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Calcium-doping effect on temperature coefficients of dielectric constants in $SrTiO_3$ capacitors

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$SrTiO_3$ ceramic capacitors were studied to improve the temperature coefficient, τ, of dielectric constants without decreasing the dielectric constants. It was indicated that an addition of calcium in an insulating reagent improved τ. From scanning electron microscopy and energy-dispersive X-ray analysis measurements, the origin of this improvement was ascribed to the following layers: (1) the oxide layers which were formed at the grain boundaries, and (2) the bismuth-oxide layers which were formed on the sample surface.

1. Introduction

$SrTiO_3$ capacitors [1] are used in electronic circuits for electro-magnetic interference (EMI). This capacitor material is also used as a capacitive varistor [2] because it has a high apparent dielectric constant together with non-linear current–voltage characteristics. The $SrTiO_3$ capacitors have smaller volume compared to other capacitors with the same capacitance. The temperature coefficient, τ, of the apparent dielectric constant is about -1600 p.p.m. K^{-1} [3, 4] which is smaller than that of a $BaTiO_3$ capacitor but much larger than that of other bulk capacitors [5, 6]. In order to improve this temperature coefficient, τ, calcium ions are normally doped to substitute strontium sites [7, 8].

From an industrial point of view, it is necessary to improve τ without decreasing the capacitance. In this work, it was shown that such improvement was made possible by controlling the insulating layers formed at the grain boundaries and the bismuth-oxide layers formed on the sample surface.

2. Experimental procedure

2.1. Sample preparation

Starting materials were $SrCO_3$, $CaCO_3$, TiO_2 (99.9%), and Nb_2O_5 (99.99%). These materials were weighed in the following ratio: $SrCO_3 : CaCO_3 : TiO_2 : Nb_2O_5 = 1 - X : X : 1 : 0.004$ where X was 0.025, 0.05, 0.075, 0.1 and 0.15. The starting materials were mixed in a plastic mill of 500 cm^3 with 200 ml pure water and nylon balls for 20 h.

The mixed slurry was dried at 398 K for 20 h. The dried powder was calcined in an alumina crucible at 1423 K for 4 h. After being roughly crushed in an agate motar, the powder was similarly mixed with pure water into the slurry form. The slurry was dried again and granulated with a polyvinyl alcohol solution. The powder was pressed under 180 MPa into discs of 10 mm diameter and 0.7 mm thick. The discs were calcined at 1273 K for 4 h in air and sintered in a molybdenum furnace at 1813 K for 4 h. The flowing gas used was 95% N_2, 5% H_2 and then was saturated with water vapour at 275 K.

An insulating reagent was smeared on to the sintered disc. Two types of insulating reagents were used: one was a mixture of 50 mol % Bi_2O_3 and 50 mol % CuO (sample A) and the other was a mixture of 47.5 mol % Bi_2O_3, 47.5 mol % CuO and 5 mol % $CaCO_3$ (sample B). The amount of insulating reagents was varied between 1.5 and 9.0 wt % to disc weight.

Both types of smeared discs were fired at 1373 K for 1 h in air. The ramping and cooling rate for both was 200 K h^{-1}. After this insulating process, silver paste was painted on to both sides of the discs and fired at 1053 K for 20 min in air.

The sample surface was observed by back-scattering electron microscopy (BSE) and analysed by energy-dispersive-X-ray analysis (EDX).

2.2. Measurements

Capacitance and dielectric loss, tan δ, of the samples were measured by an impedance analyser (YHP, 4192A) at room temperature; the measuring frequency was 1 kHz and the amplitude was 0.1 V. Resistance was evaluated from the current at 1 min after a d.c. bias of 25 V was applied.

3. Results and discussion

3.1. Effect of calcium doped in the starting materials on dielectric properties

Fig. 1 indicates electric properties as a function of the calcium content doped in the starting materials

