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Fabrication and Dielectric Properties of (Ba_{0.7}Sr_{0.3})TiO₃-Glass Composites

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Abstract

Bulk and thick-film $(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3$ (BST)-glass composites with different dielectric properties were fabricated at 1000 °C from powder mixtures of a sol-gel-derived BST and a commercial glass (GP). Increasing the calcination temperature of the BST gel powder from 850 ° to 1000 °C resulted in an increase in the sintered density of the composites with simultaneous increases in dielectric permittivity (ϵ_r) and its temperature coefficient. Similar changes were observed in composites with different GP contents. A substantial decrease in ϵ_r with a broadened ϵ_r – temperature curve for the 12% GP composite could be attributed to the inhibited densification and enhanced formation of the secondary fersite phase. The dielectric properties and dielectric tunability of the composites were examined in relation to their relative density (d_{rel}), crystallinity (L_{app}), and relative fraction of the BST phase (f_{BST}). Although changes in ϵ_r , its temperature dependence, and tunability were nominally correlated with the d_{rel} change of the sintered composites, the result that the d_{rel} of the composites was basically an increasing function of L_{app} and f_{BST} suggested the substantial contributions of L_{app} and f_{BST} to those changes.

1. Introduction

Ferroelectrics possess an important characteristic, that is, their dielectric permittivity (ϵ_r) varies as a function of dc electric field,¹⁾ giving them high potential as candidates for electrically tunable microwave applications.^{2,3)} The required material properties for such tunable microwave applications are (i) a low ϵ_r for impedance matching, (ii) a low dielectric loss, and (iii) a low temperature dependence of ϵ_r , in addition to a high dielectric tunability in certain dc bias voltage ranges. Barium strontium titanate, $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST), is the most promising material for tunable microwave devices such as phase shifters, varactors, and tunable band filters,⁴⁻⁸⁾ owing to its high tunability and low dielectric loss at room temperature. Therefore, the fabrication and dielectric tunable properties of BST materials have been extensively studied in three different forms, i.e., bulk ceramics,⁹⁻¹¹⁾ thick films,¹²⁻¹⁵⁾ and thin films.¹⁶⁻²⁰⁾

Each form of BST material has its own specific issue. That is, dielectric loss tangents of thin films are usually higher than those of other forms. Bulky samples of pure BST require very high tuning voltages. In contrast, thick films that can be obtained by a cost-effective fabrication method such as screen printing are a very attractive form, because the cofiring of BST thick films and inner electrodes such as Ag would fulfill the current demand for device miniaturization and integration in practical tunable applications. On the basis of such demand realizing the incorporation of tunable components in a low-temperature cofired ceramic (LTCC) system, the present authors have focused on BST glass-ceramics and examined the fabrication and dielectric properties including the tunability of glass-ceramic samples since a glass component would be expected to assist the samples in densifying at low-temperature, which is needed for the cofiring. In our serial studies,²¹⁻²³⁾ bulk BST glass-ceramics obtained by sintering glass powder compacts with a basic composition of 60BST-25SiO₂-15AlF₃ at 1000 °C for 24 h showed a broadened character in each ϵ_r -temperature relationship around the Curie temperature (T_c). It was also demonstrated that a thick-film sample fabricated from a glass powder with Ba/Sr = 7/3 had 27.3% tunability at 5 GHz under 10 kV/cm bias voltage.²³⁾ It is interesting to note that BST glass-ceramic samples including those reported elsewhere^{15,24,25)} possess fairly good tunability even though they are not highly densified.

It is very difficult, of course, to fabricate tunable BST materials with well-controlled dielectric properties, as mentioned in the early part of this section, since a ferroelectric material having a high ϵ_r inevitably shows high values of tunability and dielectric loss as well as a strong temperature dependence of ϵ_r around T_c . Furthermore, a material parameter that should be controlled to give the desired dielectric properties to tunable materials has not been fully understood, despite many studies

on tunable BST-based materials. Thus, a systematic study must be conducted to find out a key parameter leading to the controlled dielectric properties in each BST material system. The purpose of this study is, therefore, to fabricate BST-glass composites with different dielectric properties and then to examine the possible correlations between some material parameters and their dielectric tunable properties. We fabricated BST-glass composites from mixtures of sol-gel-derived BST and commercially available glass powders, for which the calcination temperature of the BST powder and the mixed amount of the glass powder were changed. For the BST-glass composites thus obtained, we examined the relationship between their dielectric properties (ϵ_r and its temperature dependence and tunability) and material parameters such as relative density, crystallinity, and fractional content of the BST phase of the composites.

2. Experimental Procedure

A precursor powder to $(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3$ was prepared by the sol-gel method. Fixed amounts of Ba and Sr acetates were dissolved into an acetic acid solution at 60 °C and a stoichiometric portion of Ti tetraisopropoxide was added and stirred. After a given quantity of distilled water was added, the solution was soaked at 50 °C for 4 h and dried at 130 °C. A dried gel powder was then calcined at a fixed temperature (850 – 1000 °C) for 10 h. A commercially available glass powder (GP) consisting of SiO_2 (63 mass%), CaO (19%), BaO (5%), and Al_2O_3 (7%) as major components was mixed with the calcined BST powder, for which the GP content was adjusted to be 4, 8, and 12 mass%. Disk-shaped compacts of the mixed powders, which were formed by uniaxial and isostatic pressing, were sintered at 1000 °C for 10 h to produce bulky BST-glass composites. The composite samples fabricated from the BST powders calcined at different temperatures and those with different GP contents are referred to as CT series and GP series, respectively. The sintered bulk composites were characterized in terms of the following measurements: bulk density, true density (by gas pycnometry of a pulverized powder using He gas, Quantachrome ULTRAPYCNOMETER-1000), solid phases formed and crystallite size (both by powder X-ray diffractometry, XRD; Rigaku RINT 2200), microstructure (by scanning electron microscopy, SEM; JEOL JSM-6300F), and temperature dependence of dielectric permittivity and loss tangent ($\tan \delta$) (using an LCR meter, HP-4274A).

