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Fabrication and dielectric properties of barium titanate-based glass ceramics for tunable microwave LTCC application

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Abstract

Low-fired ferroelectric glass ceramics were fabricated from glass powders with a basic composition of $0.65BaTiO_3{\cdot}0.27SiO_2{\cdot}0.08Al_2O_3$. The combined addition of SnO_2 (or ZrO_2) and $SrCO_3$ was conducted to modify the dielectric properties of the glass ceramics. The Sr-component could be incorporated preferentially in the perovskite structure after heating at 1000 °C. The bulk and thick film samples obtained by sintering glass powder with a starting composition of $0.65(Ba_{0.7}Sr_{0.3})(Ti_{0.85}Sn_{0.15})O_3{\cdot}0.27SiO_2{\cdot}0.08Al_2O_3$ at 1000 °C for 24 h showed a broadened ε_r–T relation with $T_c \approx 10\,°C$ and $\varepsilon_r(\max) \approx 280$ and microwave tunability of 32% at 3 GHz, respectively.

Keywords: Glass ceramics; Dielectric properties; $BaTiO_3$ and titanates; LTCC

1. Introduction

Electrically tunable dielectrics attract much attention in rapidly growing microwave telecommunication systems. They can be applied to tunable components such as filters, varactors, phase shifters and so on. Currently, (Ba, Sr)TiO_3 is the most studied material[1,2] and the preparation and property evaluation of (Ba, Sr)TiO_3 thin films have been widely conducted.[3,4] In addition to the usage as tunable thin films, tunable components could be assembled in microwave devices using low-temperature-cofired ceramics (LTCC) technology. LTCC shows excellent electrical performance and should be “a key material” for advanced wireless systems. Thus, the incorporation of tunable ferroelectric components in integrated microwave devices with LTCC technology would definitely lead to the further development of wireless technology.

The present authors have already attempted the fabrication of low-temperature fired bodies from glass powders with their compositions of $0.65(Ba_{1-x}Sr_x)TiO_3{\cdot}0.27SiO_2{\cdot}0.08Al_2O_3$ ($x = 0.2 \sim 0.6$).[4] Ferroelectric perovskite phase was formed from the glass powders by heating above 800 °C and curie temperature (T_c) of the heated samples could be controlled by changing the Ba/Sr ratio in the starting glasses. The tunability of a thick plate sample having Ba/Sr ratio of 7/3 heated at 1000 °C for 24 h was found to be 27% at 5 GHz. In the present study, single and combined cation substitutions for Ti and/or Ba sites in the $BaTiO_3$ phase crystallized from glass powders were conducted in order to examine the possibilities of precise control of tunability-related dielectric properties such as dielectric permittivity (ε_r) and T_c for low-temperature fired glass ceramics. SnO_2 or ZrO_2 was used as single substitute agent for the $BaTiO_3$-based glass ceramics. In the case of combined substitution, simultaneous addition of SnO_2 and $SrCO_3$ or ZrO_2 and $SrCO_3$ were made to the fundamental starting mixtures. ε_r and its temperature dependence in each heated sample were correlated to the solid phases formed, difference in crystallization behavior, lattice parameter change and compositional variation in perovskite grains in this paper.

2. Experimental procedure

Commercial chemicals used in this study were $BaCO_3$, $SrCO_3$, TiO_2, SnO_2, ZrO_2, SiO_2 and AlF_3. Glass powders with fixed compositions indicated in Table 1 were prepared by the method described in the previous paper.[5] A finely ground glass powder was mixed with an organic binder and pressed into disks. Those green compacts were heated in air in the temperature range of 900–1000 °C for up to 48 h. Crystallization temperature of each glass powder was measured with DTA. Characterization

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Table 1
Chemical compositions of powder mixtures for starting glasses (mol%)

Sample	Abbreviation	$BaCO_3$	$SrCO_3$	TiO_2	SnO_2	ZrO_2	SiO_2	AlF_3
$(B_7S_3)T$	B_7S_3T	42	18	60	–	–	25	15
$B[T_{8.5}S_{1.5}]$	BTS	60	–	51	9	–	25	15
$(B_8S_2)[T_{8.5}S_{1.5}]$	B_8S_2TS	48	12	51	9	–	25	15
$(B_7S_3)[T_{8.5}S_{1.5}]$	B_7S_3TS	42	18	51	9	–	25	15
$B[T_8Z_2]$	BTZ	60	–	48	–	12	25	15
$(B_8S_2)[T_8Z_2]$	B_8S_2TZ	48	12	48	–	12	25	15
$(B_7S_3)[T_8Z_2]$	B_7S_3TZ	42	18	48	–	12	25	15

of bulk samples thus fabricated was conducted by density measurement, solid phase identification and lattice parameter estimation (XRD: Rigaku, RINT-2000), and microstructure observation with simultaneous composition analysis (TEM: JEOL, JEM2000FX).