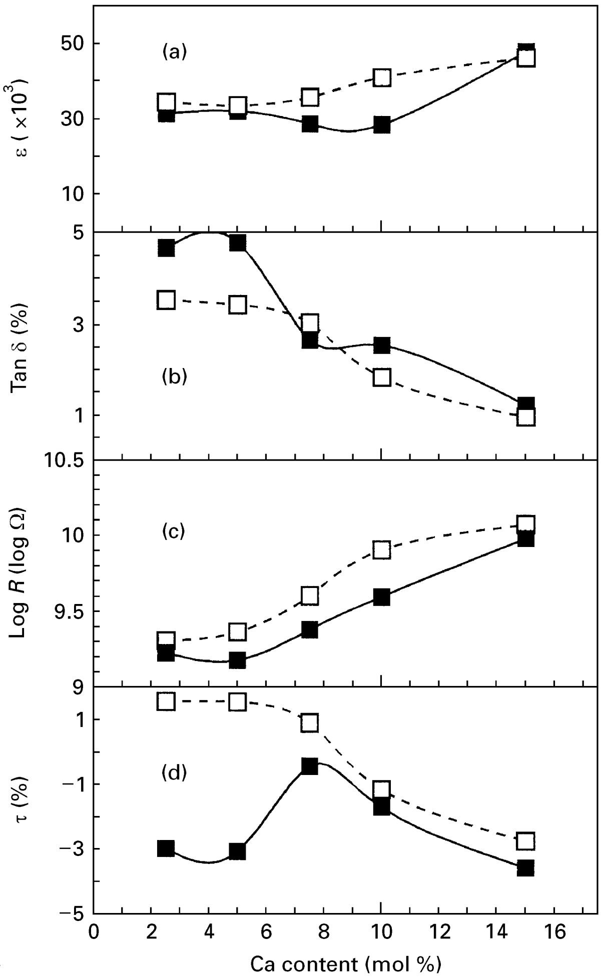

Figure 1 Dielectric properties of $(Sr_{1-x}Ca_x)TiNb_{0.004}O_3$. (–■–) Properties of the samples made by using the insulating reagent A (50% Bi_2O_3 and 50% CuO); (– –□– –) properties of samples made by using the insulating reagent B (47.5% Bi_2O_3, 47.5% CuO and 5% $CaCO_3$).

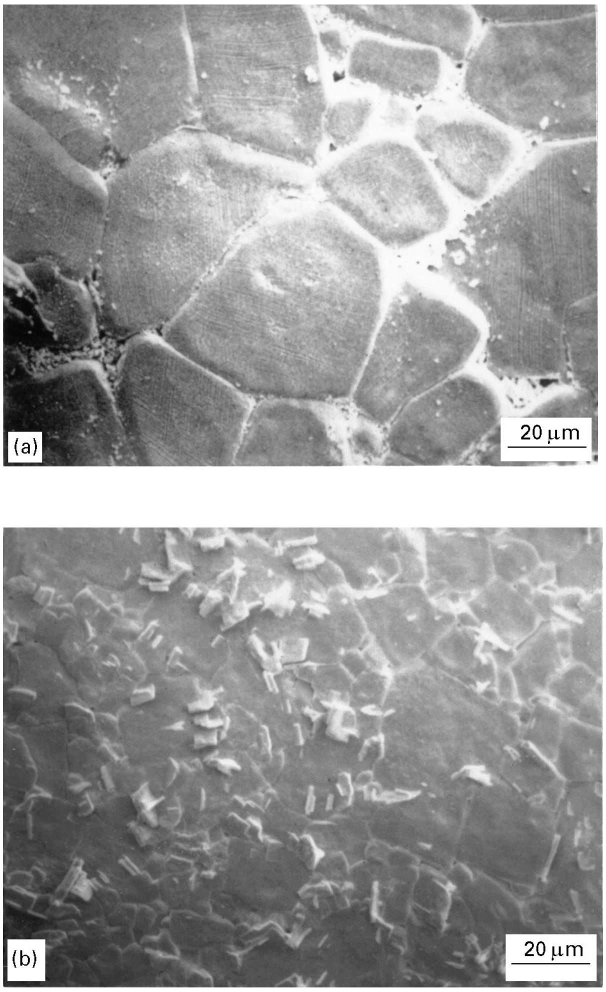

Figure 2 Secondary electron microscopy images of sample surfaces after the sample was insulated at 1373 K. (a) Insulating reagent A (50% Bi_2O_3 and 50% CuO). (b) Insulating reagent B (47.5% Bi_2O_3, 47.5% CuO and 5% $CaCO_3$).

(sample A). The apparent dielectric constant, ε (Fig. 1a) was about 40 000, and increased with increasing calcium content. The dielectric loss (Fig. 1b) decreased with increasing calcium content and it reached a minimal value (1%) at a calcium content of 15%. On the contrary, the resistance (Fig. 1c) was increased from 10^9 Ω to 10^{10} Ω corresponding to an increase of calcium content. The temperature coefficient, τ (Fig. 1d) was −3% at a calcium content of 2.5% and reached an optimal value (−0.7%) at a calcium content of about 7.5%; it was decreased to −4% with further increase of calcium content.