Thick-film composites were also fabricated by the screen printing method. A paste prepared from a powder mixture of a calcined BST and GP using a solvent of α -terpineol was printed several times through intermediate drying on a bottom Ag-Pd electrode preprinted on an alumina substrate. After a top Ag-Pd electrode was printed by a similar method, the multilayer-printed substrate was cofired at 1000 °C for 10 h under a specified heating schedule. For the thick-film composite samples thus produced, the ϵ_r change with dc bias voltages was measured at 1 MHz with an LCR

meter (HP-4285A) equipped with a fixture (Agilent 16065A). The leakage current was also measured for some selected thick-film composites.

3. Results and Discussion

3.1 Fabrication and characterization of bulk BST-glass composites

BST gel powders calcined at different temperatures were used to fabricate BST-glass composites with different dielectric properties. Figure 1 shows the effect of the calcination temperature on the relative density (d_{rel}) of the composites with a GP content of 8 mass%, which were sintered at 1000 °C for 10 h. Since the d_{rel} of the sintered composites is defined as $d_{rel} = (\text{bulk density})/(\text{true density})$, an increasing calcination temperature resulted in the production of more densified composites. A substantial enhancement in sample densification for the composite fabricated from the BST powder calcined at 1000 °C (1000CT-BST composite) was also confirmed by SEM observation, as shown in Fig. 2, where one can see a more porous and inhomogeneous microstructure in the 975CT-BST composite. Thus, the densification of the composites revealed a strong dependence on the calcination temperature of the BST gel powder. Several changes were detected in both the BST powders calcined at different temperatures and composite samples sintered at 1000 °C. An increase in the calcination temperature caused an increase in the crystallinity of the BST particles, as shown in Fig. 3, where the apparent crystallite size of each calcined BST particle (L_{app}) was calculated from its XRD profile using Scherrer's equation. A similar difference was also observed in the secondary BST particle size in the sintered composites (Fig. 2).

As can be seen in the XRD patterns of the sintered composites shown in Fig. 4, the formation of fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) can be recognized as a secondary phase in every composite (The corresponding peaks are marked with $\times$ in Fig. 4). This phase is considered to crystallize by the reaction between BST particles and glass components during sintering at 1000 °C. This is supported by the facts that no crystalline phase is formed when only the glass powder is heated at 1000 °C and that the glass powder does not contain Ti, which is one of the constituents of the fresnoite phase. A subtle change was detected in the relative fraction of the fresnoite phase (f_{fres}) formed during sintering, being $f_{fres} = 0.11, 0.14, 0.15$, and 0.10 for the 850CT-, 925CT-, 975CT-, and 1000CT-BST composites, respectively. The relative fractions of the BST (f_{BST}) and fresnoite phases were evaluated from the X-ray diffraction intensities of the BST (110) and fresnoite (210) peaks, I_{BST} and I_{fres} , respectively, and defined as $f_{BST} = I_{BST} / (I_{BST} + I_{fres})$ and $f_{BST} + f_{fres} = 1.0$. A slight increase in f_{fres} for the 925CT- and 975CT-BST composites might be attributed to the higher reactive nature of the BST powders calcined in the temperature range of 925 – 975 °C.

Another change is the amount of residual chemical groups in calcined BST powders, which decomposes to gaseous species during sintering. In our previous study on the crystallization and densification of the sol-gel-derived composite powders with a composition of $0.65(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3 - 0.27\text{SiO}_2 - 0.08\text{Al}_2\text{O}_3$, it was found that CO_2 gas release induced by the thermal decomposition of the residual carbonate groups contained in the calcined powder prohibited the composite powder compacts from densifying during sintering.²⁶⁾ Since a similar effect by the residual carbonate groups was considered to operate in this study, weight change occurring during an additional heating at 1000 °C for 10 h was measured for the calcined BST powders. On the basis of the weight loss during heating from 500° to 1000 °C (at 5 °C/min) and maintaining at 1000 °C for 10 h, the amount of residual carbonate groups was evaluated and plotted against the calcination temperature of the BST powder in Fig. 3. It is clearly seen that more than 1 mol% of the residual species was contained even in the 925CT- and 975CT-BST particles. Thus, the densification of the BST-glass composite samples, which started at approximately 1000 °C (confirmed by linear shrinkage measurement) and is promoted by the viscous flow of the glassy phase, was substantially inhibited for composites containing the BST powders calcined at lower temperatures owing to the decomposition of the residual carbonate groups involved in the BST particles.

