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A Lead Perovskite Y5U Dielectric
for Multilayer Ceramic Capacitor

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A ceramic dielectric, based on a Ba, Ti and $(Mg_{1/3}Nb_{2/3})$-substituted $Pb(Zn_{1/3}Nb_{2/3})O_3$ system, for multilayer ceramic capacitor (MLC) has been developed according to Y5U specifications in the EIA (Electronic Industries Association) standard. This ceramic dielectric, fired at 1000–1050°C, exhibits a 12000 relative dielectric constant, a 1.0% dissipation factor, a 30000 ΩF CR product (capacitance × resistance) at 25°C and a 10000 ΩF CR product at 85°C, respectively. An MLC using this dielectric and 70 Ag/30 Pd internal electrodes, has a small capacitance change of −30% at 1 kV/mm and a high breakdown voltage of 40 kV/mm. Capacitance temperature change is within −48% from −30 to +85°C. This dielectric is a promising candidate for use as a replacement for conventional barium titanate based dielectric for MLC.

§1. Introduction

Lead zinc niobate $(Pb(Zn_{1/3}Nb_{2/3})O_3$, PZN) with a perovskite crystal structure has been reported as a ferroelectric material with a 140°C Curie temperature and a 22000 relative dielectric constant at Curie temperature.[1] Although this material can be synthesized as a single crystal, it was difficult to obtain the compound as a sintered ceramic body with a perovskite structure, because of pyrochlore phase formation. The pyrochlore phase formation resulted in a low dielectric constant of 340.[2]

Therefore, many attempts have been made to synthesize such a ceramic body with a perovskite structure, in order to obtain a high dielectric constant material. Examples reported are synthesis under high pressure conditions[3] or compositional changes, *i.e.*, making solid solution with lead titanate[2] or potassium/sodium niobate.[4] The substitution for the Pb site by Ba in the PZN has also been reported from the view point of closing the tolerance factor toward unity.[5]

Some of the authors have previously presented data indicating that, in the PZN, partial substitution for the $(Zn_{1/3}Nb_{2/3})$ site by Ti and for the Pb site by Ba and/or Sr stabilized the perovskite structure, which conducted a dielectric material with a low firing temperature around 1000°C, with a high dielectric constant up to 3500–5000 and with a high electrical resistivity.[6] This fact was explained by considering the concepts of the electronegativity difference between cations and oxygen ions and of the tolerance factor in the perovskite crystal structure.

In the present study, the effects of further substitution for the $(Zn_{1/3}Nb_{2/3})$ site by $(Mg_{1/3}Nb_{2/3})$ on dielectric and electrical properties were investigated in order to obtain a higher dielectric constant material. A multilayer ceramic capacitor (MLC), fabricated using this relaxor dielectric with an appropriate composition, has also been reported.

§2. Experimental Procedure

In many cases, the temperature where the dielectric constant becomes maximum, i.e., Curie temperature (T_c), is generally shifted to around room temperature. In the present study, the Curie temperature shift was conducted by adjusting the substitution amount for the Pb site by Ba and the substitution amount for the $(Zn_{1/3}Nb_{2/3})$ site by Ti and by $(Mg_{1/3}Nb_{2/3})$. A hatched area in Fig. 1. shows a calculated plane on which the Curie temperature becomes 10°C in the Ba, Ti and $(Mg_{1/3}Nb_{2/3})$-substituted PZN system. The above calculation was made with an assumption that, for the PZN, the Curie temperature shift rates by substituting Ba, Ti and $(Mg_{1/3}Nb_{2/3})$ in deg/mol% were −11, +3.5 and −1.5, respectively. Figure 2 shows the control compositions for the PZN based system, prior to Ba substitution. Eight compositions were selected to evaluate dielectric properties, as shown in Table I, in which the numbers 1–8 correspond to the numbers 1′–8′ in Fig. 2.

Compositions examined were according to the general formula, $Pb_{1-a}Ba_a(Zn_{1/3}Nb_{2/3})_x(Mg_{1/3}Nb_{2/3})_yTi_zO_3$. Reagent grade PbO, ZnO, Nb_2O_5, TiO_2, $MgCO_3$ and $BaCO_3$ were used as starting materials. Using ordinary
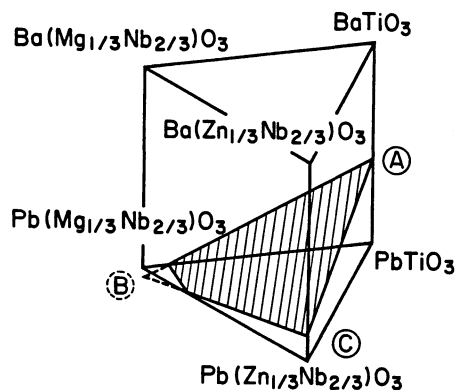