Thus, the calcium content doped in the starting material was fixed to 7.5% where the temperature, τ, was optimal, that is, the sintered body was hereafter $(Sr_{0.925}Ca_{0.075})TiNb_{0.004}O_3$.

3.2. Effect of calcium involved in the insulating reagent on dielectric properties

In the $SrTiO_3$ capacitor, the insulating layers are formed at the grain boundaries whose properties are important to improve the electric characteristics. It is therefore considered that the control of the Ca/Sr ratio in the insulating layers formed at the grain boundaries is important to cause smaller τ. Calcium ions were mixed into the insulating reagent (B) in order to improve the total device property.

The electrical properties measured are also shown in Fig. 1. The calcium content dependencies of ε, tan δ and *R* were similar to the electrical properties for sample B. However the behaviour of τ was very different. τ increased + 1.5% at a calcium content of about 2.5% and decreased to −3% with increasing calcium content. This result therefore indicates that the optimal condition for τ (i.e. τ ∼ 0) can be obtained by controlling the calcium content in the insulating reagent.

According to SEM observations, the sample surface of A (Fig. 2a) was not different from that of the as-sintered sample. However, with regard to sample B, which involved the calcium ions in the insulating reagent, a secondary phase with bright contrast was observed on the surface as shown in Fig. 2b. Fig. 3a shows part of Fig. 2b; its spatial distributions for bismuth and calcium ions were measured by EDX and are shown in Fig. 3b and c, respectively. From these figures, it is thought that the bismuth oxide phase, whose shape was flake-like, was formed on the surface

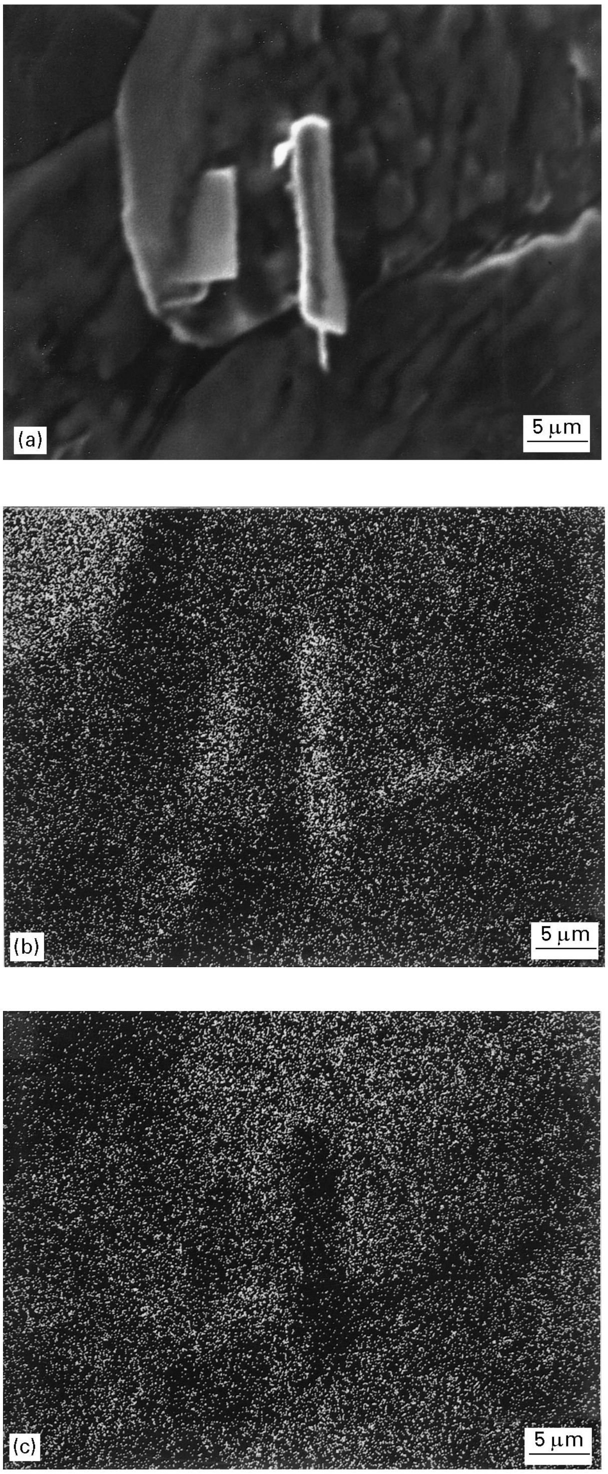

Figure 3 SEM and EDX images of bismuth oxide phase on the sample insulated at 1373 K (insulating reagent B: 47.5% Bi_2O_3, 47.5% CuO and 5% $CaCO_3$). (a) SEM image, (b) bismuth image by energy dispersive X-ray mapping, (c) calcium image by energy dispersive X-ray mapping.