Figure 5 shows ε_r – temperature relationships for the sintered bulk composites. Their ε_r values increased with an increase in the calcination temperature of the BST powder, being maximum for the 1000CT-BST composite, which showed a higher d_{rel} and consisted of higher crystallized BST particles than other composites. However, much broadened temperature dependence of ε_r and lower dielectric loss were achieved for the composites obtained from the BST powders calcined at lower temperatures.

In the following examination, we fabricated BST-glass composites with different dielectric properties from powder mixtures of 1000 °C-calcined BST and different amounts of GP and evaluated the various changes occurring in the sintered composites with the GP content. Figure 6 shows changes in the d_{rel} of the composites sintered at 1000 °C for 10 h and in the ε_r of the resulting composite at room temperature. Additionally, the L_{app} of the BST particles and the f_{fres} formed in each composite are plotted in Fig. 7. It is very interesting to recognize that the densification of the composite can be accelerated by adding a relatively small amount of GP but becomes rather inhibited at a higher GP content of 12%. As expected from this d_{rel} change, the ε_r of the composites correspondingly decreased with increasing GP content. In addition to the density decrease, it was clear that both a decreasing crystallinity of the BST phase and an increasing formation of the fresnoite phase substantially affected the decrease in the ε_r values.

The variation in the dielectric properties of BST glass-ceramics or BST-glass composites with glassy phase content generally depends on the chemical composition of the glassy phase involved. When a lead borosilicate glass frit was added to a BST powder (Ba/Sr = 0.55/0.45) at 5 - 30 wt%, the increasing content of the glass frit caused the shift of T_c to higher temperatures with suppressed broadened dependences of ε_r on temperature.²⁴⁾ In the BST glass-ceramics fabricated from composite powders containing a glass component with a composition of 0.5ZnO-0.4B₂O₃- 0.1SiO₂, it was found that the temperature dependences of ε_r became broadened with a reduction of the $\varepsilon_{r(\max)}$ temperature as the amount of the glass component increased.²⁷⁾ For the present composite system, a typical dielectric property change with GP content can be seen in the temperature dependences of ε_r and $\tan \delta$, as shown in Fig. 8. A steeper temperature dependence around T_c with larger ε_r values appears in the 4% GP (4-GP) composite consisting of more highly crystallized BST. In contrast, substantial broadening of the ε_r – temperature curve is observed for the 12-GP composite with a slight shift of T_c to a higher temperature. Thus, an increasing GP content in the present composite system resulted in the decrease in d_{rel} and simultaneous reductions of L_{app} and f_{BST} of the composites, leading to favorable dielectric properties of a broadened temperature dependence of ε_r and a low dielectric loss. On the basis of the results obtained in this study, we tried to find out a possible material parameter dominating the dielectric properties of all the bulk composites fabricated (CT series and GP series). We examined graphically the relationships between ε_r or the temperature coefficient of ε_r ($\text{TC}\varepsilon_r = (1 / \varepsilon_{r(\max)})(\partial \varepsilon_r / \partial T)$; $\partial T = -50 - 100$ °C) and a material parameter such as d_{rel} , f_{BST} , or L_{app} of the sintered composites. When both ε_r and $\text{TC}\varepsilon_r$ were plotted against a material parameter p_1 that was derived by multiplying d_{rel} by f_{BST} as $p_1 = d_{\text{rel}} \times f_{\text{BST}}$, both of which could substantially affect the dielectric properties, it was found that almost linear relationships can hold for ε_r and $\text{TC}\varepsilon_r$ changes of the bulk composites as shown in Fig. 9. The other important parameter, the crystallinity of the BST phase, could not be incorporated because no such simple correlation including the contribution of L_{app} was derived in this examination.

The relative density (d_{rel}) indicates a fractional solid content per unit volume of a sample. Let us consider here an implication of the d_{rel} change of the sintered composites as a material parameter. The composites fabricated in this study consisted of the crystalline BST and fresnoite phases (probably with a small amount of a glassy phase) and both the factional content of each solid (f_{BST} or f_{fres}) and crystallinity of the BST phase (L_{app}) inevitably changed with the calcination temperature and GP content. Since these changes in the sintered composites are closely associated with ε_r and $\text{TC}\varepsilon_r$ changes, it is important to correlate, at least qualitatively, the changes in L_{app} and f_{BST} with the d_{rel} change in each composite series (CT and GP series). In the CT series, an increase in d_{rel} was

accompanied by a simultaneous increase in L_{app} with a small variation in f_{BST} . That is, a CT series composite with a higher d_{rel} consisted of a BST phase with higher crystallinity and therefore had larger values of ϵ_r and $TC\epsilon_r$ than those with lower d_{rel} values. For the GP series, an increasing GP content led to a decrease in d_{rel} with simultaneous decreases in L_{app} and f_{BST} , which in turn resulted in the corresponding decreases in ϵ_r and $TC\epsilon_r$. Thus, the nominal dependences of ϵ_r and $TC\epsilon_r$ of the composites on d_{rel} or p_1 can be explained by the corresponding contributions of L_{app} and/or f_{BST} .

