

# Low firing and high dielectric constant X7R ceramic dielectric for multilayer capacitors based on relaxor and barium titanate composite

OSAMU FURUKAWA, MITSUO HARATA, MOTOMASA IMAI,  
YOHACHI YAMASHITA

*Research and Development Center, Toshiba Corporation, Kawasaki 210, Japan*

SATOSHI MUKAEDA

*Ceramic Capacitors Engineering Section, Marcon Electronics Co., Ltd., Nagai,  
Yamagata 993, Japan*

A temperature stable ceramic dielectric with a low firing temperature (1130 °C) and a high dielectric constant (3700 to 2600) has been developed by sintering the mixture of precalcined lead-based relaxor and prefired modified barium titanate.

This dielectric was confirmed to be a two-phase ceramic composite body, according to X-ray diffraction analysis, scanning electron microscopy, transmission electron microscopy and dielectric measurements.

A shortcoming of the high dissipation factor in the dielectric has been reduced by incorporating MnO into the barium titanate constituent prior to mixed sintering.

This ceramic dielectric meets X7R specifications in the EIA (Electronic Industries Association) standard.

## 1. Introduction

For the last few years, the current trends towards miniaturization and operation at a higher frequency in the electronic apparatus have required small electronic components with small size, high volumetric efficiency, high reliability, low cost, and compact chip configuration.

The multilayer ceramic capacitor (MLC) seems to be one of the promising candidates to meet these requirements, due to no polarity, high insulation resistance and surface-mount-device compatible configuration, compared with aluminium electrolytic or tantalum capacitors.

Dielectric materials for MLCs are classified into three categories; for temperature compensation, for temperature-stable mid dielectric constant and for high dielectric constant. X7R specifications in the EIA (Electronic Industries Association) standard [1], which are included in the temperature-stable dielectric, require the capacitance change in the temperature range from  $-55^{\circ}\text{C}$  to  $+125^{\circ}\text{C}$  to be within  $\pm 15\%$ , with reference to  $25^{\circ}\text{C}$ . Furthermore, the military specification for BX requires that the combined temperature and voltage coefficients do not exceed  $+15\%$ ,  $-25\%$  over the range from  $-55^{\circ}\text{C}$  to  $125^{\circ}\text{C}$  at working voltage. Accordingly, the MLCs using X7R or BX dielectric are widely used in the electronic circuits where the temperature stability for capacitance is required.

Table I shows the status for X7R ceramic dielectric. Conventional X7R dielectrics are mainly based on two

kinds of modified barium titanates. One of them is high firing temperature barium titanate based dielectric, sintered at about  $1350^{\circ}\text{C}$ , with a high dielectric constant of 3000 to 4200 [2]. The other is low firing temperature barium titanate based dielectric, sintered with flux at  $1093$  to  $1135^{\circ}\text{C}$  with a dielectric constant of 2700 to 3000 [3]. On the other hand, the PLZT relaxor dielectric fired at  $1100^{\circ}\text{C}$  with a dielectric constant of 2050 [4] and the  $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ – $\text{PbTiO}_3$ – $\text{PbZrO}_3$  relaxor dielectric fired at  $980^{\circ}\text{C}$  with a dielectric constant of 2300 [5] have also been reported as new candidates for low firing temperature X7R ceramic dielectric.

TABLE I Status of X7R ceramic dielectrics

Material	Firing temperature (°C)	Dielectric constant	Reference
1. BaTiO <sub>3</sub>	1350	3000–4200	[2]
2. BaTiO <sub>3</sub> + Flux	1093–1135	2700–3000	[3]
3. Relaxor PLZT	1100	2050	[4]
4. Relaxor $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ – $\text{PbTiO}_3$ – $\text{PbZrO}_3$	980	2300	[5]
5. Composite Relaxor + Ba(Ti, Zr)O <sub>3</sub>	1130	3700–2600	Present work

In order to respond to the aforementioned requirements, the reduction in capacitance temperature change has also been achieved by another technique. Takahara *et al.* have already reported the temperature stable dielectric using  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  composition by mixed-sintering technique [6]. The temperature characteristic was, however, far from the X7R specifications.