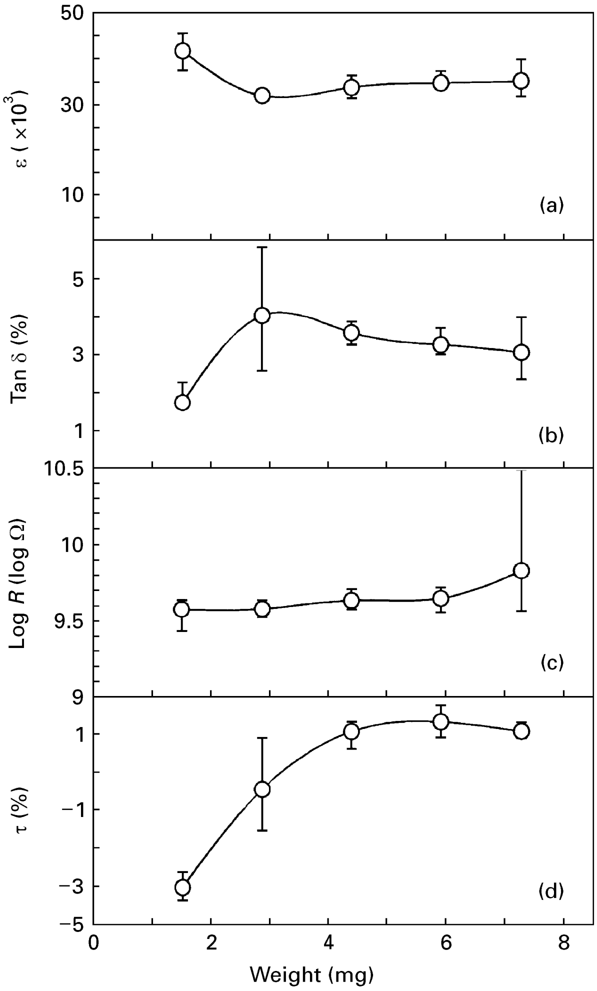

Figure 4 Dielectric properties versus weight of the insulating reagent B (47.5% Bi_2O_3, 47.5% CuO and 5% $CaCO_3$) per 1 g sintered sample, $(Sr_{0.925}Ca_{0.075})TiNb_{0.004}O_3$.

of sample B, the phase which causes τ to be smaller without reducing other electrical properties. After this insulating process, a small amount of bismuth oxide phase appeared on the surface of sample B.

3.3. Effect of amounts of insulating reagent on dielectric properties

τ was measured as a function of the amount of the insulating reagent smeared on the samples. Electrical properties measured are shown in Fig. 4. The dielectric constant, ε, was decreased from 50 000 to 35 000 with insulating reagent B, and the resistance, *R*, was increased from 4×10^9 to 6×10^9 Ω with insulating reagent.

The temperature dependence of $\Delta C/C$ is shown in Fig. 5 as a function of the amount of insulating reagents. τ ($T = 393$ K), changing from −3% to +1% with the amount of insulating reagent, corresponds to Fig. 4d. $\Delta C/C$–T curves are found to be flat in the region of 30–45 mg per 1 g sintered sample.

Back-scattered electron (BSE) images of the surfaces of three samples are shown in Fig. 6. Fig. 6a–c correspond to the samples on which insulating reagent B was smeared in amounts of (a) 15, (b) 45 and (c) 90 mg per 1 g sintered ceramics. It was determined that the amount of bright rectangular phases increased with the amount of insulating reagent.

