Japanese Journal of Applied Physics

D.C Bias and Frequency Dependence of the Dielectric Constant PZT Family ferroelectric Ceramics

To cite this article: Yoichiro Masuda and Akira Baba 1985 *Jpn. J. Appl. Phys.* **24** 113

Proceedings of the 5th Meeting on Ferroelectric Materials and Their Applications, Kyoto 1985
Japanese Journal of Applied Physics, Vol. 24 (1985) Supplement 24-3, pp. 113-116

D.C Bias and Frequency Dependence of the Dielectric Constant PZT Family ferroelectric Ceramics

Yoichiro MASUDA and Akira BABA

Department of Electrical Engineering, Hachinohe Institute of Technology

(Received May 30, 1985)

D.C bias and frequency dependence of the dielectric constant of PLLZT10/53/47 (trigonal-tetragonal phase), 10/65/35 (trigonal-phase) and 10/40/60 (tetragonal phase) compositions have been investigated. The dielectric measurements were carried out 19°C and 100°C temperature in ferroelectric phase and several frequencies between 1 kHz and 1 MHz.

Ferroelectric 180° switching and 90° rotating domain model explain the dependence of dielectric constant on electric bias and frequency.

§1. Introduction.

The investigation of polarization process and switching behavior of the ferroelectric ceramics is an important subject, owing to applying the piezoelectric, ultrasonic and light functional devices.

One of the most wide-spread methodes of gaining insight into the bahavior of ferroelectric crystal is the investigation of the D.C electric field dependence of the dielectric constant.

Many workers have been studied on this probrems. There are the wide accepted thermodynamic theory of Devonshire.[1] The variation of the dielectric constant of ferroelectric ceramics of perovskite-like structure which applied to D.C bias depends on 180° domain switcthing or 90° domain rotation. H. Diamond[2] assumed that polycrystalline ferroelectric grains around some chosen temperature are taken a Gaussian distribution and obtained the permittivity by averaging over all crystallites.

J. Janta[3] proposed the hysteresis loop of the ferroelectric crystal as the results of domain-wall motion. From this results, we can understand that there is a nonlinear field dependence of dielectric constant. M. Narutake[4] and T. Ikeda presented bias dependence of dielectric constant of $BaTiO_3$ ceramics, paying attention to piezoelectric interactions, which are the sourced of anisotropy in the crystal. M. E. Drougard[6] and D. R. Young explained the effect of "domain clamping" in $BaTiO_3$ the tetragonal state, which follows from the piezoelectric deformations of the domains.

N. Uchida[5] and T. Ikeda measured the bias dependence of Pb(Ti, Zr)O_3 family ceramics and presented at tentative model of polarization, concerning the reversal of 180° domains and rotation of 90° domains.

They considered that the contribution of 180° reversal and 90° rotatted domains separately.

This paper reports the D.C bias and frequency dependence of dielectric constant for PZT family perovskite-like ferroelectric ceramics and discussed onto the behavior of 180° and 90° domain in ferroelectric ceramics.

§2. Experimental

2.1 *Sample Preparation*

The substitution of $(La_{0.5}Li_{0.5})$ ions for Pb ions in Pb(Zr, Ti)O_3 ceramics can be shown a formula $Pb_{1-x}(La_{0.5}Li_{0.5})_x(Zr_yTi_{1-y})O_3$.

The coposition of a ceramics is indicated by PLLZTX/Y/Z, where X=100x, Y=100y and Z=100 (1−y). PbO, TiO_2, Li_2CO_3, ZrO_2 and La_2O_3 with 99.5–99.99% purities were used as raw materials. Weighed reagents were wet-milled for 16 hours in a polyethylen mill with agate stone or alulmina stone in alcohol, dried and then calcined at 800°C for 2 hours. They were then crushed, wet-milled again in alchohol.

Samples with PLLZT10/65/35 (trigonal phase), 10/53/47 (trigonal-tetragonal phase) and 10/40/60 (tetragonal phase) compositions were hot-pressed at 1150–1200°C under 200 kg/cm^2 pressure for 50 hours in oxygen enriched air atmosphere. Excess PbO (2 wt%) was added to the specimen before hot-pressing. The hot-pressed ceramics disk was sliced by a diamond-cutter.

The specimens were square plate of about 25 mm^2 in area and 0.5–0.55 mm in thickness. The sliced peaces were polished by 2000 mesh SiC powder. Shyoei-Kagaku's silver paste deposited onto the both faces of a specimen and its specimen was anneiled at 550°C for 30 minitus into the electric furnace.

2.2 *Measurements*

The properties of D.C bias and frequency dependence of dielectric constant were measured by using the equivalent circuit is illustrated in Fig. 1. Dielectric constant measurements were performed at four frequencies; 1, 10, 100 kHz and 1 MHz. The A.C measuring signal was 200 mV rms, D.C voltage was applied by using synchronous motor stepped up by 4.2 V/s. Electrical capacitance of these samples are about 300–400 pF respectively. The detecting resistance were changed from 5 Ω to 1 KΩ, after due to consider the measurement frequencies and electrical impeadance of the specimens.

