The High Frequency Properties and Crystallization of $PbTiO_3$ Glass-Ceramics by Sol-Gel Process

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Abstract. $PbTiO_3$ glass-ceramics were produced by a sol-gel process. DTA and X-ray diffraction analysis provided information about the structural transformations and crystallization temperature. The range of crystallization temperature of $PbTiO_3$ is larger than that of $PbTiO_3$ glass-ceramics. By increasing the glass composition, the crystallization temperature was increased. The phase transformation of $PbTiO_3$ from the cubic to the tetragonal phase depends on the crystal size caused by the different heat treatment temperatures. The dielectric measurements in high frequency range ($> 10^7$ Hz) exhibited evidence of a relaxation phenomena near 850 MHz. With increasing glass composition, the position of the relaxation frequency was increased. The temperature dependence of the dielectric constant of $PbTiO_3$ and $PbTiO_3$ glass-ceramics has an obvious discrepancy. The dielectric constant of $PbTiO_3$ glass-ceramics shows the characteristic dispersion at the Curie point. It indicated that the glass ceramic sample has a stronger tendency for a diffuse phase transition.

Keywords: sol-gel, $PbTiO_3$, glass-ceramic, phase transform, dielectric, relaxation

1. Introduction

Because of the potential application of ferroelectric glass-ceramics in capacitor, piezoelectric, and pyro-electric applications, numerous studies have been reported regarding the production and properties of these materials [1–5]. There have been many papers on conventional glass-ceramics such as lead titanate-boron oxide-barium oxide (PT-BaO-B_2O_3) [6] lead titanate-silica oxide (PT-SiO_2) [7] and PZT-PbO-SiO_2 [8]. Although a high crystalline phase content is desirable for a better dielectric properties, this content is quite limited using the conventional glass-ceramic technique.

Sol-gel glass-ceramics may solve this problem [9]. The perovskite $PbTiO_3$ is characterized by a high Curie temperature (490°C), a large tetragonal distortion (c/a = 1.063), and high electromechanical anisotropy. It is difficulty to use pure $PbTiO_3$ practically because of its poor sinterability and fragility. The glass-ceramic process is a method to make a dense ceramic. The sol-gel derived $PbTiO_3$-PbO-B_2O_3 system [5] was reported to have the possibility of obtaining dense ceramics. However, the drawback of the borate system was the difficulty in controlling the grain growth rate. The silicate and borate system was expected to suppress the grain growth due to its higher viscosity.

The objective of this paper was to prepare $PbTiO_3$-PbO-B_2O_3-SiO_2 glass ceramics by a sol-gel process. We have achieved levels of the ferroelectric crystalline phase that are higher than any previously reported. The lead titanate crystallization and dielectric properties of these glass ceramics were studied.

2. Experimental Procedures

The starting materials used in the present investigation included lead acetate trihydrate ($>99.0\%$ in purity), titanium tetrabutoxide ($>98.0\%$ in purity), tetraethy orthosilicate (TEOS), and tributyl borate ($>99.0\%$ in purity).

PT stock solutions were prepared by reacting lead acetate and titanium tetrabutoxide in the presence of 2-ethoxyethanol, as previously reported [10]. A

solution of acac-modified complex alkoxide was prepared by the addition of acetylacetone (acac) to the complex alkoxide solution with a molar ratio acac:Ti of 2:1. This solution of acac-modified complex alkoxide was diluted to 0.5 M with 2-ethoxyethanol. The molar composition $60PbTiO_3$-$35SiO_2$-$5B_2O_3$ (PTB-1), $80PbTiO_3$ -$17.5SiO_2$-$2.5B_2O_3$ (PTB-2), $95PbTiO_3$-$4SiO_2$ -$1B_2O_3$ (PTB-3), and $PbTiO_3$ (PTB-0) were prepared by the sol-gel process from TEOS, tributyl borate and Pb-Ti complex alkoxide. The solution of Pb-Ti complex alkoxide was added to a mixture of TEOS, tributyl borate, 2-ethoxyethanol and water, with a molar ratio of 1:4:2 for TEOS: 2-ethoxyethanol:water, followed by stirring for 30 min at room temperature. This Pb-Ti complex alkoxide, TEOS and tributyl borate, were mixed in a desired proportion to form the PbO-TiO_2-SiO_2-B_2O_3 solutions that are shown in above. The resultant mixture, was poured into glass vessel and covered for three days at 70°C to form a gel, followed by drying on covered for 10 days at 70°C. The translucent gel was heated at 2°C/min to 450°C for 4 h. Then this gel-like glass was reheated to crystallize at desired temperature for desired times. The gels were dried at a temperature of 250°C or desired temperature in air for differential thermal analysis with a System 7/4 PE-1700. The crystallization behavior of powders was observed with Rigaku K/max 2400 XRD. FT-IR spectra were measured with a Nicolet 5DXC. Microstructures of cross sections of the sintered samples were examined using a Shimadzu EPMA-8750.