In the present study, a ceramic dielectric composite material for MLCs, which satisfies the X7R specifications, has been developed using the composition based on a lead perovskite relaxor and a modified barium titanate by mixed-sintering technique at low firing temperature. In this paper, dielectric properties and microstructure for the composite material are discussed.

## 2. Sample preparation and measurement

Lead-based complex perovskite dielectrics with low firing temperature (900 to 1200 °C) are known to be attractive materials for MLCs, because of their excellent dielectric properties and a compatibility with less expensive silver-rich internal electrodes. The authors have already reported a Y5S compound based on  $(\text{Pb}_{1-x}\text{Sr}_x)(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{Ti}_z\text{O}_3$  (hereafter abbreviated as PSZT 100x/100y/100z) [7]. In the present study, the composition PSZT 15/85/15 was used as a lead-based relaxor constituent, because its Curie temperature is at around room temperature and the composition can be fired at 1050 °C or below, while the composition  $\text{Ba}(\text{Ti}_{1-z}\text{Zr}_z)\text{O}_3$  with  $z = 0$  to 0.04 (hereafter abbreviated as BTZ 100(1 – z)/100z) was used as a modified barium titanate to shift the Curie temperature to 120 °C and the average particle size for BTZ was controlled to be 2 to 3 μm in order to decrease the reactivity of pure  $\text{BaTiO}_3$ .

Reagent grade  $\text{PbO}$  (purity 99.52%),  $\text{SrCO}_3$  (purity 69.71% as SrO),  $\text{ZnO}$  (purity 99.90%),  $\text{Nb}_2\text{O}_5$  (purity 99.36%),  $\text{TiO}_2$ ,  $\text{BaCO}_3$  (purity 77.39% as BaO),  $\text{ZrO}_2$  (purity 99.07%) and  $\text{MnCO}_3$  (purity 57.75% as MnO) were used as starting materials. The relaxor (PSZT) and modified barium titanate (BTZ) were preformed separately by calcining the mixture of raw material powders at 800 °C for 2 h and at 1300 °C for 8 h, respectively. The resultant calcined BTZ powder was carefully crushed for 2 h with zirconia media and distilled water, whereas the calcined PSZT relaxor powder was milled for 22 h with zirconia media and distilled water. The resultant average particle sizes were 2 to 3 μm for BTZ and less than 1 μm for PSZT powder. Then, 100 to 60 mol % of the PSZT powder and 0 to 40 mol % of the BTZ powder were mixed with distilled water for 3.3 h. After drying, the resultant powders were pressed into discs 17 mm in diameter and 1.5 mm thick and fired typically at 1130 °C for 4 h. The fired discs were then analysed for microstructure by scanning electron microscope (SEM) and transmission electron microscope (TEM) and for X-ray analysis. The fired discs were lapped to 1 mm or 100 μm thickness. Silver paste was printed onto both surfaces of the 1 mm thick discs and fired at 800 °C for 10 min as electrodes. For samples of 100 μm

thickness, silver was evaporated onto both surfaces for use as electrodes, to avoid a change in electrical properties due to glass frit contamination in silver paste. Dielectric measurements were made at various ambient temperatures ranging from –55 °C to +125 °C, using an automatic capacitance bridge (model YHP4270A or YHP4274A, Yokogawa Hewlett Packard Co., Ltd, Tokyo, Japan). Insulation resistance was measured by applying 100 V mm<sup>-1</sup> d.c. across the specimen, using an ultra megohm meter (model SM10E, Toa Electronics Co., Ltd, Tokyo, Japan) with the value being measured after 2 min to calculate the electrical resistivity.