Fig. 1. A calculated plane (hatched area) on which the Curie temperature becomes 10°C in the Ba, Ti and $(Mg_{1/3}Nb_{2/3})$-substituted $Pb(Zn_{1/3}Nb_{2/3})O_3$ system. A, B and C denote calculated chemical compositions described below:
A: $Pb_{0.564}Ba_{0.436}TiO_3$, B: $Pb_{1.016}Ba_{-0.016}(Mg_{1/3}Nb_{2/3})O_3$, C: $Pb_{0.882}Ba_{0.118}(Zn_{1/3}Nb_{2/3})O_3$.
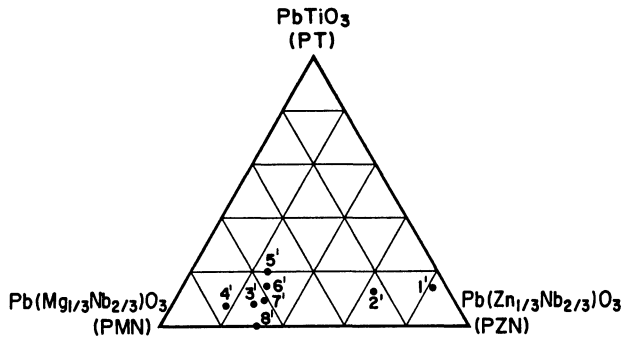
Fig. 2. Control compositions for the $Pb(Zn_{1/3}Nb_{2/3})O_3$ based system prior to Ba substitution. Numerical values $1'-8'$ correspond to sample numbers 1–8 in Table I.

ceramic techniques, these raw materials were mixed in a resin pot mill with distilled water for 22 hours. The mixture was dried, calcined at 800°C for 2 hours, and milled for 22 hours. After drying, the resultant powders were granulated with binder, and then pressed into disks, 17 mm in diameter and 2.0 mm thick. The disks were fired at 1000°C for 8 hours. Then, they were ground down to a 1.0 mm thickness, silver paste was painted as electrodes on both surfaces and fired at 700°C.

An MLC was fabricated as follows: The above calcined powders were cast into ceramic green sheets by doctor blade tape casting method. Then, an Ag 70/Pd 30 paste was screen-printed on the sheets as internal electrodes. The green sheets were stacked and cut into chips. The chips were heated to 400°C to burn out binder, then fired at 1000–1050°C. Termination electrodes were attached to them individually.

For measuring dielectric properties, an automatic capacitance bridge, 4270A (Yokogawa Hewlett Packard Co., Ltd.), was used. The dielectric constant (K) was calculated using measured capacitance and dimension of the specimen. Capacitance and dissipation factor (DF) measurements were made at 1 kHz and 1 V_{rms}. Insulation resistance was measured by applying 100 V/mm dc across the specimen, using an ultra megohm meter, SM10E (Toa Electronics Co. Ltd.). The value was recorded after 2 minutes, to calculate the electrical resistivity (ρ).

§3. Results and Discussion

Table I shows dielectric properties for the Ba, Ti and $(Mg_{1/3}Nb_{2/3})$-substituted PZN system. In this table, K_{25} denotes K value at 25°C, K_{max} indicates the maximum

value of K, DF_{25} shows the DF value at 25°C, ρ_{25} and ρ_{125} indicates ρ values at 25°C and at 125°C, $\Delta C/C$ presents capacitance change with reference to 25°C, and P.A. indicates the relative amount of perovskite phase, calculated from the peak intensities of X-ray diffraction pattern with CuK_α radiation as follows;

$$P.A.(\%) = I_{per.(110)} / (I_{per.(110)} + I_{pyro(222)}) \times 100$$

where $I_{per.(110)}$ shows the intensity for a perovskite (110) line, and $I_{pero(222)}$ is the intensity for a pyrochlore (222) line.

As a result, samples 3, 6–8 in Table I showed more than 10000 relative dielectric constant (K) values, more than $10^{13}\ \Omega$ cm electrical resistivity at 25°C. These capacitance temperature characteristics showed within the $+22$, -56% range, which met Y5U specifications in the EIA (Electronic Industries Association) standard.

The perovskite structure is regarded as an ionic crystal in the first approximation.[7] It has been shown that the perovskite crystal structure ABO_3 can be enhanced by increasing the amount of ionic bond component p and by closing the tolerance factor t toward unity,[6] where p and t are defined as

$$p = 1 - \exp\left(-(1/4)(\Delta X_{AB-O})^2\right),$$

and

$$t = (r_A + r_O)/(\sqrt{2}(r_B + r_O))$$

in which ΔX_{AB-O} denotes the electronegativity difference between A or B ions and oxygen ions, and r_A, r_B and r_O are the ionic radii for A, B and oxygen ions, respectively.

