344-51 (1986).
- 12) O. Parkash, D. Kumar and R. Rajgopalan, *Bull. Mater. Sci.*, **8**, 13-21 (1986).
- 13) D. G. Grossman and J. O. Isard, *J. Am. Ceram. Soc.*, **52**, 230-31 (1968).
- 14) C. G. Bergeron and C. K. Russel, *J. Am. Ceram. Soc.*, **48**, 115-18 (1965).
- 15) S. M. Lynch and J. E. Shelby, *J. Am. Ceram. Soc.*, **67**, 424-27 (1984).
- 16) T. Kokubo and M. Tashiro, *Bull. Inst. Chem. Res., Kyoto Univ.*, **54**, 301-06 (1976).
- 17) J. Marillet and D. Bourret, *J. Non-Cryst. Solids*, **147&148**, 266-70 (1992).
- 18) A. Herczog, *J. Am. Ceram. Soc.*, **47**, 107-15 (1964).
- 19) T. Kokubo, C.-T. Kung and M. Tashiro, *Yogyo-Kyokai-Shi*, **76**, 89-94 (1968).
- 20) The Society of Calorimetry and Thermal Analysis, Japan, "Thermodynamic Database MALT2", Kagakugijutsusha, Tokyo (1993).
- 21) R. F. Geller and E. N. Bunting, *J. Research Nat. Bur. Standards*, **18**, 585-89 (1937).
- 22) E. Kordes, *Z. Anorg. Allgem. Chem.*, **241**, 1-38 (1939).
- 23) D. G. Grossman, J. O. Isard, *J. Phys. D: Appl. Phys.*, **3**, 1058-67 (1970).