

Properties of SrTiO₃ based relaxors

Yukio Sakabe, Kunisaburo Tomono, Yukio Hamaji, Hirotsugu Yano and Kikuo Wakino

Murata Manufacturing Co., Ltd., 2-26-10 Tenjin, Nagaokakyo-shi, Kyoto, 617, Japan

Relaxor dielectric ceramics of SrTiO₃-Bi₂O₃-2TiO₂ modified with MgO and PbO were studied. Addition of MgO and PbO increased the dielectric constant from original value of 1000 up to 4200 with stable temperature dependence, and also prolonged the relaxation time. Activation energies of relaxation time were 0.27 eV and 0.39 eV for SrTiO₃-Bi₂O₃-2TiO₂ and SrTiO₃-Bi₂O₃-2TiO₂-MgO-PbO, respectively. The monolithic ceramic capacitors prepared with these dielectrics showed stable capacitance and low dissipation factor under high AC and DC bias field, small surface temperature rise and low harmonic distortion.

1. INTRODUCTION

Dielectric materials showing a pronounced change in dielectric properties with applied frequency are called relaxors. Most popular and useful ferroelectric relaxor is complex perovskite oxide with lead ion such as Pb(Mg_{1/3}Nb_{2/3})O₃ and Pb(Ni_{1/3}Nb_{2/3})O₃¹⁻⁴. These relaxors are practically being used for dielectrics for small size monolithic capacitors (MLCs) with large capacitance because of their high dielectric constants (~20,000) and relatively low sintering temperatures (~950°C).

Another typical relaxor material is SrTiO₃-Bi₂O₃-nTiO₂. Extended works have been also done for this system⁵⁻⁷.

In this paper, effects of the addition of MgO and PbO on dielectric and relaxor behaviors of this system and the application for high voltage MLCs are discussed.

2. EXPERIMENTAL PROCEDURES

Industrial grade raw materials ; SrCO₃, MgCO₃, PbO, TiO₂ and Bi₂O₃ were mixed to obtain the following three formulations;

#1 0.84SrTiO₃-0.16(Bi₂O₃-2TiO₂)

— — Designated as ST-Bi·T

#2 0.84SrTiO₃-0.16(Bi₂O₃-2TiO₂)-0.12MgO

— — ST-Bi·T-M

#3 0.84SrTiO₃-0.16(Bi₂O₃-2TiO₂)-0.12MgO
-0.13PbO — — ST-Bi·T-M-P

Calcium titanate was also added to formulation of #2(ST-Bi·T-M) for some samples.

The powder, calcined at 950°C, was mixed with organic binder and pressed to discs with 10mm in diameter by 1mm in thickness. The sample discs were then sintered in air atmosphere for 2 h at 1200°C through 1250°C. Silver paste was applied on the both sides of the sintered discs and they were fired at 800°C to form the electrode.

Capacitance and dissipation factor were measured at 1kHz/1Vrms by YHP4274A LCR autobridge. HP4192A LF impedance analyzer was used for frequency characteristics at various temperatures. DC bias and high voltage AC field dependence of capacitance and dissipation factor were measured by Sosin Electric Type 1210-A high voltage bridge. Harmonic

wave distortion analysis was performed using YHP4333A distortion analyzer and Anritsu MS420A Network Analyzer.

The samples were also submitted to X ray diffraction (XRD) analysis.

3. RESULTS AND DISCUSSION

3.1. Structural analysis

X ray diffraction analysis indicated that the dielectrics used in this study had cubic perovskite structure. The same result has been obtained in the previous work by Skanavi et al.⁵⁾ They considered that vacancies were produced in strontium sites due to the replacement of some of strontium ions with bismuth ions resulting in the relaxation behavior. Lattice constants change with MgO, PbO and CaTiO₃ contents are shown in Fig.1a, 1b and 1c. The addition of PbO increased the lattice constant. On the other hand, CaTiO₃ decreased the lattice constant. These tendencies are usually seen in SrTiO₃ or BaTiO₃ based system. However, the lattice constant increased with the amount of MgO up to x=0.24, which is particular to this system. Ionic radius of Mg(0.072nm) is much smaller than that of Sr(0.12nm) and a little larger than that of Ti(0.061nm). These data suggest that Mg ion can substitute Ti site to increase the lattice constant in this system.

