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Dielectric properties of (Ba, Sr)O–(Sm, La)$_2$O$_3$–TiO$_2$ ceramics at microwave frequencies

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The dielectric properties of (Ba, Sr)O–(Sm, La)$_2$O$_3$–TiO$_2$ material at microwave frequencies were investigated. By varying the amount of strontium from 0–25 mol % in the 0.15(Ba$_{1-x}$Sr$_x$)O–0.15Sm$_2$O$_3$–0.7TiO$_2$ composition, it was possible to adjust the frequency temperature coefficient, τ_f, from -13 p.p.m. °C^{-1} to $+30$ p.p.m. °C^{-1}. When 7 mol % Sr was substituted for barium, $\tau_f = 0$ p.p.m. °C^{-1} was obtained. TiO$_2$ with rutile phase ($\tau_f \approx 400$ p.p.m. °C^{-1}) acted as a dominant element in τ_f variation of the 0.15(Ba$_{1-x}$Sr$_x$)O–0.15(Sm$_{1-y}$La$_y$)$_2$O$_3$–0.7TiO$_2$ ($0 \leqslant x \leqslant 0.25$, $0 \leqslant y \leqslant 0.6$) system. Additionally, increasing the quantity of lanthanum substitution for samarium had a greater positive effect on τ_f than strontium substitution for barium. When 60 mol % La was substituted for samarium with 7 mol % Sr substitution barium, τ_f of the system reached 95 p.p.m. °C^{-1}. The effect on microwave dielectric characteristics of the 0.15(Ba$_{0.93}$Sr$_{0.07}$)O–0.15Sm$_2$O$_3$–0.7TiO$_2$ (BSST) ceramics by varying the calcination and/or sintering conditions or doping additives, were studied. The added SnO$_2$ acted as a firing agent to lower the sintering temperature, and the dielectric Q (Q_d) value was improved by properly adding CdO. With 1 wt % CdO addition, the highest Q_d value of the BSST resonator, after calcination at 1100 °C/2 h and sintering at 1370 °C/4 h, reached 4180 at 4 GHz with a small τ_f of -4 p.p.m. °C^{-1} and an ε_r of 80.7 was obtained.

1. Introduction

The use of dielectric material to act as a resonator was first proposed by Richtmyer [1] in 1939. In recent years, dielectric resonators (DRs) [2] with a small frequency temperature coefficient, τ_f, low loss and high permittivity (small size for a given resonant frequency) have been widely used as frequency-determining elements in microwave integrated circuits, such as dielectric resonator oscillators (DROs) [3], dielectric resonator filters (DRFs) [4], etc.

The TiO$_2$ material (rutile phase) was first found by Okaya [5] with a high Q_d value ($Q_d \approx 10000$) at 4 GHz. However, the frequency temperature coefficient, $\tau_f \approx +400$ p.p.m. °C^{-1}, was too large to be applied in practice. Until the last few years, DRs with a relative dielectric constant, ε_r, of around 20–90, such as complex perovskite structure [6], the ZrO$_2$–SnO$_2$–TiO$_2$ composition [7], and the BaO–Re$_2$O$_3$–TiO$_2$ (Re = La, Nd, Sm, etc.) system [8–12] have been studied for more practical uses at broadband frequencies. The BaO–Sm$_2$O$_3$–TiO$_2$ system with high permittivity (ε_r = 70–90) was commonly applied in the 800 MHz mobile telephone system, *L* (1–2 GHz), or *S* (2–4 GHz) band frequencies for miniaturizing circuit dimensions.

The main intention in the present work was to survey the microwave dielectric properties of (Ba, Sr)O–(Sm, La)$_2$O$_3$–TiO$_2$ material and to determine its best composition with the fabrication process. Moreover, the effect of lanthanum substitution for samarium, strontium substitution for barium, the second phases and doping additives of CdO and SnO$_2$ on the BaO–Sm$_2$O$_3$–TiO$_2$ system were also studied.