3.2 Tunable property of thick-film composites

Pastes for screen printing were prepared from the same powders of calcined BST and GP as those used for bulk composites. After the required components were screen printed on an alumina substrate, they were cofired at 1000 °C for 10 h to produce thick film BST-glass composites with a thickness of ~ 25 µm. ϵ_r and its change with dc bias voltage were measured at room temperature and relative tunability; n_r ³⁾ was calculated using the equation, $n_r (\%) = 100 \times [\epsilon_r(0) - \epsilon_r(E_0)] / \epsilon_r(0)$, where $\epsilon_r(0)$ and $\epsilon_r(E_0)$ are relative permittivities at a zero bias and a given bias voltage E_0 , respectively. A typical dc bias voltage dependence of n_r can be seen in Fig. 10 for the thick films with different GP contents. Measured ϵ_r and calculated n_r at a dc bias voltage of 50 kV/cm are summarized in Table I. The values of $\epsilon_r(0)$ measured for the thick film composites are lower than those of the corresponding bulk composites. In general, different from the production of bulk ceramics by conventional sintering, the shrinkage of a film is substantially restricted in the direction parallel to the plane of the film because of constrained sintering induced by a substrate.^{13, 28)} A similar effect of constrained sintering could be applied to the cofiring of the multilayer structure of the present thick films (upper electrode/BST layer/lower electrode/substrate). Thus, the porous microstructure of the thick films was responsible for the decrease in $\epsilon_r(0)$. The highest n_r , 46.4%, was obtained for the thick-film composite with a combination of 1000 °C-calcined BST and 4% GP.

Different studies have been conducted on the dielectric tunable properties of BST-based materials. Zhang et al. studied the relationships among sintering conditions, microstructure, and dielectric properties of glass-ceramics with a composition of 0.95BST (Ba/Sr = 65/35) – 0.02Glass (BaO-SiO₂-B₂O₃) fabricated at 1050 – 1200 °C. They reported that n_r increased with increasing sintering duration, and a maximum value of 39.8% at 30 kV/cm was achieved for a glass-ceramic sintered at 1150 °C for 4 h.²⁵⁾ The n_r change was explained by a decrease in the internal stress among grains resulting from grain growth. For Li-doped BST (Ba/Sr = 55/45) thick films fabricated by screen printing and sintering at 900 °C, the effect of the prereaction temperature (500, 700, and 900 °C) of a Li₂O and BST mixture on the dielectric properties of the thick films was examined.¹²⁾

The BST thick films showed similar broadened ε_r vs temperature characteristics and a similar n_r of about 32% at 30 kV/cm, irrespective of the film density and initial particle size. Divya et al. fabricated BST thick-film capacitors at 1070 °C from a sol-gel-derived powder of 0.95BST (Ba/Sr = 7/3) – 0.1 glass component ($B_2O_3 \cdot SiO_2$). A 35- μ m-thick film of the glass ceramic indicated n_r of 32% at 35 kV/cm.¹⁵⁾ In most of these studies, however, few examinations were attempted to correlate the n_r changes with some parameter of the fabricated BST-based materials. Theoretically, the trend “the higher the dielectric constant, the higher the tunability” generally holds in an ideal ferroelectric where the dielectric response is controlled by the lattice dynamics of the material. That is, one can see that n_r of the ideal ferroelectric is an increasing function of ε_r of the material. However, this trend does not always hold for ferroelectric materials containing imperfections or nontunable secondary phases. According to three basic models for ferroelectric/dielectric bicomponent composite (layered, columnar, and spherical inclusion models), the results of the simulation of the n_r vs ε_r dependence for them showed that these dependences may be very different from each other.³⁾ Therefore, it is essential to obtain information on the actual n_r vs ε_r dependence for a given practical system.

In order to find out some material parameter correlating with n_r of all the thick film composites fabricated in this study, measured n_r at 50 kV/cm was plotted against some selected parameters. Figure 11 shows each correlation with (a) ε_r of the thick films, (b) the same parameter of p_1 as that shown in Fig. 9, and (c) d_{rel} of the bulk composites fabricated under the same conditions. In the n_r vs ε_r plot shown in Fig. 11(a), which is based on the theoretical background described above, a tendency for n_r to increase with an increase in ε_r can be recognized with a deviation from a linear relation in a lower ε_r range. From this plot, it was found that a basic relationship derived for an ideal ferroelectric, that is, the tunability of a material is an increasing function of ε_r of the material, can hold for the present composite system. By comparing the plots of Figs. 11(b) and 11(c), a better linear correlation can be seen in the plot against d_{rel} . This result reveals that n_r of the present BST-glass composites changes in proportion to the fractional solid content in each composite. However, this correlation seemed to be nominal because the composites with different d_{rel} values consisted of different ratios of solid phases (crystalline BST and fresnoite and possibly a glassy phase) and, additionally, the BST phase in each composite was in a different crystalline state, as shown in Table I. As mentioned in a previous section, the d_{rel} change had a significant correlation with those in L_{app} and f_{BST} in the way that d_{rel} is an increasing function of L_{app} and f_{BST} . This fact indicates that a higher n_r would be a result of the combined effect of d_{rel} , L_{app} , and f_{BST} . Although no simple correlation was observed in the plots of n_r vs L_{app} and n_r vs f_{BST} , it can be assumed that both

L_{app} and f_{BST} strongly affect the dielectric tunability of the present composites. Therefore, a further study on the fabrication and characterization of the present BST-glass composites with controlled L_{app} and f_{BST} is required to derive a new parameter taking into account the combined contribution of L_{app} and f_{BST} .