The results of point analysis by EDX are given in Table I. The numbers 1, 2 and 3 in the table accord with the numbers 1, 2 and 3 in Fig. 6, respectively. It was determined that the oxide formed on the surfaces consisted of bismuth, strontium and titanium ions; the strontium content was decreased with the amount of insulating reagent and that of bismuth was inversely increased. The calcium content in the oxide phase did

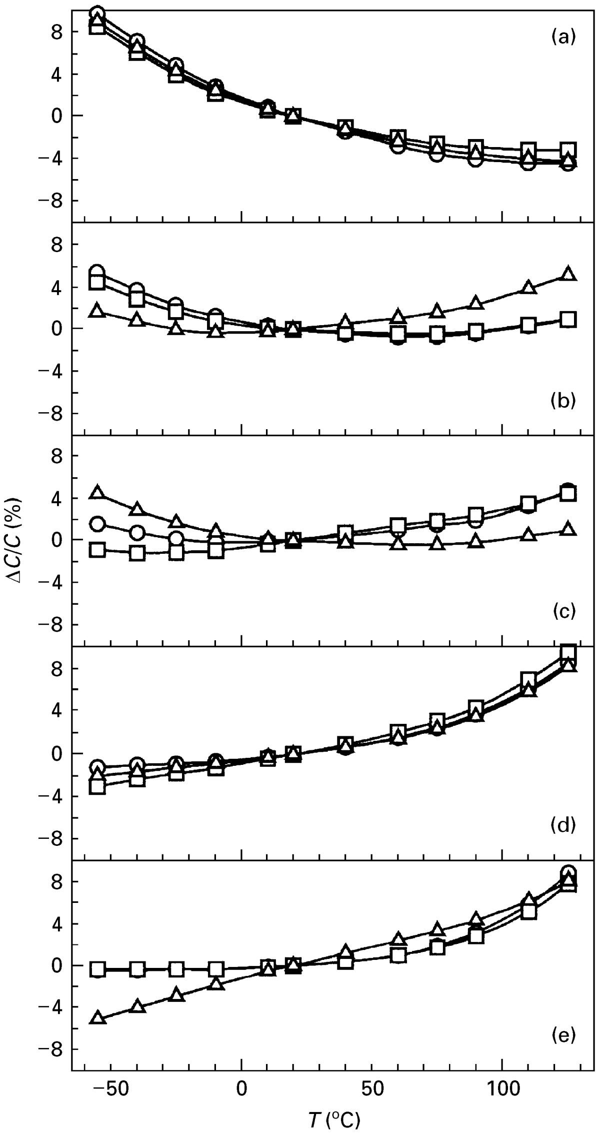

Figure 5 Temperature coefficients of dielectric constant versus weight of the insulating reagent B. The sintered body was the same as given in Fig. 4. Smeared amounts of insulating reagent per 1 g sintered sample, were (a) 18 mg, (b) 36 mg, (c) 54 mg, (d) 72 mg, and (e) 90 mg.

not vary. The layers formed at the grain boundaries by insulating reagent B was $SrBi_4Ti_4O_{15}$ or one of the other Bi–Ti oxides [9, 10].

τ for these oxides has a plus sign. However, τ for the bismuth oxide phases formed on the sample surface, slightly conceivably has a slightly minus sign. The amount of bismuth oxide phase formed on the sample surface increased with the amount of insulating reagent B.

Because such Bi–Ti oxides are generally insulating, calcium ions do not vary the resistance and capacitance even if they diffuse into the grain boundaries. However, calcium ions make Sr–Ca–Bi–Ti oxide, in which τ has a slightly minus sign, on the sample surface. The sign of τ at the grain boundaries is inverse to the sign of that on the surface, and thus τ of the Sr–Ca–Bi–Ti oxide on the sample surface compensates τ at the grain boundaries.