Dielectric properties of the bulk samples were separately measured in low frequency region (HP-4274A) and microwave region (HP-4194, HP-4291). Prior to each measurement, both sides of sintered sample were coated with Ag paste (N.E.CHEMCAT, A-2735), which was followed by firing at 650 °C for 30 min to form Ag electrodes. The ε_r change with temperature was measured in the temperature range from −150 °C to 150 °C at low frequency (1 kHz or 100 kHz). Measurement of microwave tunability was carried out for a thick plate sample fabricated by the method described earlier[5] using vector network analyzer (HP-8510C) with applying dc vias voltage.

3. Results and discussion

3.1. Ba(Ti, Sn)O_3- and Ba(Ti, Zr)O_3-based bulk samples

Temperature dependence of ε_r at 100 kHz are given in Fig. 1 for bulk samples of BTS, B_8S_2TS and B_7S_3TS obtained by sintering the corresponding glass powder compacts at 1000 °C for 24 h. The BTS sample derived from a glass powder of Ti/Sn = 85/15 showed a broadened ε_r curve without any appreciable change in T_c compared with that of $BaTiO_3$ (120 °C). Since the addition of a larger amount of SnO_2 to the starting powder mixture made its melting temperature much higher and homogeneous glass formation more difficult, no further incorporation of the Sn-component was attempted. On the contrary, for the samples with the fixed Ti/Sn ratio but containing variable Sr contents, B_8S_2TS and B_7S_3TS, substantial lowering in T_c can be clearly seen with the corresponding increase in Sr content, becoming $T_c \approx 50$ °C and 10 °C, respectively. It is well known that the cation substitution with Sr^{2+} and Sn^{4+} for $BaTiO_3$ crystal definitely causes a decrease in T_c.[6,7] From the XRD result shown in Fig. 2, very small diffraction peaks of SnO_2 appear for both BTS and B_7S_3TS samples. This XRD result together with the ε_r–temperature curve of the BTS sample suggested that little amount of Sn^{4+} could substitute for the Ti^{4+}-site in the

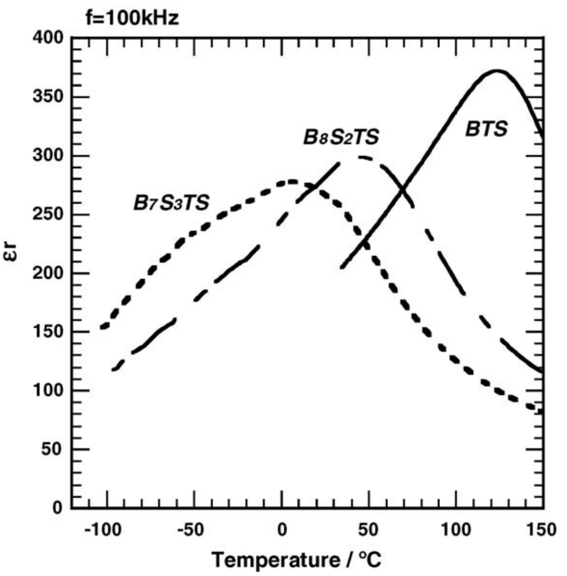

Fig. 1. Temperature dependence of ε_r for bulk samples derived from SnO_2-containing glasses.

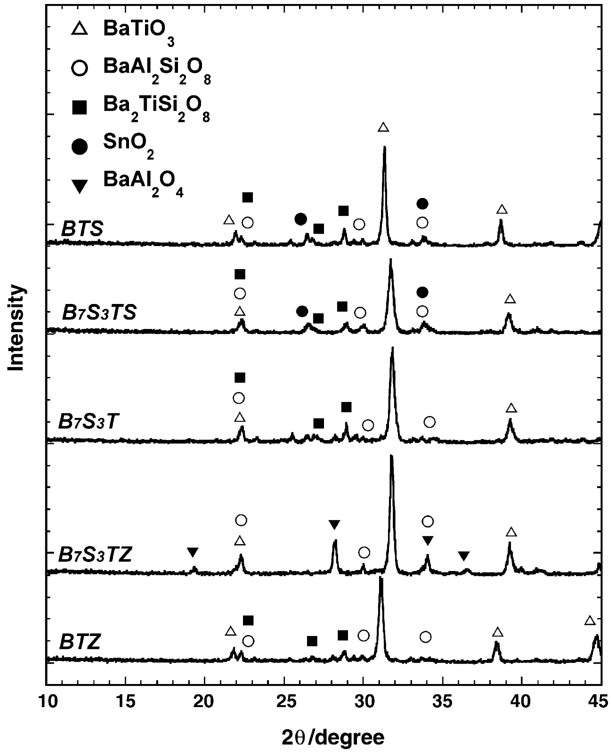

Fig. 2. XRD patterns of glass ceramics sintered at 1000 °C for 24 h.