4. Conclusions

BST(Ba/Sr = 7/3)-glass composites were fabricated by sintering powder mixtures of a sol-gel-derived BST and a commercial glass at 1000 °C for 10 h. Dielectric permittivity (ϵ_r), its temperature dependence ($TC\epsilon_r$), and dielectric tunability (n_r) were evaluated for bulk and thick-film composites. The calcination temperature of the BST gel powder markedly affected the sample density and the resulting dielectric properties. The increase in calcination temperature caused an increase in the sintered relative density (d_{rel}) of the bulk composites, which was accompanied by both an increasing ϵ_r and its steeper $TC\epsilon_r$ around T_c . The inhibited densification of the composites containing the BST powders calcined at lower temperatures would be predominantly attributed to the decomposition of residual carbonate groups involved in the calcined BST particles during sintering. Similar changes were detected for composites with different GP contents. An increase in the GP content from 4 to 12% resulted in simultaneous decreases in the d_{rel} and ϵ_r . A substantial decrease in ϵ_r with a broadened ϵ_r – temperature curve for the 12% GP-contained composite could be explained by the accelerated formation of the fresnoite phase. Measurement of the dc bias voltage dependence of ϵ_r for thick-film composites showed a basic tendency for their n_r to increase with increasing ϵ_r of the composites. The examinations on the relationships between dielectric properties and material parameters (the d_{rel} , L_{app} , and f_{BST} of the composites) indicated that the dielectric properties of the composites were nominally correlated with d_{rel} or a modified parameter, p_1 . However, from the result that an increasing d_{rel} was accompanied by simultaneous increases in the L_{app} and/or f_{BST} of the composites, it was strongly suggested that changes in L_{app} and f_{BST} substantially affect the resulting ϵ_r , $TC\epsilon_r$, and n_r of the BST-glass composites in the present system.

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Figure captions

- Fig. 1 Relative density change of sintered composites with calcination temperature of BST powder.
- Fig. 2 SEM images of composites fabricated from BST powders calcined at (a) 975 °C and (b) 1000 °C.
- Fig. 3 Changes in apparent crystallite size (L_{app}) and amount of residual carbonate groups of BST powders calcined at different temperatures.
- Fig. 4 XRD patterns of composites fabricated from (a) 850 °C-calcined and (b) 1000 °C-calcined BST powders.
- Fig. 5 Temperature dependences of (a) ε_r and (b) $\tan\delta$ at 10 kHz for bulk composites sintered at 1000 °C.
- Fig. 6 Changes in relative density and ε_r of sintered composites with GP content.
- Fig. 7 Changes in L_{app} of BST and relative fraction of fresnoite phase formed during sintering for composites with different GP contents.
- Fig. 8 Temperature dependences of (a) ε_r and (b) $\tan\delta$ at 10 kHz for bulk composites with different GP contents.
- Fig. 9 Plots of (a) ε_r at room temperature and (b) $TC\varepsilon_r$ against a parameter, p_1 , for bulk composites showing almost linear correlation between them.
- Fig. 10 Relative tunability changes with dc bias voltage for thick-film composites with different GP contents.
- Fig. 11 Correlations between relative tunability and (a) ε_r of the thick-film composites, (b) material parameter, p_1 , and (c) relative density of bulk composites.

Table I Dielectric permittivity and tunability of thick-film composites and calculated crystallite size and fractional content of BST of the corresponding bulk samples.

Sample	$\epsilon_r(0)^a$	$n_r(\%)^b$	L_{app}^c	f_{BST}
CT series				
CT-850	250	13.5	39	0.89
CT-925	300	23.3	44	0.86
CT-975	335	28.9	46	0.85
CT-1000	475	37.2	50	0.90
GP series				
4-GP	635	46.4	66	0.95
8-GP	475	37.2	50	0.90
12-GP	310	29.0	37	0.80

a) At room temperature

b) Under a dc bias voltage of 50 kV/cm

c) Apparent crystallite sizes measured for bulk samples (nm)

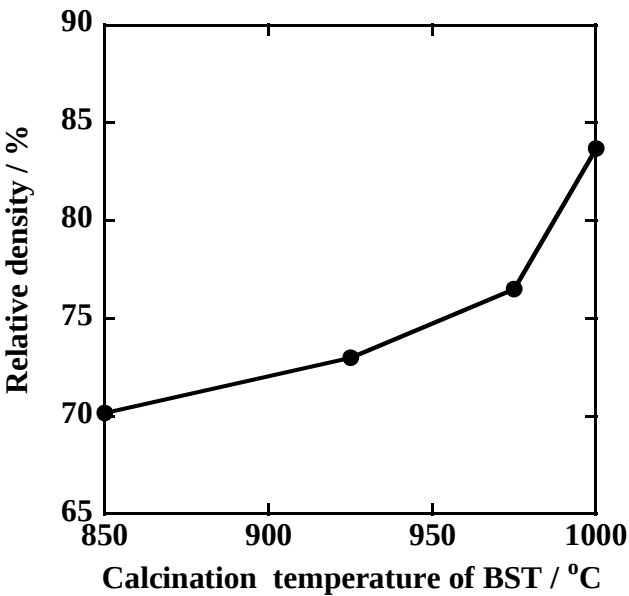


Fig. 1 Relative density change of sintered composites with calcination temperature of BST powder.