Figures 3 and 4 show p and t distributions on the calculated plane on which the Curie temperature becomes 10°C. In these figures, the electronegativity values, proposed by Pauling,[8] were used and the tolerance factor was calculated, using the ionic radii proposed by Shannon.[9]

For samples 1–4 in Table I, whose compositions have a p value of approximately 0.58, selected by considering the sinterability of the ceramics, the P.A. ratio was decreased in the region where the $(Mg_{1/3}Nb_{2/3})$ ratio is large. One of the reasons for this may be attributed to a decrease in the t value from unity, as shown in Fig. 4. Another reason for this may center on inadequate firing conditions, such as a relatively lower firing temperature. Electrical resistivity values became higher with increasing $(Mg_{1/3}Nb_{2/3})$ ratio. The highest K value was obtained in the vicinity of around 60 mol% $(Mg_{1/3}Nb_{2/3})$ composi-

Table I. Dielectric properties of the Ba, Ti and $(Mg_{1/3}Nb_{2/3})$-substituted PZN system. "a" denotes Ba substitution amount. Other symbols or abbreviation can be seen in the text.

| No.	a (mol%)	T_c (°C)	K_{25}	K_{max}	DF_{25} (%)	ρ_{25} (Ω cm)	ρ_{125} (Ω cm)	$\Delta C/C$ (%) −30°C	$\Delta C/C$ (%) +85°C	P.A. (%)
1	16	12	7100	7200	1.9	1.0×10^{13}	7.0×10^{12}	−28	−18	98
2	13	12	8300	8500	1.8	1.1×10^{13}	9.1×10^{12}	−34	−25	99
3	6	12	11100	11700	1.2	2.7×10^{13}	1.5×10^{13}	−43	−41	97
4	4	12	8000	8200	1.1	3.3×10^{13}	1.1×10^{13}	−39	−37	92
5	11	20	8500	8500	2.0	2.3×10^{13}	9.1×10^{12}	−41	−27	99
6	9	20	10400	10500	1.5	$2,1 \times 10^{13}$	1.2×10^{13}	−44	−34	99
7	7	12	11100	11600	1.0	1.6×10^{13}	1.5×10^{13}	−44	−39	98
8	3	5	11700	13000	0.3	1.6×10^{13}	1.4×10^{13}	−44	−47	96
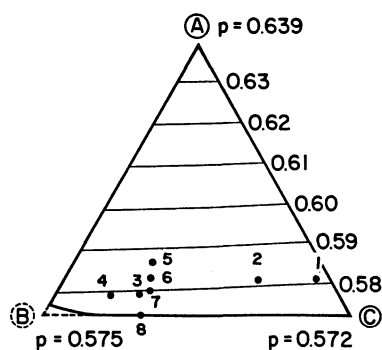
Fig. 3.   Ionic bond component amount p distribution on the plane with $T_c = 10°C$. A, B and C denote calculated compositions cited in Fig. 1. Symbol (.) denotes the present experimental composition. Sample numbers 1-8 correspond to those in Table I.

Fig. 4.   Tolerance factor t distribution on the plane with $T_c = 10°C$. A, B and C denote calculated compositions cited in Fig. 1. Symbol (.) denotes the present experimental composition. Sample numbers 1-8 correspond to those in Table I.
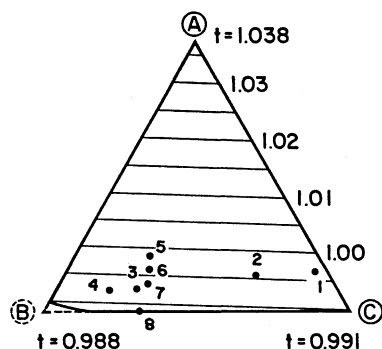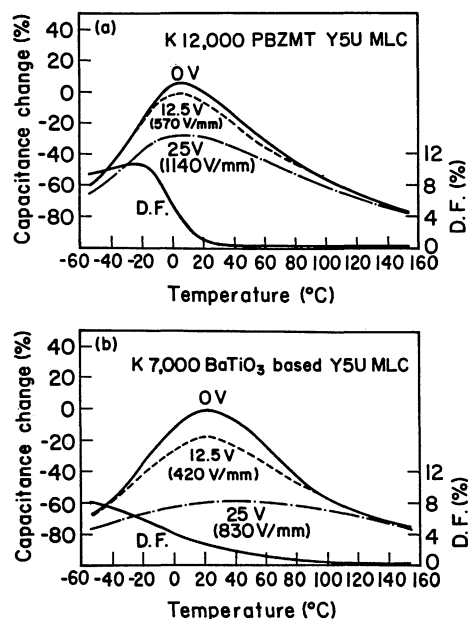