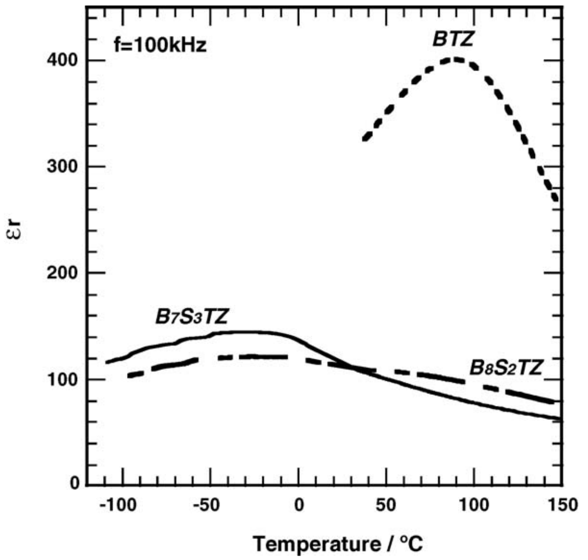

Fig. 3. Temperature dependence of ε_r for bulk samples derived from ZrO_2-containing glasses.

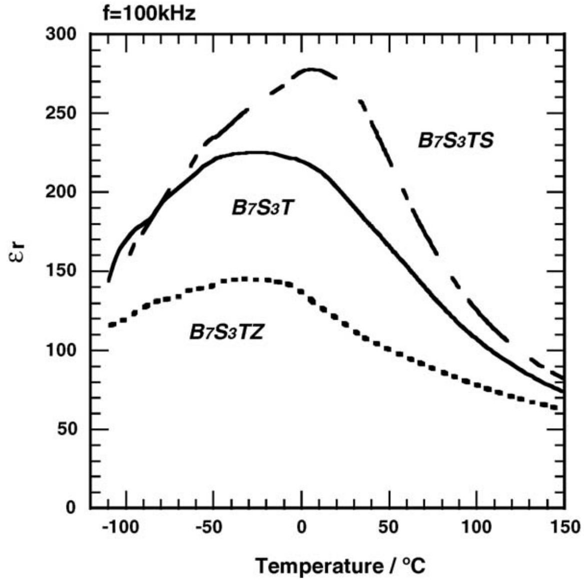

Fig. 4. ε_r–T relations for bulk glass ceramics with a fixed ratio of Ba/Sr = 7/3.

perovskite structure of the bulk samples obtained by heating the corresponding glass powders at 1000 °C. However, the considerable decrease in T_c observed for the B_8S_2TS and B_7S_3TS samples would be explained by the fact that the incorporation of Sr^{2+} into the perovskite structure could much easily occur even in the glass ceramics thus fabricated.

Fig. 3 indicated the ε_r versus temperature relationship of the Ba(Ti, Zr)O_3-based bulk samples heated under the same conditions. It is clearly seen that the single addition of ZrO_2 into the basic glass composition caused a small decrease in T_c. The measured lattice parameter of $a = 0.4043$ nm for the bulk BTZ sample was slightly larger than that of well-crystallized $BaTiO_3$. According to the results of the Zr-substituted $BaTiO_3$,[6,8] several percent of Zr^{4+} cation might be incorporated in the perovskite structure for the BTZ glass ceramic sample heated at 1000 °C for 24 h. Substantially suppressed ε_r curves can be seen for the B_8S_2TZ and B_7S_3TZ samples to which ZrO_2 and $SrCO_3$ were simultaneously added. The intensity and broadness of the XRD peaks of the perovskite phase indicated in Fig. 2 are similar to those of other glass ceramic samples sintered under the same heating conditions, except that the $BaAl_2O_4$ phase newly formed only in both Zr- and Sr-containing samples. The compositionally inhomogenized perovskite phase with the formation of $BaAl_2O_4$ might be responsible for the suppressed character of the ε_r–T curves.