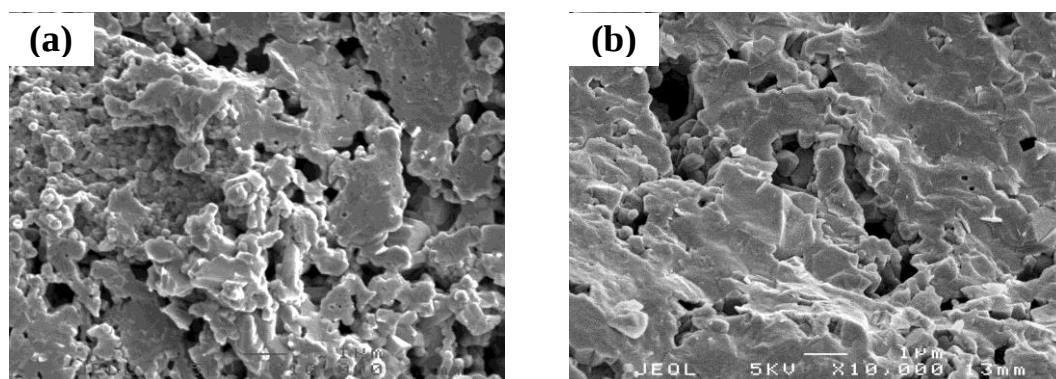


Fig. 2 SEM images of composites fabricated from BST powders calcined at (a) 975 °C and (b) 1000 °C.

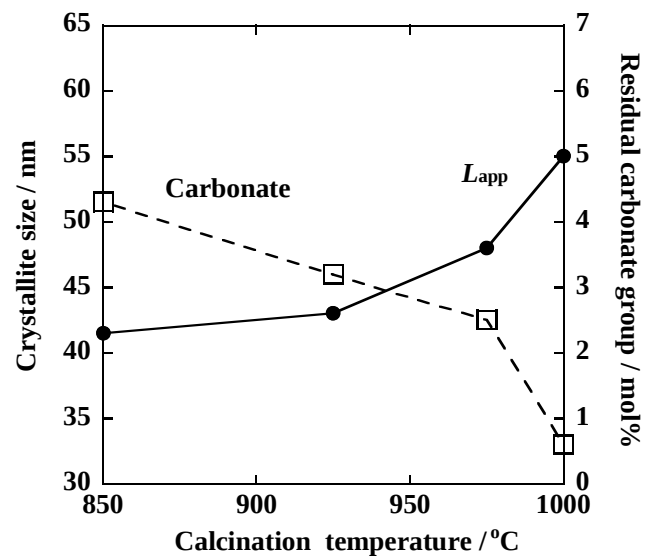


Fig. 3 Changes in apparent crystallite size (L_{app}) and amount of residual carbonate groups of BST powders calcined at different temperatures.

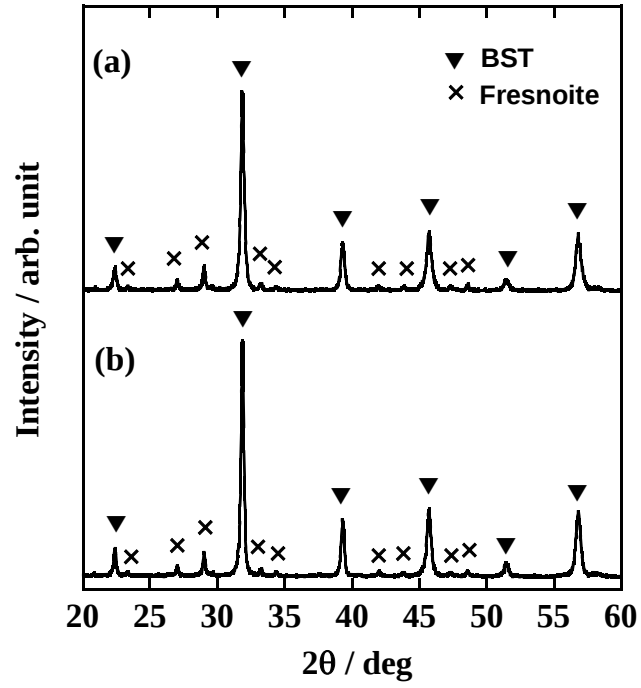


Fig. 4 XRD patterns of composites fabricated from (a) 850 °C-calcined and (b) 1000 °C-calcined BST powders.