## 3. Results and discussion

### 3.1. Features of two-phase ceramic composite dielectric

The PSZT 15/85/15 ceramic has a dielectric constant maximum at around 0 °C, while the BTZ 96/4 ceramic has two dielectric constant maxima at 50 °C and at 125 °C, as shown in Fig. 1. When the PSZT ceramic and the BTZ ceramic are mixed-sintered, it is expected that the sintered body must have three dielectric constant maxima. As a matter of fact, it is clearly shown in Fig. 2 that the composite has three dielectric constant maxima within the temperature range from –55 °C to +125 °C. The peak at the lowest temperature side shifted towards the higher temperature side with increasing frequency, while the two peaks at a higher temperature side did not change with frequency increase as shown in Fig. 3. The former peak having large frequency dispersion was, therefore, identified to be based on the PSZT relaxor. The latter two peaks were based on the BTZ ceramic. This result suggests that the present mixed-sintering ceramic body has a composite structure.

The formation of the composite ceramic dielectric, composed of mixed phases, was also confirmed by X-ray diffraction patterns. Fig. 4 shows the (222)

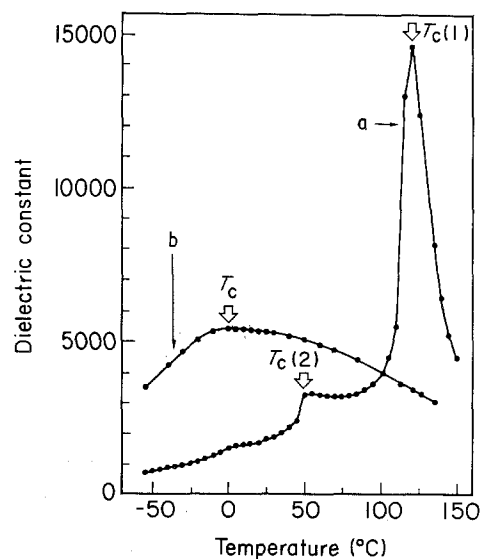


Figure 1 Temperature dependence of dielectric constant for (a) PSZT 15/85/15 ceramic sintered at 1050 °C and for (b) BTZ 96/4 ceramic sintered at 1300 °C, 1 kHz.

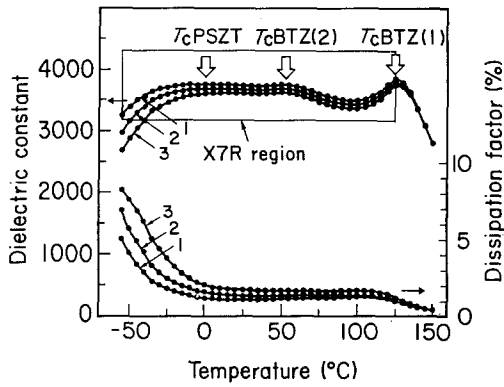


Figure 2 Frequency dependence of dielectric constant and dissipation factor for 0.6 PSZT 15/85/15 + 0.4 BTZ 96/4 mixed-sintering ceramic composite sintered at 1130 °C for 4 h as a function of temperature (1 1 kHz, 2 10 kHz, 3 100 kHz).

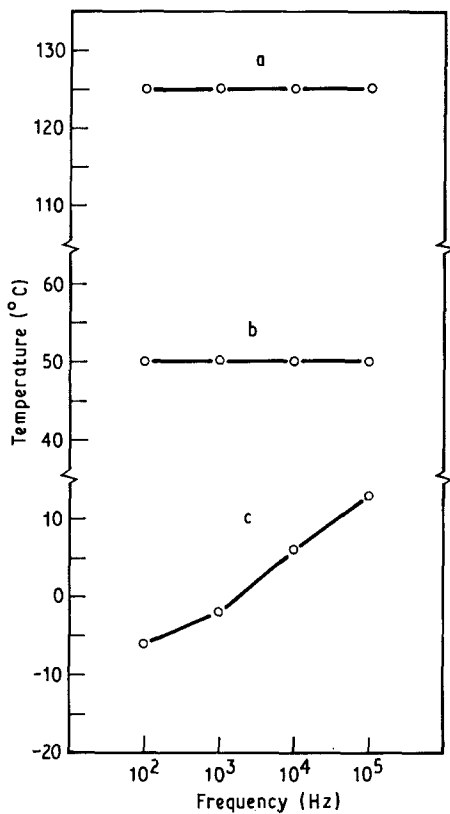


Figure 3 Frequency dependence of dielectric constant maximum. (a  $T_c$  BTZ(1), b  $T_c$  BTZ(2), c  $T_c$  PSZT)