3.2. Effect of the combined addition of cation components on crystallization and resulting dielectric properties

The ε_r–T relationship among three kinds of bulk samples with a fixed ratio of Ba/Sr = 7/3 are comparatively shown in Fig. 4 to elucidate the effect of the combined addition of the second component (Sn and Zr). They clearly affected the relationship in a very different manner. Compared with the B_7S_3T character, the co-addition with Sn and Sr caused an increase in T_c with an increasing ε_r(max), whereas a substantial lowering of ε_r over a wide temperature range without any T_c change took place for the Zr-containing sample. In the sintering of glass powder that can crystallize during heating, two different processes, the densification due to viscous flow and crystallization, should occur competitively. In general, crystallization prior to full densification can lead to keeping the considerably high porosity in the sintered body.[9] As can be seen in DTA curves in Fig. 5, the thermal behavior of the glass powder used in this study was characterized with two or more exothermic peaks caused by

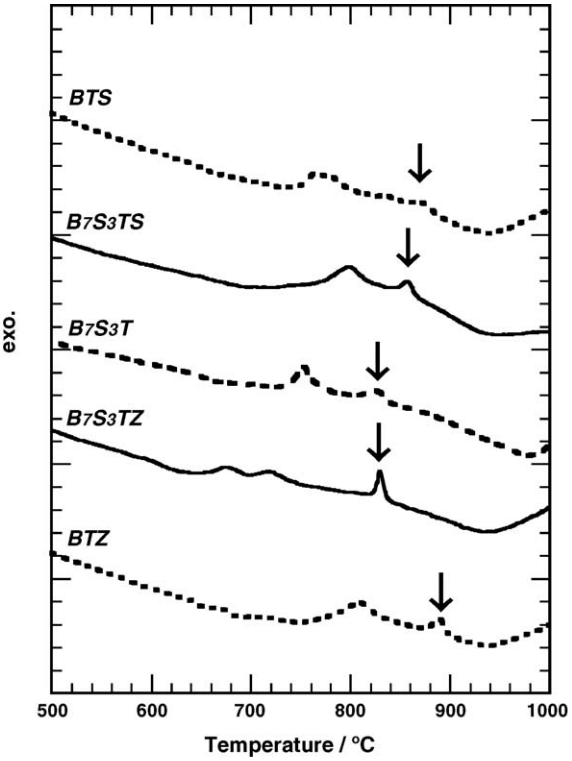

Fig. 5. DTA curves of glass powders.

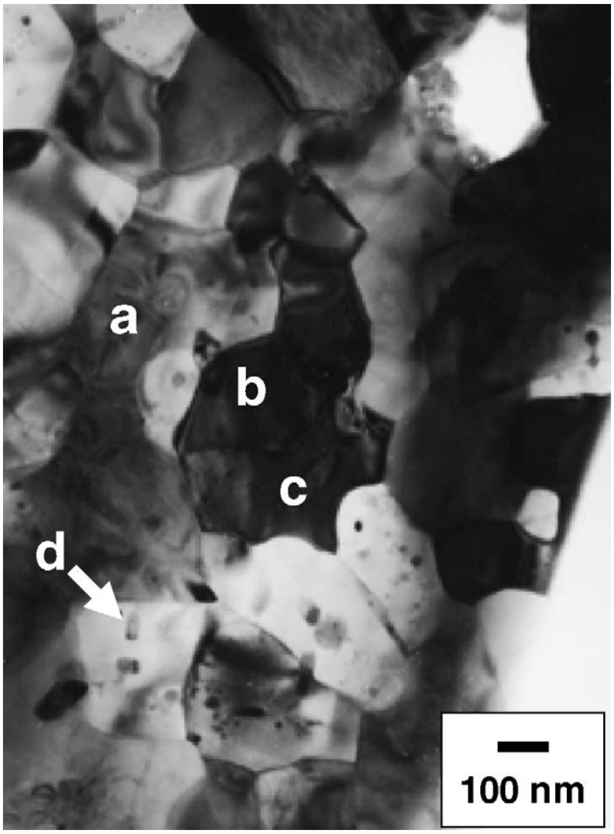

Fig. 6. Typical TEM image of the B_7S_3TS sample sintered at 1000 °C for 24 h, showing: (a) $BaAl_2Si_2O_8$; (b) (Ba, Sr)TiO_3 with Ba/Sr = 64/36; (c) (Ba, Sr)TiO_3 with Ba/Sr = 56/44; and (d) SnO_2 grains.

crystallization, for which the peaks marked with arrow corresponded to the crystallization of the perovskite phase.[10] Based on the liner shrinkage measurement of some glass powder compacts, it was recognized that the general relationship between densification and crystallization as mentioned above should necessarily hold for the present glass powders. That is, the higher the first crystallization temperature became, the higher the temperature at which shrinkage started proportionally and also the larger the total amount of shrinkage could be. Thus, the lowest value of the bulk density of B_7S_3TZ sample could be interpreted by the inhibited densification due to the lowest crystallization temperature among all the samples. It is concluded that the suppressed ε_r–T curve of the B_7S_3TZ sample could be attributed to the poor densification combined with less compositional homogeneity of the corresponding perovskite phase.