2. Experimental procedure

Samples were prepared from reagent-grade BaCO$_3$, SrCO$_3$, TiO$_2$, Sm$_2$O$_3$ and La$_2$O$_3$. The purity of these raw powders were higher than 99.9%. In accordance with the 0.15BaO–0.15Sm$_2$O$_3$–0.7TiO$_2$ composition investigated by Nishigaki *et al.* [8], the raw materials prepared for experiments were weighed to the system of 0.15(Ba$_{1-x}$Sr$_x$)O–0.15(Sm$_{1-y}$La$_y$)$_2$O$_3$–0.7TiO$_2$ ($0 \leqslant x \leqslant 0.25$, $0 \leqslant y \leqslant 0.6$).

The starting powders were mixed in a plastic jar with agate balls for 15 h. After drying, the powder was then calcined from 1000–1150 °C for 2 h. Subsequently, organic binder was added to produce granulation. Cylindrical specimens were pressed under a pressure of 2500 kg cm^{-2} then debindered at 600 °C 20 h^{-1}. Afterwards, these pellets were sintered in air between 1350 and 1390 °C for 4 h.

The post method, first introduced by Hakki and Coleman [13] and then modified by Courtney [14] and Kobayashi and Katoh [15], was applied with a radial dielectrometer (Fig. 1) to estimate the relative dielectric constant, ε_r, of a DR. The ε_r of a cylindrical DR can be accurately determined by measuring the

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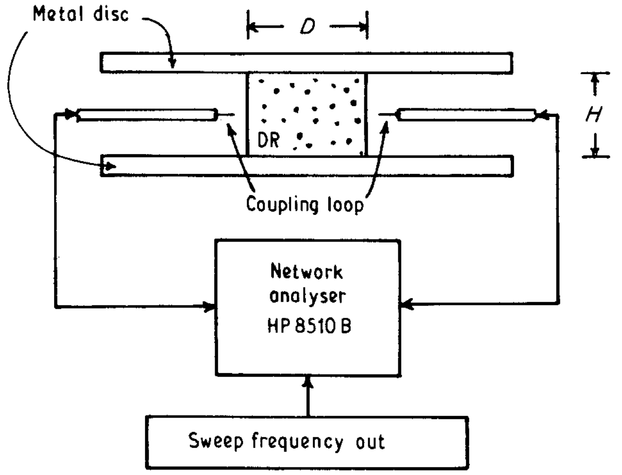

Figure 1 The post method with a radial dielectrometer for microwave dielectric measurements.

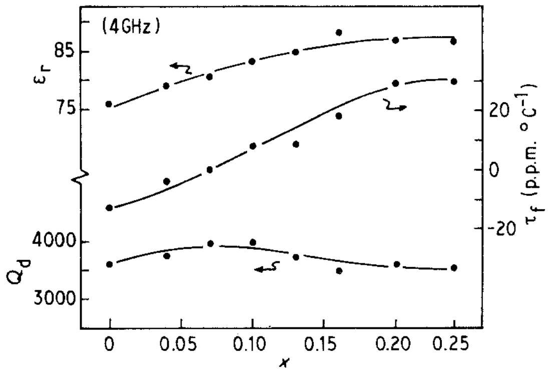

Figure 2 Dielectric characteristics of the $0.15(Ba_{1-x}Sr_x)O$–$0.15(Sm_{1-y}La_y)2O_3$–$0.7TiO_2$ ceramics with various strontium substitutions while $y = 0$.

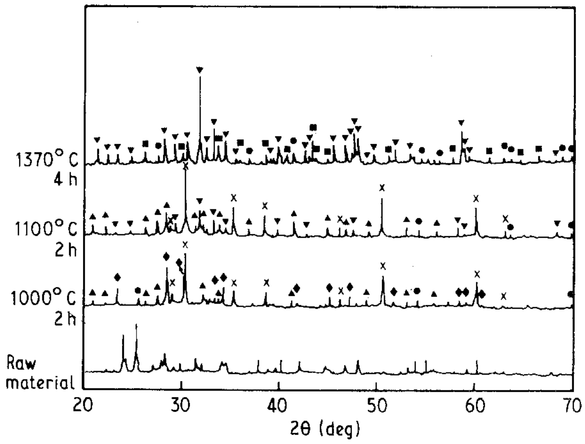

Figure 3 XRD patterns of the $0.15(Ba_{0.93}Sr_{0.07})O$–$0.15Sm_2O_3$–$0.7TiO_2$ (BSST) dielectric ceramics: (▲) $Ba_4Ti_{13}O_{30}$, (×) $Sm_2Ti_2O_7$, (▼) BaO–Sm_2O_3–$5TiO_2$, (■) $Ba_2Ti_9O_{20}$, (◆) $BaTi_4O_9$, (●) TiO_2 (rutile).