reflection lines for the composite phase, the PSZT phase and the BTZ phase. In the composite reflection lines, peak 1 corresponds to that for the PSZT and shoulder peak 2 corresponds to that for the BTZ. It is obvious that the obtained ceramic body is a two-phase composite, not a single solid solution.

The microstructure observed using an SEM also showed that the ceramic is a two-phase composite. From Fig. 5, it is shown that the grain size is around 5  $\mu\text{m}$  and that the sintered body has a dense structure. According to the observation of a TEM photograph for the composite dielectric, three kinds of grains, A, B and C existed as shown in Figs 6 and 7. The energy dispersive spectroscopy (EDS) spectra from the A

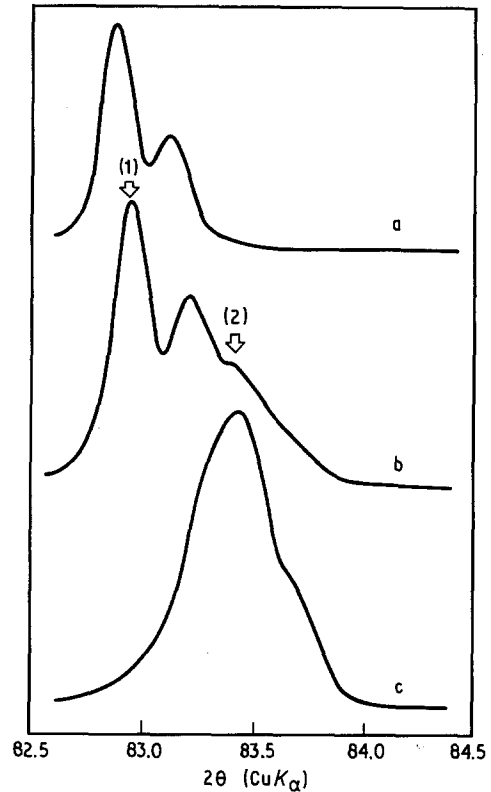


Figure 4 X-ray diffraction patterns for  $\text{CuK}\alpha$  (222) reflection lines. (a) For PSZT 15/85/15 ceramic. (b) For 0.6 PSZT 15/85/15 + 0.4 BTZ 96/4 mixed-sintering ceramic. (c) For BTZ 96/4 ceramic.