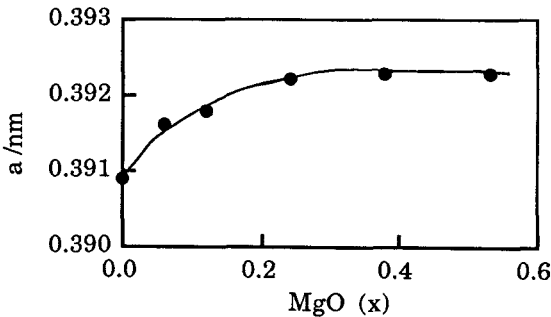


Fig.1a. Effect of MgO on lattice constant of 0.84SrTiO₃-0.16Bi₂O₃ · 2TiO₂-xMgO.

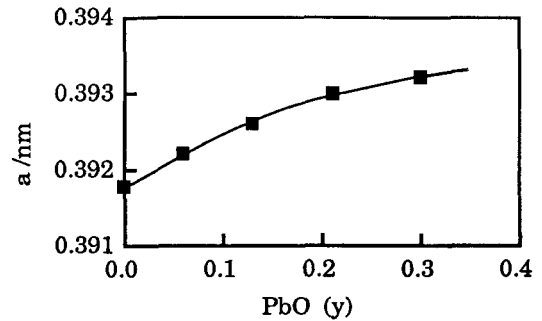


Fig.1b. Effect of PbO on lattice constant of 0.84SrTiO₃-0.16Bi₂O₃ · 2TiO₂-0.12MgO-yPbO.

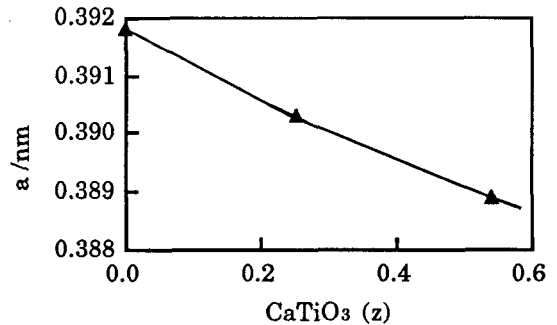


Fig.1c. Effect of CaTiO₃ on lattice constant of 0.84SrTiO₃-0.16Bi₂O₃ · 2TiO₂-0.12MgO-zCaTiO₃

3.2. Dielectric properties

Figure 2 shows the temperature dependence of dielectric constant for the three samples. The dielectrics of ST-Bi · T-M-P has much higher dielectric constant than the other two samples. Figure 3 shows the dependence

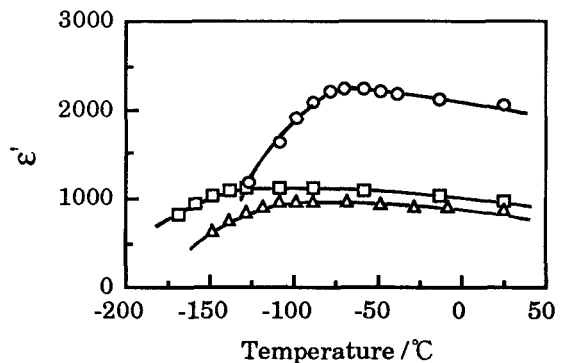


Fig.2. Temperature dependence of dielectric constant at 1kHz.

□ :ST-Bi · T, △ :ST-Bi · T-M, ○ :ST-Bi · T-M-P,

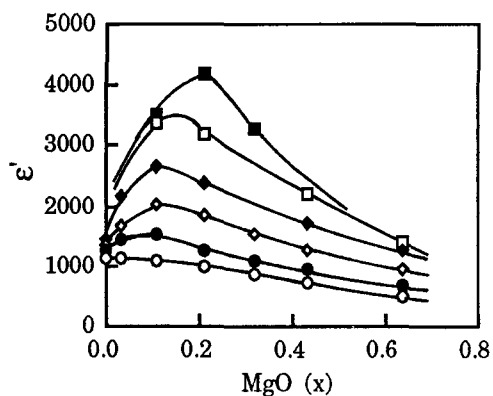


Fig.3. Effect of MgO and PbO on dielectric constant of $0.84\text{SrTiO}_3 \cdot 0.16\text{Bi}_2\text{O}_3 \cdot 2\text{TiO}_2 \cdot x\text{MgO} \cdot y\text{PbO}$.