resonant frequency of the TE_{011} mode and verified by other resonant modes. The Kobayashi and Katoh's method [15] and Courtney's method [14] were also utilized in this work, for measuring DR Q_d and τ_f values, respectively. Experimental equipment for measuring the microwave dielectric properties of DRs include the HP8510B network analyser and the HP8350B + HP83592A sweep oscillator.

X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), and electron probe microanalysis (EPMA), which includes wavelength X-ray spectrometry (WDS) and energy dispersive X-ray spectrometry (EDS) were utilized to investigate the microstructures of the dielectric materials.

3. Results and discussion

The results in Fig. 2 show that ε_r, τ_f and Q_d are functions of strontium substitution in the $0.15(Ba_{1-x}Sr_x)O$–$0.15(Sm_{1-y}La_y)_2O_3$–$0.7TiO_2$ system with $y = 0$. When the strontium quantity substituted increased from 0–25 mol %, τ_f increased from -13 to $+30$ p.p.m. °C^{-1} in which the Q_d value was in the range 3500–3950, and ε_r increased ranging from 76 to 88. Evidently, the extent of the available τ_f of a DR offers more space to compensate for a circuit's frequency temperature drift.

The existent main phase and second phases of $0.15(Ba_{1-x}Sr_x)O$–$0.15(Sm_{1-y}La_y)_2O_3$–$0.7TiO_2$ (at $x = 0.07$ and $y = 0$) composition were identified from the XRD patterns in Fig. 3. After calcination at 1050 °C/2 h and sintering at 1370 °C/4 h, the composition $0.15(Ba_{0.93}Sr_{0.07})O$–$0.15Sm_2O_3$–$0.7TiO_2$ (BSST) had $\tau_f \approx 0$ p.p.m. °C^{-1} and $Q_d = 3950$. The main whisker-shaped crystals of the BSST were (Ba, Sr)O–Sm_2O_3–$5TiO_2$ (Fig. 4a, b). In addition, small amounts of the second phases of $Ba_2Ti_9O_{20}$ and TiO_2 (rutile) were found randomly dispersed in the bulk (Fig. 4c, $x = 0.07$; Fig. 4d, $x = 0.15$).

The BSST composition is located on the tie line between the ternary phases of BaO–Sm_2O_3–$3TiO_2$ and BaO–Sm_2O_3–$5TiO_2$. Strontium dissolved in the main phase forming a solid solution of (Ba, Sr)O–Sm_2O_3–$5TiO_2$; however, a small content of strontium was difficult to detect by EPMA. According to the chemical balance theory of composition, the ternary phase of (Ba, Sr)O–Sm_2O_3–$5TiO_2$ should contain some samarium-rich and titanium-deficient compound to compensate for the segregation of TiO_2 and $Ba_2Ti_9O_{20}$. Hence, the excess samarium seems to form a substitutional solid solution as the matrix [8] in (Ba, Sr)O–Sm_2O_3–$5TiO_2$ with titanium deficiency. The XRD pattern (Fig. 3) of the BSST ceramics (1370 °C/4 h) showed that it coincided approximately with the ternary phase BaO–Sm_2O_3–$5TiO_2$, which was same as the orthorhombic structure of BaO–Nd_2O_3–$5TiO_2$ [12].