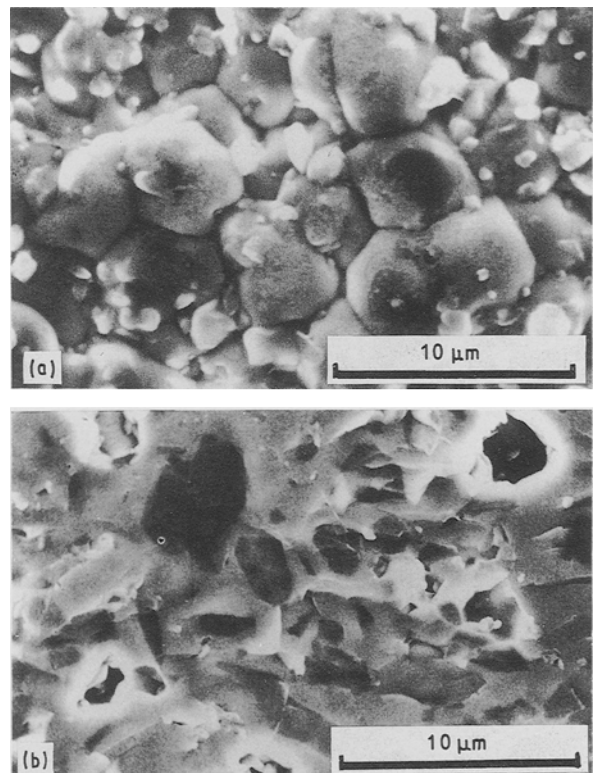


Figure 5 Microstructure for 0.6 PSZT 15/85/15 + 0.4 BTZ 96/4 ceramic sintered at 1130 °C for 4 h. (a) As-sintered surface. (b) Fracture surface.

region gave Pb, Sr, Zn, Nb and Ti element peaks, showing that the composition of the grain in the A region corresponds to the PSZT constituent. The spectra from the B region gave Ba, Ti and Zr element

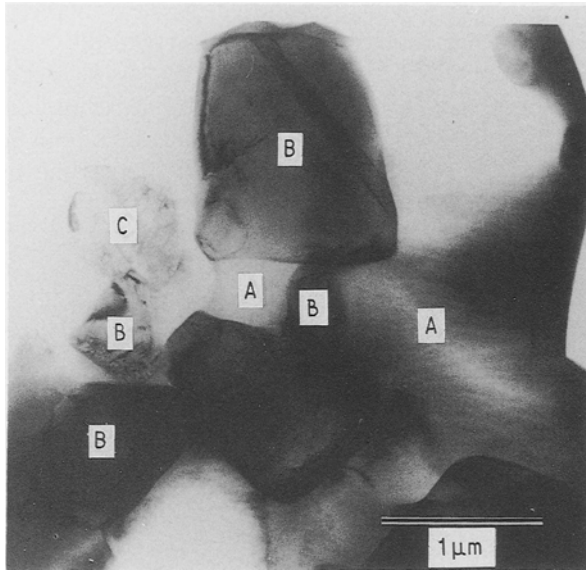


Figure 6 Transmission electron microscope image for 0.6 PSZT 15/85/15 + 0.4 BTZ 96/4 ceramic sintered at 1130°C for 4 h.

peaks, in addition to a trace amount of Pb and Nb peaks, revealing that this portion corresponds to the BTZ constituent. The spectra from the C region gave all the peaks of the elements mentioned above. This fact means that the solid solution is already formed in the C region. In the present observation, however, the C grains rarely existed. According to these microstructural observations, it is also shown that the obtained ceramic is a composite.

### 3.2. Reduction in dissipation factor

For making use of the present two-phase ceramic composite as a dielectric for MLCs, it is necessary for the dissipation factor to be less than 2.5%, when measured at 1 V<sub>r.m.s.</sub> for the 25 μm (= 1 mil) dielectric thickness at room temperature. Unfortunately, it was found that the present ceramic dielectric does not meet this requirement strictly. To clarify the reason for this, a.c. voltage dependence of the dissipation factor for various 100 μm thick dielectrics were measured under 1 to 5 V<sub>r.m.s.</sub> a.c. voltage at room temperature. From Fig. 8, it was clear that the BTZ constituent essentially causes the high dissipation factor values at high a.c. voltage.

In order to reduce the dissipation factor, 0.7 mol % manganese oxide (MnO) was added to the BTZ constituent, for the effect of manganese oxide addition to lead-based dielectric or piezoelectric has been reported to enhance the sinterability of the ceramic body and to reduce the dissipation factor [8] and the same effects are expected even in the present PSZT–BTZ composite ceramic dielectric. Fig. 8 also shows that the addition of MnO to the BTZ constituent is very effective for the reduction in dissipation factor for the present composite ceramic dielectric.