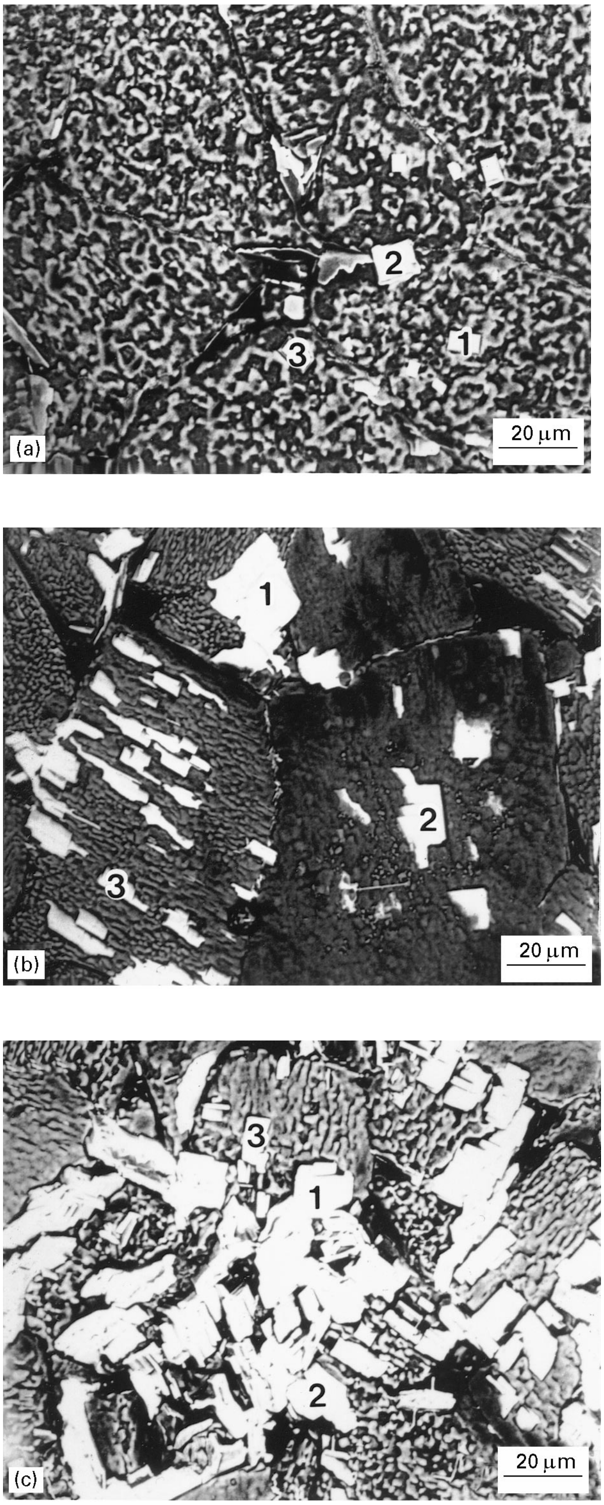

Figure 6 Back-scattered electron images of sample surfaces when the weight of the insulating reagent B varies. The sintered body was the same as given in Fig. 4. Smeared amounts of insulating reagent per 1 g of the sintered sample were (a) 18 mg, (b) 54 mg, and (c) 90 mg.

4. Conclusion

We attempted to improve the temperature coefficient, τ, of the apparent dielectric constant of $SrTiO_3$ capacitors. From SEM and EDX measurements, an addition of calcium in an insulating reagent acted to form bismuth oxide on the surface of the sintered sample and to improve τ. This change of τ was ascribed to the formation of two layers: one was the oxide phase

TABLE I Energy-dispersive X-ray analysis of bismuth oxides formed on sample surfaces when the weight of the insulating reagent B varies. The sintered body was the same as given in Fig. 4. The numbers 1, 2 and 3 in the table accord with numbers 1, 2 and 3 in Fig. 6, respectively

Smeared amount of insulating reagent (mg/g sample)	Point 1	Point 2	Point 3	Average
18				
Sr	6.00	6.59	6.10	6.23
Ca	3.63	3.03	2.85	3.17
Ti	22.02	22.26	22.06	22.11
Bi	5.87	5.59	6.36	5.94
Bi/(Sr + Ca)	0.58	0.58	0.71	0.63
Ti/(Sr + Ca)	2.3	2.3	2.3	2.4
54				
Sr	4.95	5.24	5.21	5.13
Ca	1.87	2.78	1.98	2.21
Ti	22.31	21.70	22.16	22.06
Bi	7.77	7.54	7.65	7.65
Bi/(Sr + Ca)	1.1	0.94	1.1	1.0
Ti/(Sr + Ca)	3.3	2.7	3.1	3.0
90				
Sr	3.72	4.66	4.54	4.31
Ca	2.14	2.76	2.24	2.38
Ti	21.90	21.72	21.94	21.85
Bi	9.03	8.00	8.25	8.43
Bi/(Sr + Ca)	1.5	1.1	1.2	1.3
Ti/(Sr + Ca)	3.7	2.9	3.2	3.3

which was formed at the grain boundaries by the insulating reagent, and the other layer was the bismuth oxide phase which was formed on the sample surface. It was determined that the temperature coefficient of the $SrTiO_3$ capacitor could be controlled by the amount of insulating reagent smeared on the surface.

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