Compared with Fig. 4c (Sr = 7 mol %), the second phases of the $0.15(Ba_{1-x}Sr_x)O$–$0.15Sm_2O_3$–$0.7TiO_2$ composition in Fig. 4d (Sr = 15 mol %) obviously increased, making τ_f of the DR more positive. Based on the logarithmic mixing rule, Wu and Chang [10] determined τ_f of the BaO–Sm_2O_3–$5TiO_2$ crystal to be -30 p.p.m. °C^{-1}. However, owing to the presence of $Ba_2Ti_9O_{20}$ [16] and TiO_2 (rutile) phases having $\tau_f \approx 15$ p.p.m. °C^{-1} and 400 p.p.m. °C^{-1}, respectively, the amount of these second phases had positive contributions in τ_f of the BSST dielectric resonator. In

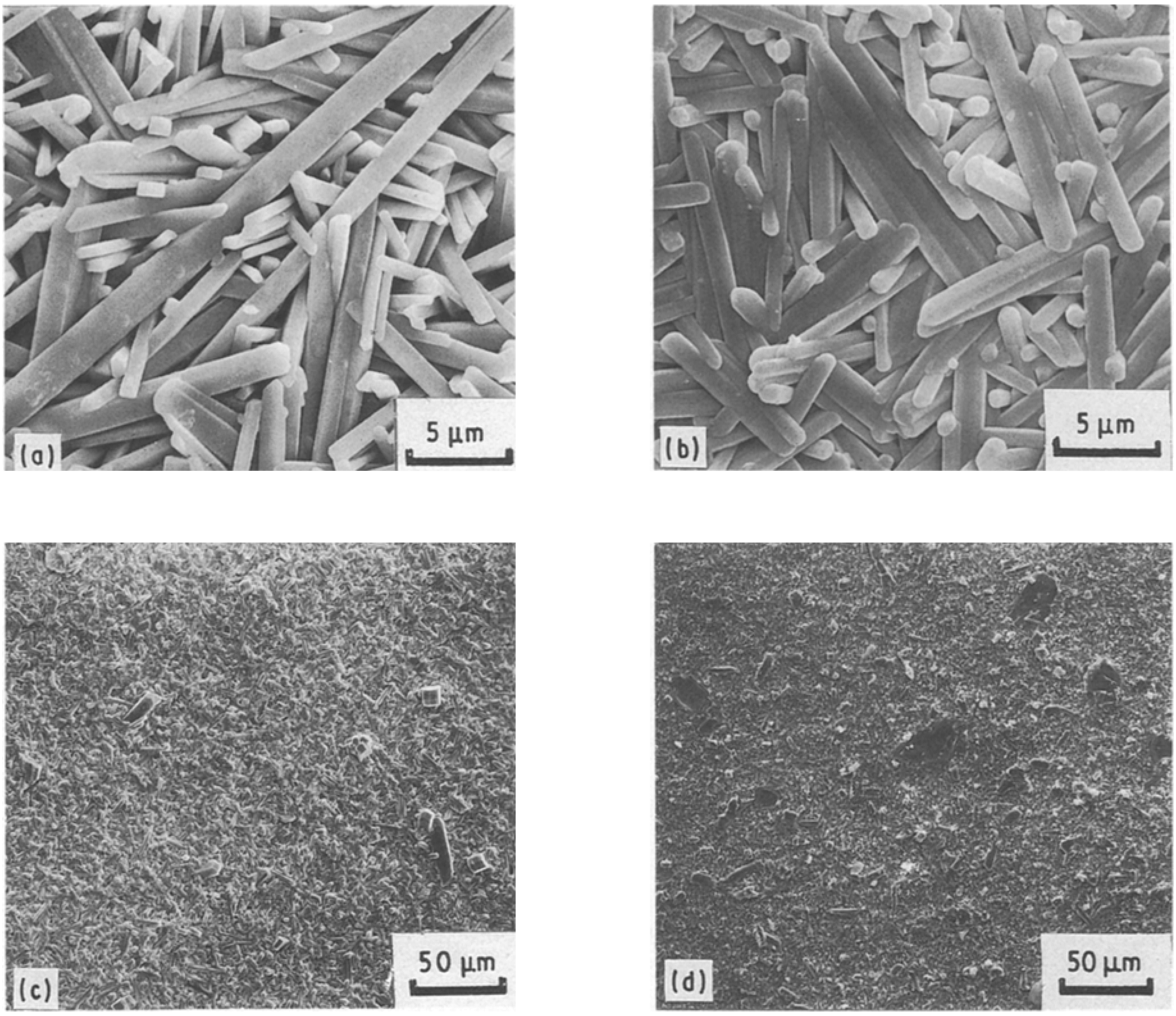

Figure 4 The uniform crystals in the DRs of $0.15(Ba_{1-x}Sr_x)O$–$0.15Sm_2O_3$–$0.7TiO_2$ calcined at 1050 °C 2 h^{-1}. (b, c) $x = 0.07$, sintered at 1370 °C/4 h; (a) $x = 0.07$, sintered at 1390 °C/4 h; (d) $x = 0.15$, sintered at 1370 °C/4 h.

particular, the larger the quantity of TiO_2 (rutile), the more positive was the τ_f.

The existent phases of the BSST ceramics (1370 °C/4 h) were mainly (Ba, Sr)O–Sm_2O_3–$5TiO_2$ accompanied by a small amount of $Ba_2Ti_9O_{20}$ and TiO_2 phases (Fig. 3). The XRD patterns in Fig. 3 indicated that if the BSST powder was calcined at 1000 °C/2 h or 1100 °C/2 h, intermediate phases of $Sm_2Ti_2O_7$, $BaTi_4O_9$ and $Ba_4Ti_{13}O_{30}$ appeared, and then were consumed after sintering at 1370 °C/4 h. The X-ray line profile obtained by WDS shown in Fig. 5 confirmed the existent TiO_2 phase (long, dark) in the BSST ceramics, and this phase was also proved by EDS analysis.