The reason for the reduction in dissipation factor, when MnO was added to the BTZ constituent, is not known explicitly. Mn addition to BaTiO<sub>3</sub> has, however, been reported to form oxygen vacancies [9] and to prevent the decrease in the electrical resistivity, which arises from the reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> [10]. The above situation has been taken into consideration

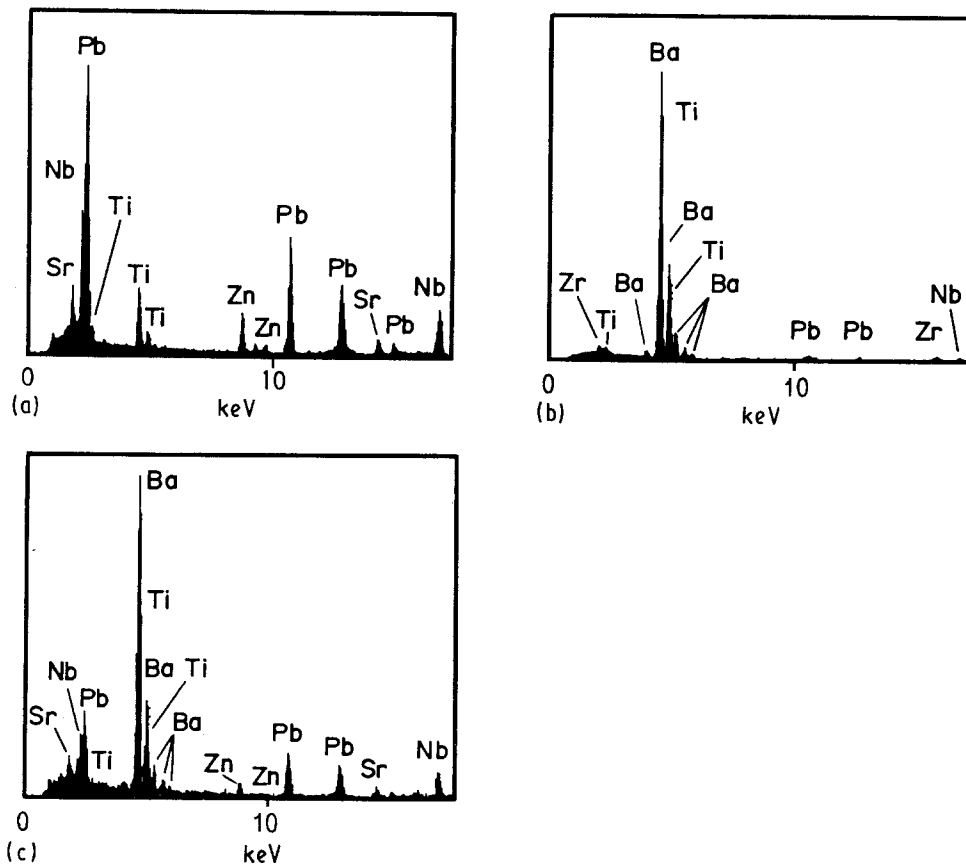


Figure 7 Energy spectrum obtained from regions A, B and C in Fig. 6.

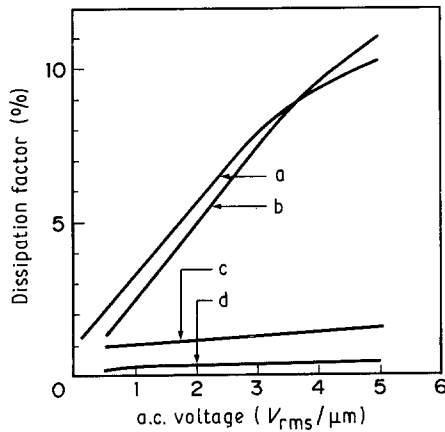


Figure 8 A.c. voltage dependence of dissipation factor for various 100  $\mu\text{m}$  thickness specimens at 1 kHz, 25  $^{\circ}\text{C}$ . (a 0.6 PSZT (15/85/15) + 0.4 BTZ (96/4), b BTZ (96/4), c PSZT (15/85/15), d 0.6 PSZT (15/85/15) + 0.4 BTZ (96/4) doped with MnO)