Fig. 5.   Capacitance change vs. temperature with various dc bias voltages. (a) In the present Pb perovskite (PBZMT) Y5U MLC. (b) In the conventional barium titanate based Y5U MLC.
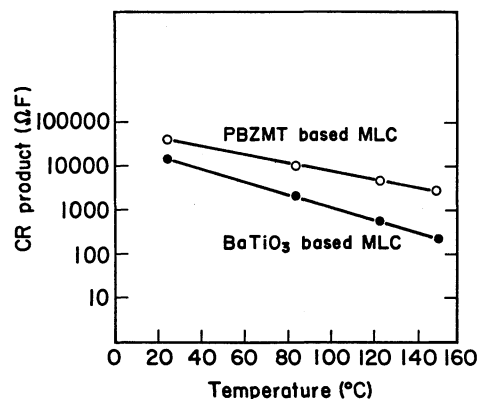

Fig. 6.   CR product temperature dependence in the present Pb perovskite (PBZMT) based MLC and conventional barium titanate based MLC.

tion.

For samples 5-8 in Table I, whose compositions include about 50-70 mol% $(Mg_{1/3}Nb_{2/3})$, the P.A. ratio increased with increasing Ti ratio, i.e., Ba substitution amount. This also can be explained by considering the behaviour of p and t values.

§4.   Several Properties of Multilayer Ceramic Capacitor

An MLC was fabricated using the dielectric composition, $Pb_{0.875}Ba_{0.125}(Zn_{1/3}Nb_{2/3})_{0.30}(Mg_{1/3}Nb_{2/3})_{0.50}Ti_{0.20}O_3$ with small additives (hereafter abbreviated as PBZMT). The resultant PBZMT based MLC showed a 12000 relative dielectric constant (K) and the capacitance temperature characteristics met Y5U specifications in the EIA standard.

Figure 5 shows capacitance change vs. temperature characteristics under 50% of rated voltage and 100% of rated voltage in the PBZMT based MLC (a) as well as the conventional barium titanate (BaTiO$_3$) based MLC with K 7000 (b). When rated voltage is applied to the BaTiO$_3$ based MLC, the remaining capacitance is only 40% of the initial value. However, the PBZMT based MLC shows 70% of the initial value, under the same conditions. This means that PBZMT based 33 μF MLC is equivalent to conventional BaTiO$_3$ based 60 μF MLC, under the practical rated voltage conditions.

Figure 6 represents CR product for the present PBZMT based MLC and the conventional BaTiO$_3$ based

MLC as a function of temperature. The CR product is usually represented as a product of capacitance and resistance for the MLC and has a unit of ΩF or second. High CR product is an essential requirement for a highly reliable MLC. Table II summarizes several characteristics for the present PBZMT based MLC, compared with the conventional Y5U BaTiO$_3$ based MLC. The most outstanding features are excellent dc bias characteristic, higher CR product and lower ageing rate.

§5.   Conclusion

A low temperature fired Pb perovskite Y5U dielectric composition, promising for multilayer ceramic capacitor (MLC), has been obtained by substituting Ba for the Pb site and $(Mg_{1/3}Nb_{2/3})$ and Ti for the $(Zn_{1/3}Nb_{2/3})$ site in the $Pb(Zn_{1/3}Nb_{2/3})O_3$ system.

An MLC, fabricated using the present Pb perovskite dielectric, has superior characteristics, especially in regard to high electrical resistivity and in small dc bias dependence, in comparison with the higher temperature

Table II. MLC characteristics for Y5U specification.

Characteristics		PBZMT based MLC	BaTiO$_3$ based MLC
Chip Size (mm)		$10.5 \times 9.5 \times 3.0$	$10.5 \times 10 \times 3.0$
Cielectric Thickness (μm)		22	30
Number of Active Layers		100	30
Internal Electrode		70 Ag/30 Pd	100 Pd
Firing Temperature (°C)		1050	1350
Capacitance (μF)		33	4.7
Dissipation Factor 1 kHz 25°C (%)		1.0	2.0
Relative Dielectric Constant K 25°C		12000	7000
Capacitance	−55°C	−62	−80
Change (%)	−30°C	−36	−50
	85°C	−48	−55
	125°C	−65	−80
CR Product (ΩF)	25°C	30000	17000
	85°C	10000	2500
	125°C	5000	1000
	150°C	2000	200
Capacitance Change under dc Bias	1/2 rated	−10	−20
(%)	rated	−30	−60
Breakdown Voltage (V)		400–600	400–600
Aging Rate (%/decade)		1–2	4

fired conventional barium titanate based MLC.

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