$y =$: \circ ; 0.0, \bullet ; 0.06, \diamond ; 0.13, \blacklozenge ; 0.17, \square ; 0.22, \blacksquare ; 0.28

Table 1. Effect of PbO with the existence of MgO.

PbO	ϵ	$\Delta\epsilon/\epsilon$ %
0	1100	-12.0
0.06	1550	-10.9
0.11	1960	-13.2
0.17	2610	-15.3

of dielectric constant on MgO at various PbO contents. Table 1 shows the dielectric constants at room temperature and the maximum change of the dielectric constant between -25°C and $+85^\circ\text{C}$ with the reference temperature of 20°C . Dielectric constant is not so sensitive to PbO without MgO. However, with the existence of MgO, the dielectric constant increases with PbO. MgO has an optimum content between $x=0.1$ and 0.2 for a given PbO content. As evident from these results, coexistence of MgO and PbO raises the dielectric constant without significant change in its temperature dependence.

3.3 Dielectric relaxation

Temperature dependence of dielectric constant was measured for the three compositions at frequency range from 500Hz to 4 MHz. Fig-

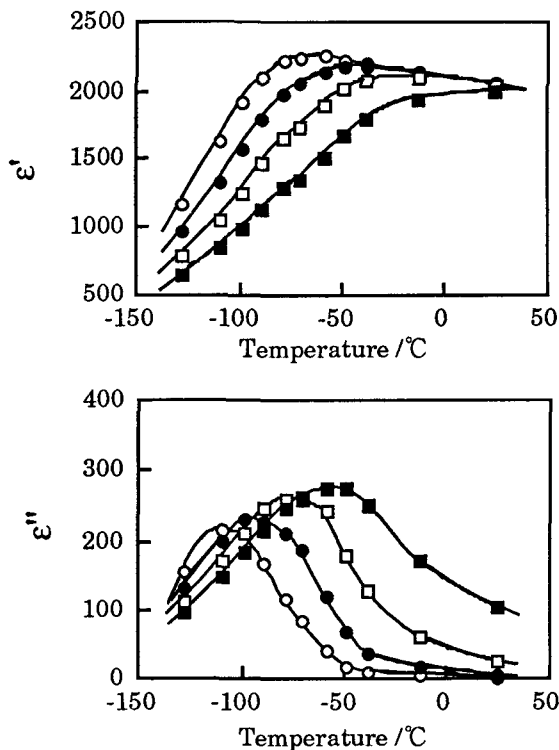


Fig.4. Frequency dependence of ϵ' and ϵ'' for ST-Bi · T-M-P

\circ ;1 kHz, \bullet ;10 kHz, \square 100 kHz, \blacksquare ;1MHz,

ure 4 is for the results of ST-Bi · T-M-P which shows a typical relaxation behavior similar to the previous work⁵). The other two samples also showed similar behaviors.

Relaxation time τ was calculated from the equation of

$$\tau = \frac{1}{2\pi f_0}$$

where f_0 is the relaxation frequency at which ϵ'' has the maximum value. Figure 5 shows the relaxation time change with the reciprocal of absolute temperature. The relaxation time is significantly prolonged with the addition of MgO and PbO. Since the plots show straight line, activation energies E can be obtained using the following equation;

$$\tau = \tau_0 \exp\left(\frac{E}{kT}\right)$$

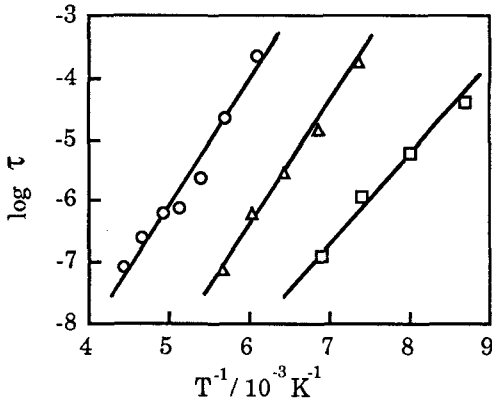


Fig.5. Arrhenius plots of relaxation time.

□ ; ST-Bi T, △ ; ST-Bi T-M, ○ ; ST-Bi T-M-P

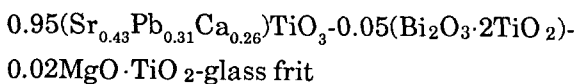
Table 2. Relaxation time and activation energy.