3. Results and Discussion

3.1. *Crystallization of PbTiO₃ Glass-Ceramics*

The gels were dried at a temperature of 250°C in air for DTA (heating ratio 10°C/min). The exothermic peaks observed at 505.3°C, 544.6°C and 622.4°C is the crystallization temperature of $PbTiO_3$ for the compositions PTB-0, PTB-2 and PTB-1 (Fig. 1). Crystallization temperatures increase when the ratio of glass phase increases, because the glass phase former acts as an obstacle to form crystalline $PbTiO_3$. We could not develop a quantitative relationship for the glass content versus the $PbTiO_3$ glass-ceramics crystallization temperatures in these DTA experiments. The exothermic peak of pure $PbTiO_3$ is the
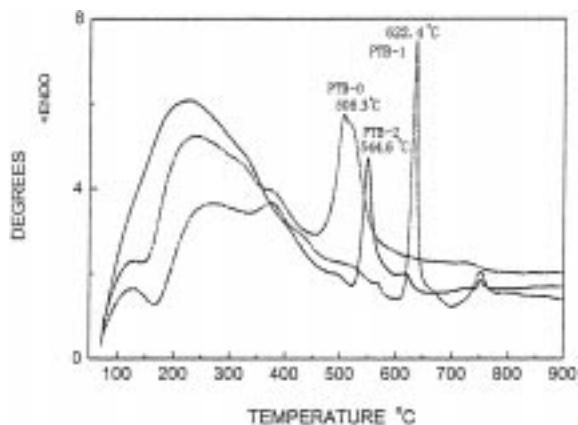

Fig. 1. DTA of $PbTiO_3$ gel-like glass.

combination of two exothermic peaks. This means that it is a two-step process to form crystallines $PbTiO_3$ from the glass-state of the sample. This result most likely reflects the formation of pyrochlore phase as the first crystal phase in the pure $PbTiO_3$, then a phase transition to the perovskite phase occurs at higher temperature. However, no pyrochlore phase was observed in the X-ray diffraction patterns for the glass-ceramic (Fig. 3). It is likely that the perovskite phase crystallized directly from a homogeneous amorphous mixture of glass-ceramic-components.

The pure $PbTiO_3$ undergoes a phase transformation from the tetragonal to the cubic perovskite phase at the Curie temperature on heating. To investigate the effect of crystal size on the $PbTiO_3$ glass-ceramic, the samples of PTB-2 were heated at 600°C, 700°C and 800°C for 2 h, respectively, for crystal growth before DTA runs. DTA data (Fig. 2) were obtained by heating at 5°C/min. An endothermic peak caused by the phase transformation of $PbTiO_3$ from tetragonal to the cubic is observed on heating. The endothermic peak shifts to higher temperature with increasing heat treatment temperature. It is obvious that the appearance of the endothermic peak is affected only by the crystal size. Ishikawa et al. [11] have expressed the size dependence of T_c as

$$T_c = 500 - 588.5 \big/ (d - 12.6)$$

where d is the grain size. The Curie temperature was decreased with decreasing grain size. The
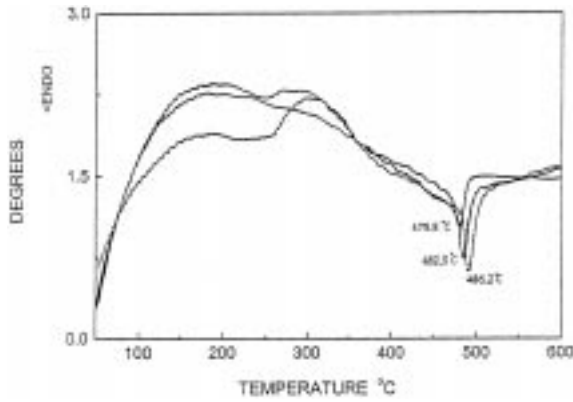
Fig. 2. DTA of PbTiO₃ glass-ceramics heated at different temperatures.

crystallization behavior of PbTiO₃ in glass agrees with pure PbTiO₃.