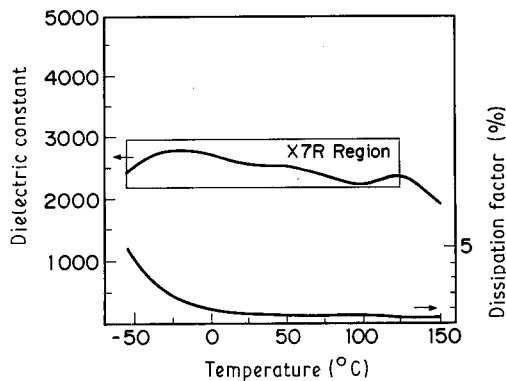


Figure 9 Temperature dependence of dielectric constant and dissipation factor for 0.6 PSZT 15/85/15 + 0.4 (BTZ 96/4 + 0.007 MnO) ceramic dielectric composite sintered at 1130  $^{\circ}\text{C}$  for 4 h and measured at 4  $V_{\text{r.m.s.}}$  in 100  $\mu\text{m}$  thickness at 1 kHz,  $K_{25^{\circ}\text{C}} = 2600$ ,  $\Delta C/C = +9\%$ ,  $\text{DF}_{25^{\circ}\text{C}} = 0.5\%$ .

TABLE II Properties of developed X7R dielectric

Material	0.6PSZT15/85/15 + 0.4BTZ96/4	0.6PSZT15/85/15 + 0.4(BTZ96/4 + 0.007MnO)
Dielectric constant	3700	2600
Temperature coefficient of capacitance (%)	+ 13 to -13	+ 9 to -13
Dissipation factor (%)		
at 1 $V_{\text{r.m.s.}}$ $\text{mm}^{-1}$	1.1	0.3
at 1 $V_{\text{r.m.s.}}$ $\text{mil}^{-1}$	8.0	0.5
Insulation resistance		
at 25 $^{\circ}\text{C}$ ( $\Omega\text{F}$ )	3800	3200
at 125 $^{\circ}\text{C}$ ( $\Omega\text{F}$ )	4700	480
d.c. bias dependence (%)		
at 1 $\text{kV mm}^{-1}$	- 9	- 0.3
at 2 $\text{kV mm}^{-1}$	- 27	- 14
Firing temperature ( $^{\circ}\text{C}$ )	1130	1130
	X7R at 1 mm thickness	X7R at 25 $\mu\text{m}$ (1 mil) thickness

in the ferroelectric region below the Curie temperature. In the present case, the similar mechanism may be dominant, resulting in the dissipation factor reduction.

Fig. 9 shows the temperature dependence of dielectric constant and dissipation factor for the MnO doped composite ceramic dielectric. It is clearly shown, in Fig. 9, that the MnO modified composite ceramic dielectric meets X7R specifications both regarding the capacitance temperature change and the dissipation factor at room temperature.

Table II summarizes several properties for the newly developed X7R dielectric ceramic. The present two-phase composite ceramic dielectric, without MnO, has a high dielectric constant of 3700 and meets X7R specifications at a 1 mm thickness. On the other hand, the composite with 0.7 mol % MnO also has a high dielectric constant of 2600 and meets X7R and BX 25 V/25  $\mu\text{m}$  specifications at the 25  $\mu\text{m}$  (= 1 mil) thickness.

#### 4. Summary

A composite ceramic dielectric with a low firing temperature and a high dielectric constant has been developed by sintering a mixture of preformed lead perovskite relaxor and modified barium titanate.

This dielectric, sintered at 1130  $^{\circ}\text{C}$ , was confirmed to be structurally and electrically a two-phase ceramic composite, using several investigatory methods.

A reduction in dissipation factor for the composite dielectric was achieved by incorporation of a small amount of MnO into the modified barium titanate portion prior to mixed sintering.

The composite ceramic dielectric with dielectric constant of 3700 meets X7R specifications and the MnO added composite ceramic dielectric with dielectric constant of 2600 meets both X7R and BX 25 V/25  $\mu\text{m}$  specifications.

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