	τ at 25°C /s	E /eV
ST-Bi·T	2.55×10^{-12}	0.27
ST-Bi·T-M	2.91×10^{-12}	0.38
ST-Bi·T-M-P	4.34×10^{-10}	0.39

Activation energy E and relaxation time τ at room temperature for the three samples are shown in Table 2.

3.4. Application for monolithic capacitors

When high voltage monolithic capacitors are designed, the material for internal electrode, which is cofired with the dielectric material at high temperature, must be considered. The composition of ST-Bi·T-M-P includes bismuth ion and has firing temperature above 1200°C. Therefore, the internal electrode must consist of expensive platinum or platinum alloys to prevent the attack from bismuth ion. In order to employ less expensive 70%Ag-30%Pd alloy for the internal electrode, the dielectric material was modified to the following formulation;



Bismuth oxide was reduced to minimize the influence to the internal electrode. Calcium oxide was added to improve DC bias characteristics and lead oxide was increased to compensate the decrease of the dielectric constant with the addition of calcium oxide. Glass frit consisting of SiO_2 , Nb_2O_5 and ZnO was added to lower the sintering temperature. This material is designated as STD. Monolithic chip capacitor samples with this material were fired at 1060°C and terminated with silver paste. An active dielectric thickness of the samples was 80 μm . The monolithic chip capacitor samples with BaTiO_3 based X7R material were prepared with the same dielectric thickness for comparison. The sintering temperature of this sample was 1120°C. This material is designated as BTD.

Table 3. Basic electrical properties.

Dielectrics	STD	BTD
Dielectric constant at 1kHz 1Vrms	2320	2100
Dissipation factor at 1kHz 1Vrms /%	0.52	1.02
TCC	N4700	X7R
Insulation resistance / Ωcm		
25°C	1×10^{14}	2×10^{13}
125°C	5×10^{12}	7×10^{11}

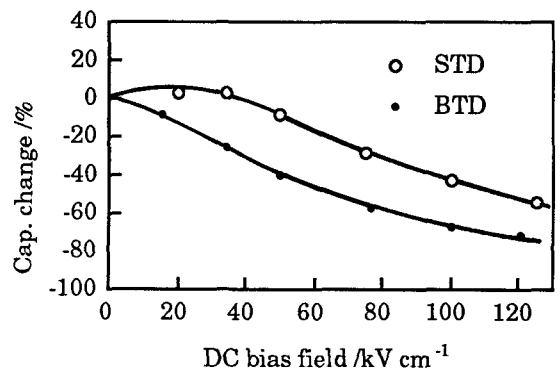


Fig.6. Effect of DC bias field on capacitance change.

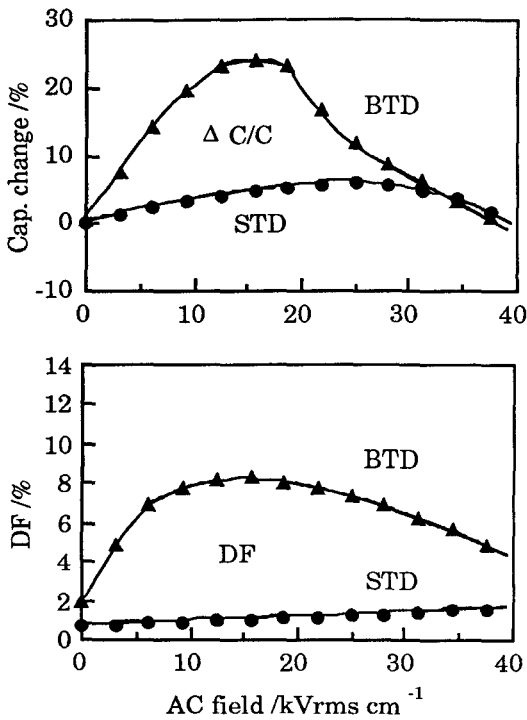


Fig.7. Effect of AC field on capacitance change and dissipation factor.