Figure 3 shows XRD patterns of the gel-like glass and the glass-ceramics heated at various temperature for 2 h. For pure PbTiO₃, the pyrochlore phase and perovskite phase of PT were observed in trace amounts at 350°C and the perovskite phase becomes more prominent at temperatures >450°C. Pure perovskite phase is achieved only at 500°C. No crystalline phase was detected in the gel-like glass obtained by heating for 2 h at 450°C (PTB-2) and 500°C (PTB-1). The pyrochlore phase was not observed from the XRD patterns in the glass-ceramic system. The crystallization behavior observed by XRD agrees well with DTA results.

SEM imagines for the crystallized samples (PTB-1, PTB-2) are shown in Fig. 4. In order to remove glassy phases, the samples were polished and then etched in 1M HF solution for 2 min at room temperature. In the PTB-2 sample that was crystallized at 950°C, The size of PbTiO₃ crystals is about 1 μm (Fig. 4a) and show the ferroelectric domains in the cross sections of the grains (Fig. 4b). With increasing crystallization temperature, these particles grow to a size of 10–12 μm and are aggregated into clusters (Fig. 4c). The EDAX analysis indicated that the composition of the crystal grain was only Ti, Pb and O element. The images (Fig. 4d, 4e,) for PTB-1 sample crystallized at 1050°C a shows that these PbTiO₃ crystals are discrete in the glass phase and the grain size is about 8 μm. The backscattered image of a
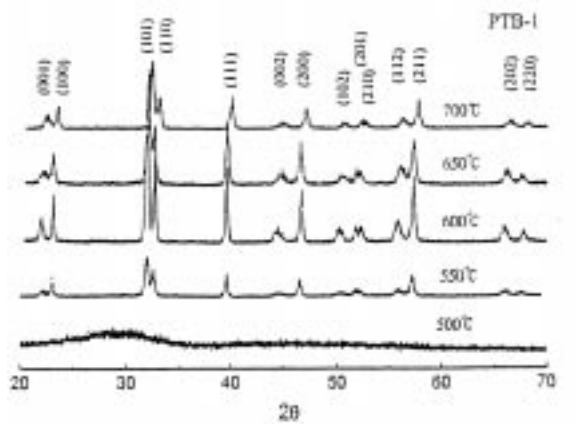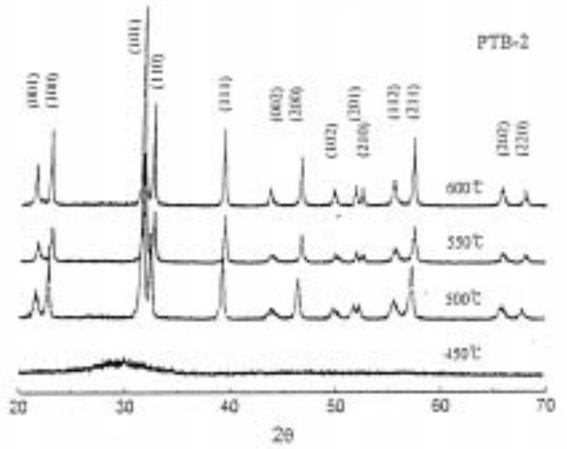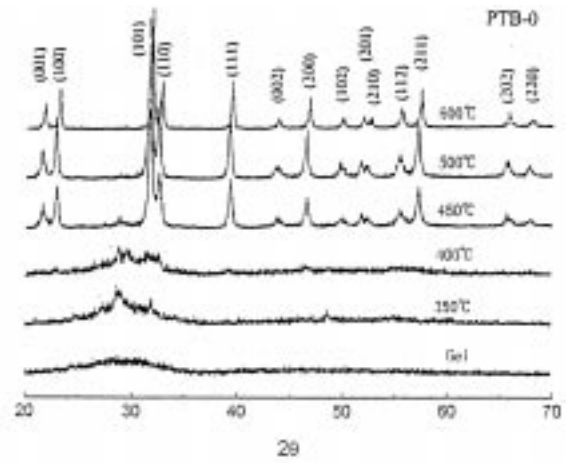
Fig. 3. XRD patterns of PbTiO₃ gel-like glass heated at different temperatures.