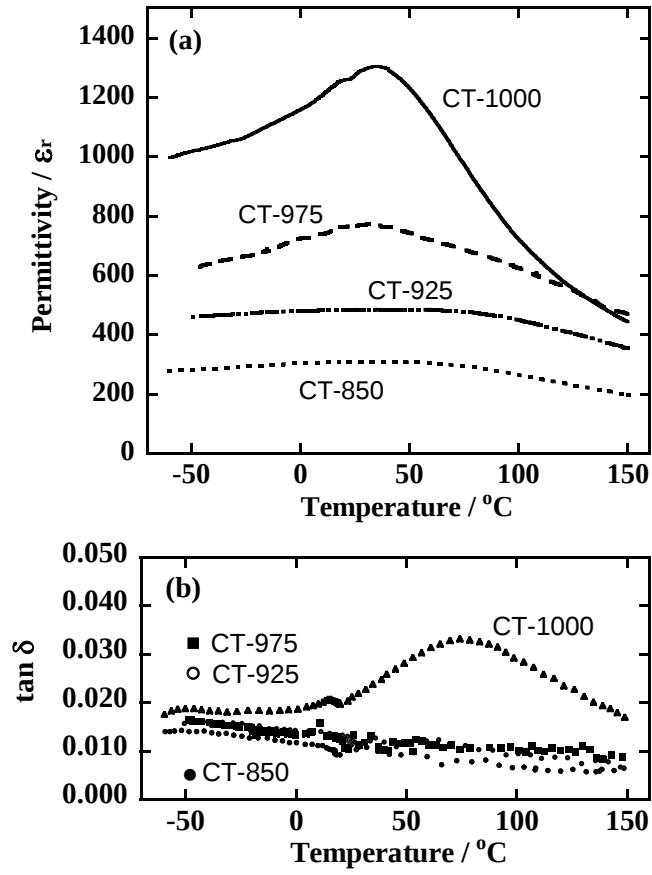


Fig. 5 Temperature dependences of (a) ϵ_r and (b) $\tan \delta$ at 10 kHz for bulk composites sintered at 1000 °C.

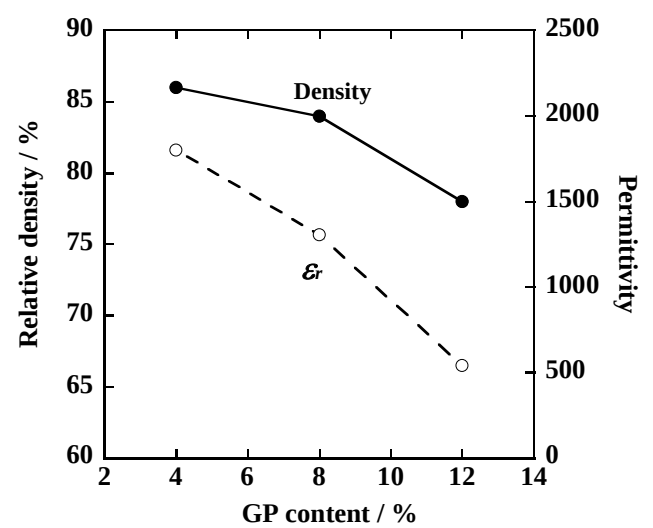


Fig. 6 Changes in relative density and ϵ_r of sintered composites with GP content.

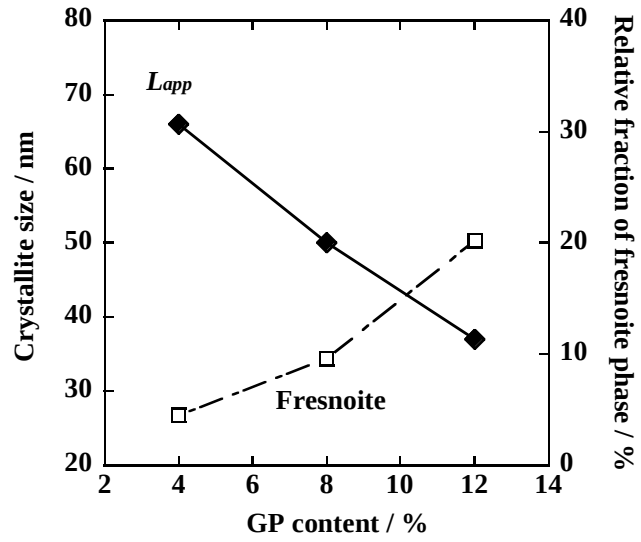


Fig. 7 Changes in L_{app} of BST and relative fraction of fresnoite phase formed during sintering for composites with different GP contents.

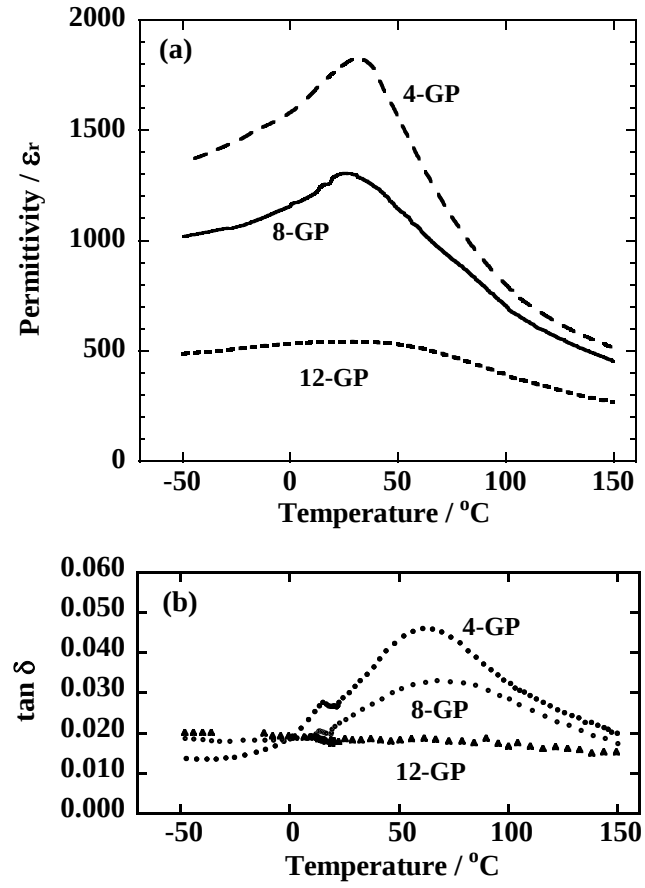


Fig. 8 Temperature dependences of (a) ϵ_r and (b) $\tan \delta$ at 10 kHz for bulk composites with different GP contents.