Basic electrical properties of these two dielectrics are shown in Table 3. DC and AC voltage characteristics are shown in Fig. 6 and 7. The dielectric constant of STD is higher than that of BTD, whereas voltage dependences of STD are much smaller. DC breakdown voltages of $0.1 \mu\text{F}$ chip capacitor samples with the dielectric thickness of $80 \mu\text{m}$ were 2.8kV for STD and 1.6kV for BTD, respectively.

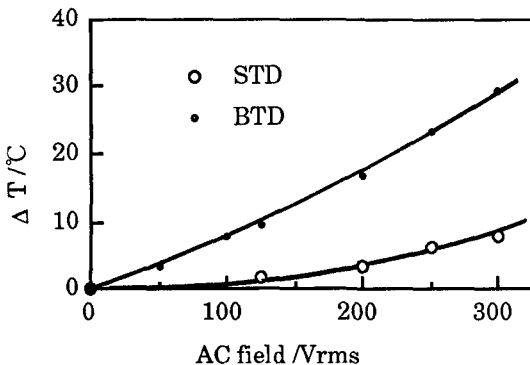


Fig.8. Surface temperature rise ΔT at 60Hz.

Figure 7 shows a large increase of dissipation factor in the case of BTD. This causes a significant surface temperature rise in BTD capacitor when used under AC field. The temperature rise when AC field of 60Hz was applied was measured with a thermocouple at 25 °C. The results are shown in Fig.8. Temperature rises at 250Vrms were 7°C and 24°C for STD and BTD, respectively.

Harmonic wave distortion at 10kHz was also measured to compare the linearity of the polarizations. Samples with the capacitance of 1000pF were used for this measurement. The dielectric thickness was $80 \mu\text{m}$. The results were shown in Table 4. A 25-30dB difference at the 3rd and 5th harmonic wave frequencies indicates that STD has smaller wave distortion than BTD under low field.

Table 4. Harmonic wave distortion at 10 kHz.

	Vrms	Harmonic wave distortion /dB				
		Total	2nd	3rd	4th	5th
MLCs with STD	1.0	-85.8	-107.1	-96.1	-113.7	-99.1
	3.0	-78.5	-105.5	-80.0	-109.2	-90.2
MLCs with BTD	1.0	-61.3	-105.5	-63.3	-114.6	-75.4
	3.0	-5.17	-103.8	-53.4	-106.2	-67.3

Figure 9 shows the frequency dependence of capacitance and dissipation factor for STD.

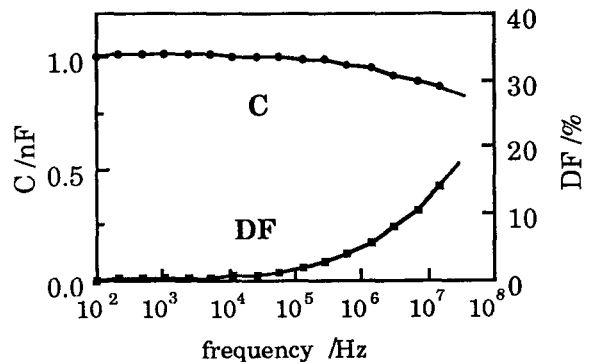


Fig.9. Frequency dependence of capacitance and dissipation factor for STD.

Both capacitance and dissipation factor are stable at lower frequency than the dielectric dispersion frequency at around 10^6 Hz. However, they become unstable with the increase of frequency. From these results, it is apparent that this material is suitable for high voltage monolithic capacitors under the frequency up to 1 MHz.

4. SUMMARY

- Addition of MgO and PbO to $\text{SrTiO}_3\text{-Bi}_2\text{O}_3\text{-}2\text{TiO}_2$ increases the dielectric constant from 1000 up to 4200 with stable temperature dependence, and also prolongs the relaxation time significantly.
- Activation energies of relaxation time are 0.27 eV and 0.39 eV for $\text{SrTiO}_3\text{-Bi}_2\text{O}_3\text{-}2\text{TiO}_2$ and $\text{SrTiO}_3\text{-Bi}_2\text{O}_3\text{-}2\text{TiO}_2\text{-MgO-PbO}$, respectively.
- Monolithic capacitors prepared with these dielectrics show stable capacitances and low dissipation factors under high AC and DC bias field.
- Surface temperature rise is much smaller

- than BaTiO_3 based material under AC field.
- This material has a linear dielectric property at low field.
- This material is suitable for high voltage monolithic capacitors under the frequency up to 1 MHz.

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