Typical microstructure observed with TEM is shown in Fig. 6 for the B_7S_3TS sample. It consisted of various crystalline phase without any detectable amorphous phase. Grain size of those crystals ranged from 100 to 400 nm. The outstanding feature of the microstructure was the presence of very small SnO_2 grains with about 50 nm in the long-axis, which distributed inside some grains. The elemental analysis of several perovskite grains showed an average value of about 60/40 for the Ba/Sr ratio calculated from relatively scattered ones. In addition, a very small fraction of the Sn signal was detected in the perovskite grains. Fig. 7 reveals the microwave tunability at 3 GHz as a function of dc vias voltage for the B_7S_3TS thick film sample (20 μm in thickness). This sample indicated 32% tunability under 50 kV/cm vias voltage. Comparing with the B_7S_3T thick film reported elsewhere,[5] a relatively larger vias voltage was needed to attain a comparable tunability for the B_7S_3TS sample obtained in the present study. Although the ferroelectric glass ceramics derived from glass powders in the BaO(SrO)–TiO_2(SnO_2)–SiO_2–Al_2O_3 system would be a candidate material for microwave tunable LTCC application, further examination on the relationship between tunable sensitivity of glass ceramics and their material characters including process parameters has to be made in detail.

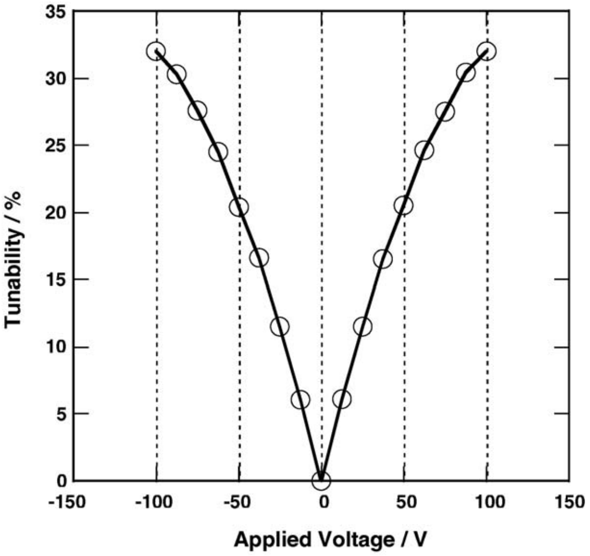

Fig. 7. Microwave tunability at 3 GHz as a function of dc vias voltage for the B_7S_3TS thick film sample.

4. Conclusion

Glass ceramics containing ferroelectric crystalline perovskite phase were fabricated from glass powders with a basic composition of $0.65(Ba_{1-x}Sr_x)TiO_3 \cdot 0.27SiO_2 \cdot 0.08Al_2O_3$. The effect of changing the glass compositions on the dielectric properties of the corresponding bulk samples was examined by the addition of SnO_2 or ZrO_2 combined with or without changing the Ba/Sr ratio. Little amount of Sn^{4+} or a small amount of Zr^{4+} might be incorporated into the Ti-site of the perovskite structure by heating at 1000 °C for 24 h. On the other hand, Sr^{2+} could easily and preferentially substitute for the Ba-site in both the Sn- and Zr-added samples. For bulk samples to which both Zr and Sr were simultaneously added, substantially suppressed ε_r–T curves were obtained, which might be attributed to poor densification and/or inhomogeneous formation of the ferroelectric perovskite phase. The combined addition of Sn and Sr components caused shifting of T_c towards higher temperature with higher ε_r at T_c, compared with those of the B_7S_3T sample. A thick film sample obtained from a glass powder with a starting composition of $0.65(Ba_{0.7}Sr_{0.3})(Ti_{0.85}Sn_{0.15})O_3 \cdot 0.27SiO_2 \cdot 0.08Al_2O_3$ showed microwave tunability of 32% at 3 GHz under 50 kV/cm vias voltage.

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