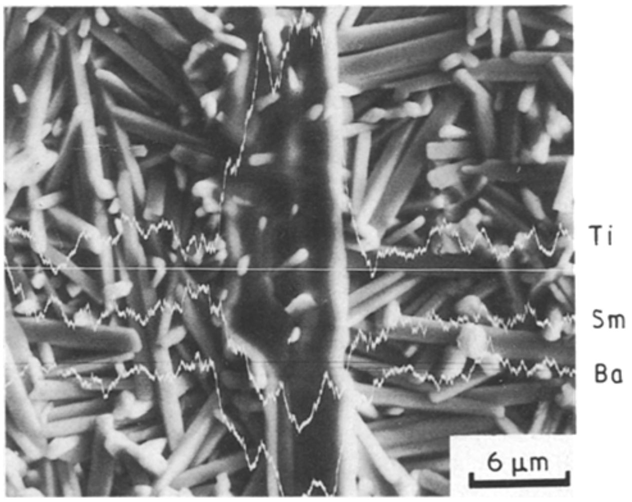

Figure 5 The TiO_2 phase in the BSST dielectric resonator analysed by WDS X-ray line profile.

After sintering at 1390 °C for 4 h, the voids became more prominent as the length of the whisker-shaped crystals increased. The main whisker-shaped crystals grew in the longitudinal direction (Fig. 4a, b) at the expense of short ones, which produced new voids in which short crystals were originally located. As long crystals came into contact with others, the sintered specimen expanded and the bulk density decreased. The size distribution of the whisker-shaped crystals was mainly determined by the sintering temperature, where the crystals in Fig. 4a (1390 °C/4 h) were greater than in Fig. 4b (1370 °C/4 h). Fig. 6 ($d_{1370\,^{\circ}C} > d_{1350\,^{\circ}C} > d_{1390\,^{\circ}C}$) indicates that the bulk density, d, of the BSST resonator was related to its sintering temperature and sintering time.

The microwave properties of the BSST dielectric resonators under various calcination and sintering conditions are shown in Table I. ε_r of a DR was

TABLE I Microwave dielectric properties of the $(Ba_{0.93}Sr_{0.07})O$–Sm_2O_3–$5TiO_2$ (BSST) ceramics under various calcination and sintering conditions