polished cross section without etch for PTB-1 heat treatment at 950°C is shown in Fig. 4f. It is indicated that the content of glass plays an important role in the
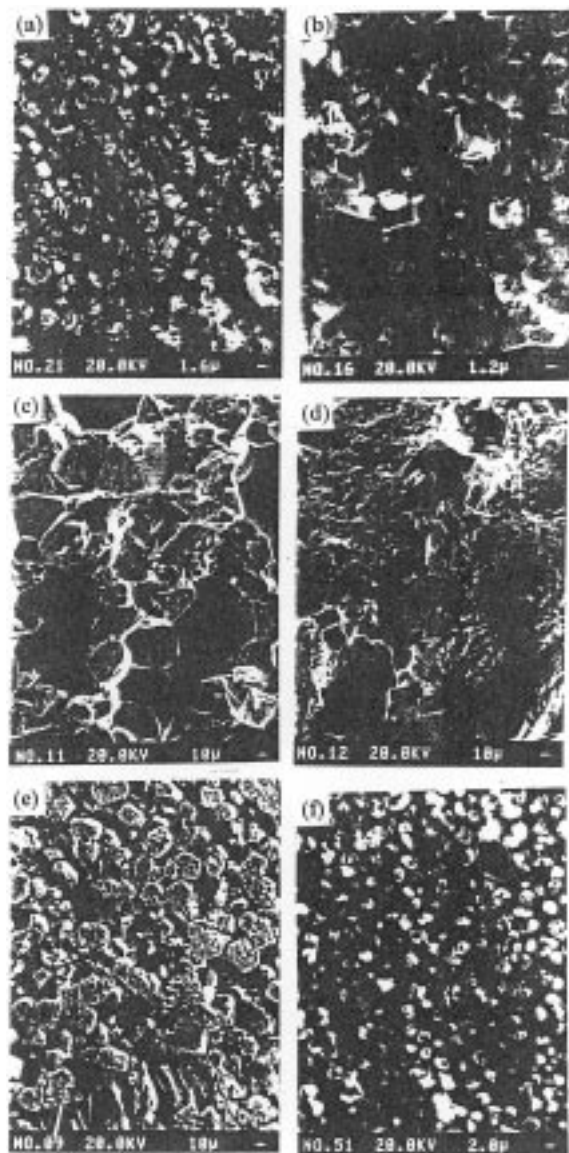
Fig. 4. SEM imagines of PbTiO$_3$ glass-ceramics heated at different temperatures (a) PTB-2, 950°C for 4 h, etched. (b) PTB-2, 950°C for 4 h. (c) PTB-2, 1050°C for 4 h (d) PTB-1, 1050°C for 4 h (e) PTB-1, 1050°C for 4 h, etched (f) PTB-1, 950°C for 4 h, backscattered image.

degree of dispersion for crystalline PbTiO$_3$ in the glassy matrix and controlling the PbTiO$_3$ grain size.

3.2. Dielectric Properties of PbTiO$_3$ Glass-Ceramic

Relative permittivity and loss measurements from 1 MHz to 1 GHz were carried out using HP4286

and HP16194A (Range: $\sim$ 2 GHz) high-temperature component test fixture. The temperature dependence of the dielectric constant and dielectric loss was measured with HP4284. The electrodes were applied to the sample faces.

The dimension of samples for microwave dielectric measurement is $1.6\,mm \times 2.4\,mm \times 2\,mm$ (equal to the dimensions of calibration sample provided by HP company). We have measured the high frequency dielectric properties of BaTiO$_3$ ceramic. Its position of relaxation frequency is about 790 MHz. This result is the same as Mark P. McNeal reported [2]. In the process of measurement, the samples have been incised into two pieces. The position of the relaxation frequency of sample is the same as the incised sample. We conclude that the results obtained from the high frequency dielectric measurement in HP4286 are the material properties.

Microwave dielectric measurements (Fig. 5) exhibited evidence of relaxation phenomena for PTB-2 and PTB-3. The relaxation is characterized by a decrease in the relative permittivity with frequency, accompanied by a peak in the dielectric loss. The origins of this relaxation phenomenon have been attributed to the existence of domain structures [12,13]. From their dielectric spectra we can see that the position of the relaxation frequency shifted to higher frequency with increasing of the glass composition. The position of the relaxation frequency of PTB-2 and PTB-3 were at 850 MHz and 800 MHz, respectively. The relaxation peak is not observed up to $\sim$ 1000MHz in PTB-1 material. The grain size of
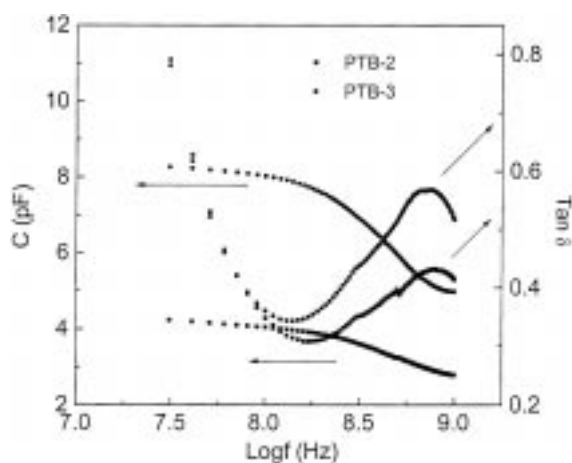

Fig. 5. The dielectric spectrum of PbTiO$_3$ glass-ceramics heated at 950°C for 4 h.