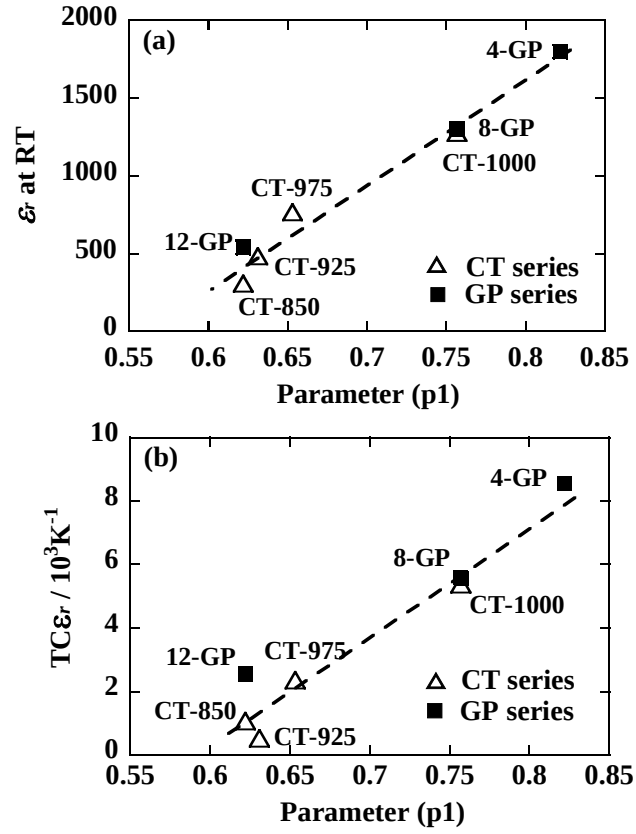


Fig. 9 Plots of (a) ϵ_r at room temperature and (b) $TC\epsilon_r$ against a parameter, p_1 , for bulk composites showing almost linear correlation between them.

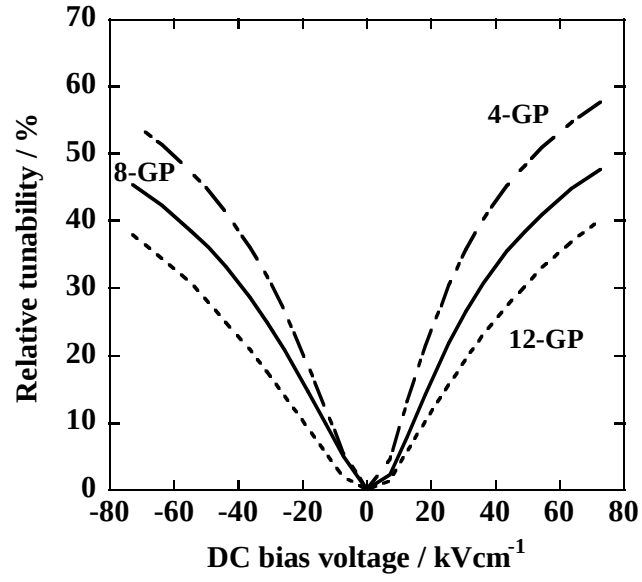


Fig. 10 Relative tunability changes with dc bias voltage for thick film composites with different GP contents.

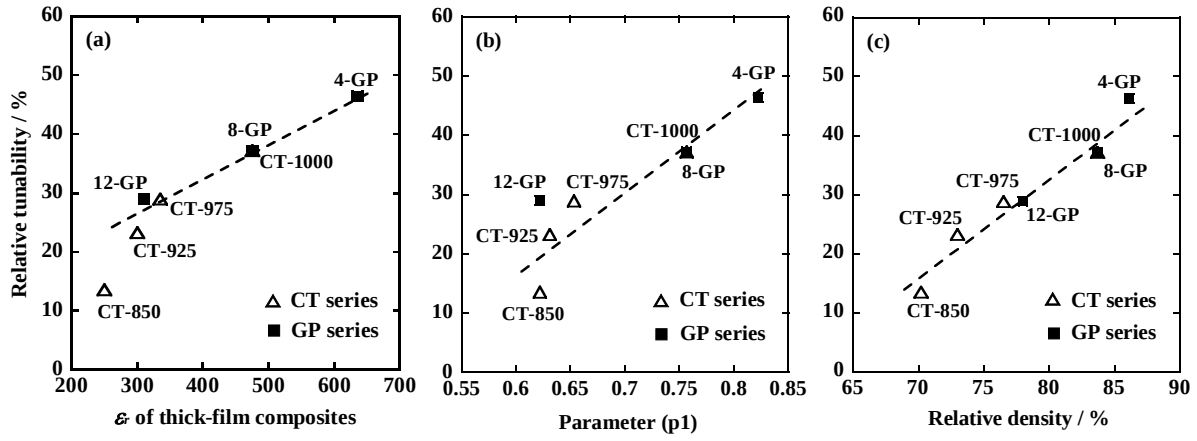


Fig. 11 Correlations between relative tunability and (a) ϵ_r of the thick film composites, (b) material parameter, p_1 , and (c) relative density of bulk composites.