Calcination temp. (°C/2 h)	Sintering temp. (°C)	Sintering time (h)	τ_f (p.p.m. °C^{-1})	d (g cm^{-3})	Q_d	ε_r
1000	1350	4	− 8	5.61	3710	77.8
	1370	4	− 5	5.52	3820	79.2
	1390	4	− 2	5.54	3780	78.3
1050	1350	4	− 7	5.63	3850	79.6
	1370	4	0	5.62	3950	81.4
	1390	4	+ 3	5.51	4020	78.3
1100	1350	4	− 4	5.60	3920	78.6
	1370	4	+ 3	5.68	4080	79.5
	1390	4	− 6	5.42	3540	77.7
1150	1350	4	− 9	5.57	3420	79.1
	1370	4	+ 5	5.50	3300	80.3
	1390	4	+ 13	5.41	3160	78.0

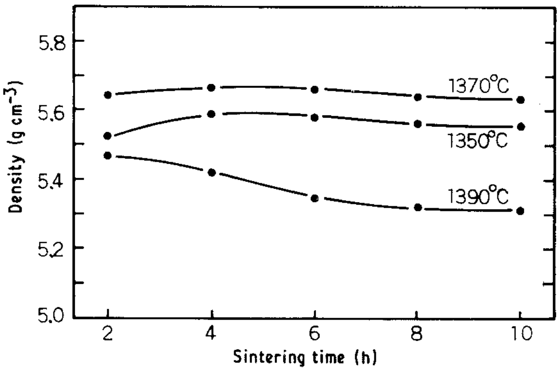

Figure 6 Variation of bulk density, d, of the BSST ceramics versus sintering time at various temperatures, after calcining at 1100 °C/2 h.

TABLE II Microwave dielectric properties of the 0.15 $(Ba_{0.93}Sr_{0.07})O$–$0.15(Sm_{1-y}La_y)_2O_3$–$0.7TiO_2$ (BSSLT) ceramics with various lanthanum substitutions

y	d (g cm^{-3})	τ_f (p.p.m. °C^{-1})	Q_d	ε_r
0.2	5.54	+ 21	4020	83.7
0.4	5.51	+ 48	3990	85.0
0.5	5.49	+ 82	4120	85.8
0.6	5.48	+ 95	4170	86.2

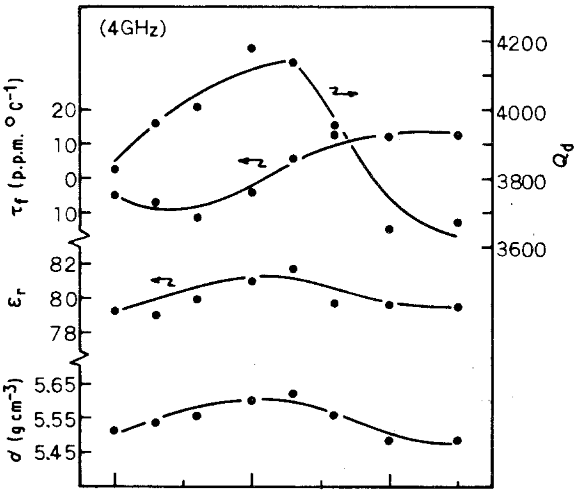

Figure 7 Microwave dielectric properties (ε_r, Q_d, and τ_f) of the BSST ceramics doped with various quantities of CdO.

generally proportional to the bulk density, d, especially for the specimens sintered at 1390 °C, at which lower ε_r and bulk density were obtained. The Q_d qualities in Table I primarily ranged from 3700–4100, and the highest value was 4080 with the BSST dielectric resonator calcined at 1100 °C/2 h and sintered at 1370 °C/4 h.

τ_f values in Table I seemingly possessed no regular relationship with the calcination and sintering temperature. Actually, τ_f of a DR is a function of the thermal expansion coefficient, α, and the temperature coefficient of ε_r (τ_ε), i.e. $\tau_f \approx -(\alpha + \frac{1}{2}\tau_\varepsilon)$ [17]. The Q_d value in Table I generally decreased with the fall in bulk density, except for the samples calcined at 1050 °C/2 h and 1150 °C/2 h. Easier moisture absorption of the DRs with lower density might explain the decrease of the Q_d value, in particular for specimens sintered at 1390 °C/4 h but calcined at 1100 °C/2 h or 1150 °C/2 h.