PbTiO$_3$ in PTB-1 glass-ceramics is smaller than that of the PTB-2 and PTB-3, The relaxation peak is possible at >1000 MHz.

The relaxation frequency, f_r is related to the grain size d. The relation follows that [12]

$$f_r = \frac{\sqrt{c_{55}/\rho}}{\pi d}$$

ρ is the density, c_{55} is the stiffness constant. From this equation, f_r varies inversely with grain size, d. The particle size of PbTiO$_3$ was restrained greatly in the higher glass content. Therefore, the particle size of PbTiO$_3$ in PTB-2 is smaller than that of PTB-1. The change rule of measured relaxation frequencies is consistent with this equation.

The temperature dependence of the dielectric constant of PbTiO$_3$ and PbTiO$_3$ glass-ceramic has an obvious discrepancy (Fig. 6). The dielectric constant of PbTiO$_3$ crystals surrounded by a glassy matrix shows the characteristic dispersion at the Curie point. It is indicated that the sample has a strong tendency of diffusion phase transition. The dielectric peak value of PbTiO$_3$ single crystal reaches about 10,000 while that of the glass ceramic is below 5500 for PTB-2. The reason seems that the glass ceramic contains SiO$_2$ or other phase in a continuous position of the matrix, which results in a diffused and a low dielectric peak. The dielectric constant of PbTiO$_3$ glass-ceramics at T_c does not obviously drop with increasing temperature. At higher frequency, the decrease in dielectric constant for PbTiO$_3$ glass-ceramic is more evident than at lower frequency. The trend for the temperature dependence of the dielectric loss of PbTiO$_3$ glass-ceramic agrees with the dielectric constant. Above the Curie temperature, it is evident that the value of dielectric loss of PbTiO$_3$ glass-ceramic increases markedly as the measuring temperature is increased. The apparent increase in dielectric constant at elevated temperatures (Fig. 6) is due to increased loss in this temperature range. This trend is consistent with the PbTiO$_3$ glass-ceramic having a higher electrical conductivity at higher temperature.

4. Conclusion

PbTiO$_3$-PbO-SiO$_2$-B$_2$O$_3$ glass-ceramics were produced by a sol-gel process. The temperature range of the crystallization temperature of PbTiO$_3$ is larger than that of PbTiO$_3$ glass-ceramics. As the glass composition increases, the crystallization temperature increased. The phase transformation of PbTiO$_3$ from the cubic to the tetragonal depends on the crystal size caused by the different heat treatment temperatures. The glass-ceramics exhibited evidence of relaxation phenomena in their dielectric spectra. By increasing the glass composition, the relaxation frequency was increased. The temperature dependence of the dielectric constant of PbTiO$_3$ glass-ceramic revealed that the glass has a higher electrical conductivity in the range of higher temperature.

Acknowledgment

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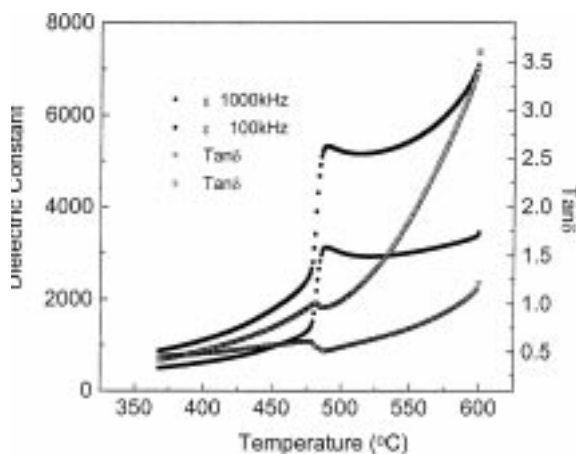5. Kunio Saegusa, *J. Am. Ceram. Soc.*, **79**(12), 3282 (1996).

Fig. 6. The temperature dependence of the dielectric constant of PbTiO$_3$ glass-ceramic heated at 950°C for 4 h.

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