Table II shows the microwave properties of 0.15 $(Ba_{0.93}Sr_{0.07})O$–$0.15(Sm_{1-y}La_y)_2O_3$–$0.7TiO_2$ (BSSLT) ceramics with various lanthanum substitution for samarium. Experimental results indicated that increasing the quantity of lanthanum substitution for samarium ($0 \leq y \leq 0.6$) had a greater effect on τ_f than strontium substitution for barium. With 60 mol % La substitution, the former had τ_f up to 95 p.p.m. °C^{-1}. From SEM surface observation, the quantity of the TiO_2 second phase ($\tau_f \approx 400$ p.p.m. °C^{-1}) obviously increased. The dielectric constant, ε_r, in Table II increased with the decreasing bulk density. These phenomena might be due to the fact that TiO_2 possesses a higher dielectric constant ($\varepsilon_r \approx 100$) and lower theoretical density ($d = 4.25$ g cm^{-3}).

With 1.5 wt % SnO_2 added in the BSST composition, ε_r and τ_f were found to be not sensitive to this additive. However, the sintering temperature could be reduced to 1300 °C without apparent degradation of Q_d. When more SnO_2 was added, the grain size increased and bulk density decreased under the same sintering conditions. Added SnO_2, therefore, was thought to act as a firing agent for the BSST ceramics. The dielectric characteristics of the BSST material doped with CdO are shown in Fig. 7, in which Q_d can be improved to 4180 with 1 wt % CdO addition. Nevertheless, a larger quantity of this additive leads to a drastic drop in Q_d. When the doping amount of CdO was more than 0.6 wt %, τ_f of the BSST resonators increased; ε_r also gradually increased to 81.7 when the dopant amount increased to 1.3 wt %. Yet, the Q_d value reduced when > 1 wt % CdO was added. These results, caused by doping with CdO in the BSST system, might reflect the microstructural alternation which warrants further study.

4. Conclusion

A frequency temperature coefficient, τ_f, of 0 p.p.m. $°C^{-1}$ was obtained when 7 mol % Sr was substituted for barium in the $0.15(Ba_{1-x}Sr_x)O$–$0.15(Sm_{1-y}La_y)_2O_3$–$0.7TiO_2$ system with $y = 0$. It was possible to adjust τ_f from -13 to $+30$ p.p.m. $°C^{-1}$ when the amount of strontium was increased from 0 and 25 mol %. The variation of microwave dielectric properties of the $0.15(Ba_{1-x}Sr_x)O$–$0.15Sm_2O_3$–$0.7TiO_2$ composition on strontium substitution for barium might be interpreted as a consequence of the TiO_2 rutile phase ($\varepsilon_r = 100$, $\tau_f \approx 400$ p.p.m. $°C^{-1}$, $Q_d = 10000$ at 4 GHz) in the bulk.

In the $0.15(Ba_{1-x}Sr_x)O$–$0.15(Sm_{1-y}La_y)_2O_3$–$0.7TiO_2$ system at $x = 0.07$ (BSSLT), increasing the amount of lanthanum substitution for samarium had greater positive effect on τ_f than strontium substitution for barium in the system at $y = 0$. When 60 mol % La was substituted for samarium, τ_f of the BSSLT resonator increased to 95 p.p.m. $°C^{-1}$. The amount of segregation of the TiO_2 was thought to be a major factor affecting τ_f of the BSSLT system. Because the TiO_2 second phase has a lower theoretical density ($d = 4.25$ g cm^{-3}) and a higher dielectric constant ($\varepsilon_r = 100$), the ε_r of the BSSLT dielectric resonators increased as the bulk density decreased.

The dielectric Q (Q_d) value of the $0.15(Ba_{0.93}Sr_{0.07})O$–$0.15Sm_2O_3$–$0.7TiO_2$ (BSST) ceramics was improved with a proper amount of CdO addition. The added SnO_2 acted as a firing agent in lowering the sintering temperature for the BSST ceramics. With 1 wt % CdO addition in the BSST composition, the highest Q_d value reached was 4180 (at 4 GHz) with $\varepsilon_r = 80.7$, and a small τ_f of -4 p.p.m. $°C^{-1}$ was obtained.

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