Samples were setted into silicone oil bath. Temperature stabilization was ±0.5°C. Temperature measurements wre carried out by a alumel-chromel thermocou-

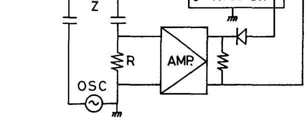

Fig. 1. Schematic picture of bias and frequency dependence measurement.

ple, which was in contact with the sample.

Remanent polarization and coercive field were obtained from 50 Hz D-E hysteresis loop using modified Sowyer-Tower curcuit.

The elastic and electromechanical measurements were made with the resonance-antiresonance method in radial mode vibration.

§3. Results and Discussions.

The results of the dielectric measurements of three compositions are shown in Fig. 2(a), (b) for PLLZT10/53/47 near the trigonal-tetragonal phase transition, Fig. 3(a), (b) for trigonal phase PLLZT10/65/35 and Fig. (a), (b) tetragonal phase PLLZT10/40/60 compositions, respectively. The dielectric measurement of specimen are made by depolarized vergin state annealed into the electric furnace.

Measurement temperature are at 19 and 100°C, respectively.

The D.C bias was applied to specimen in alphabetical order A, B, C,. . . N. From the examining result of the Fig. 2–4, the following interesting phenomena were observed.

(a) When the biasing field is varied from at point K to E, two dielectric peaks appear in vicinity of point J and N in the figure.

(b) The d.c bias dependence of the dielectric constant is

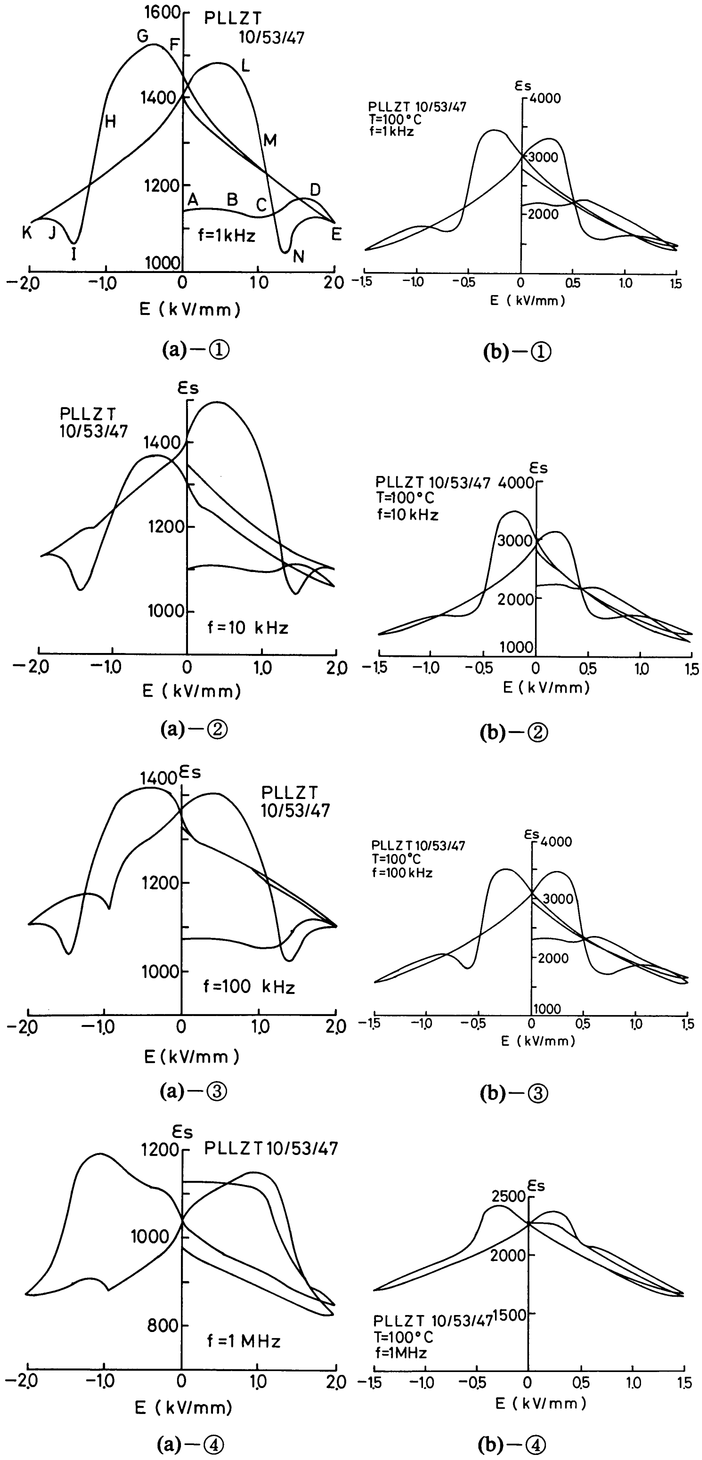

Fig. 2. (a) The d.c bias and frequency dependence of dielectric constant for PLZZT10/53/47 ceramics at 19°C.
(b) The d.c bias and frequency dependence of dielectric constant for PLLZT10/53/47 ceramics at 100°C.

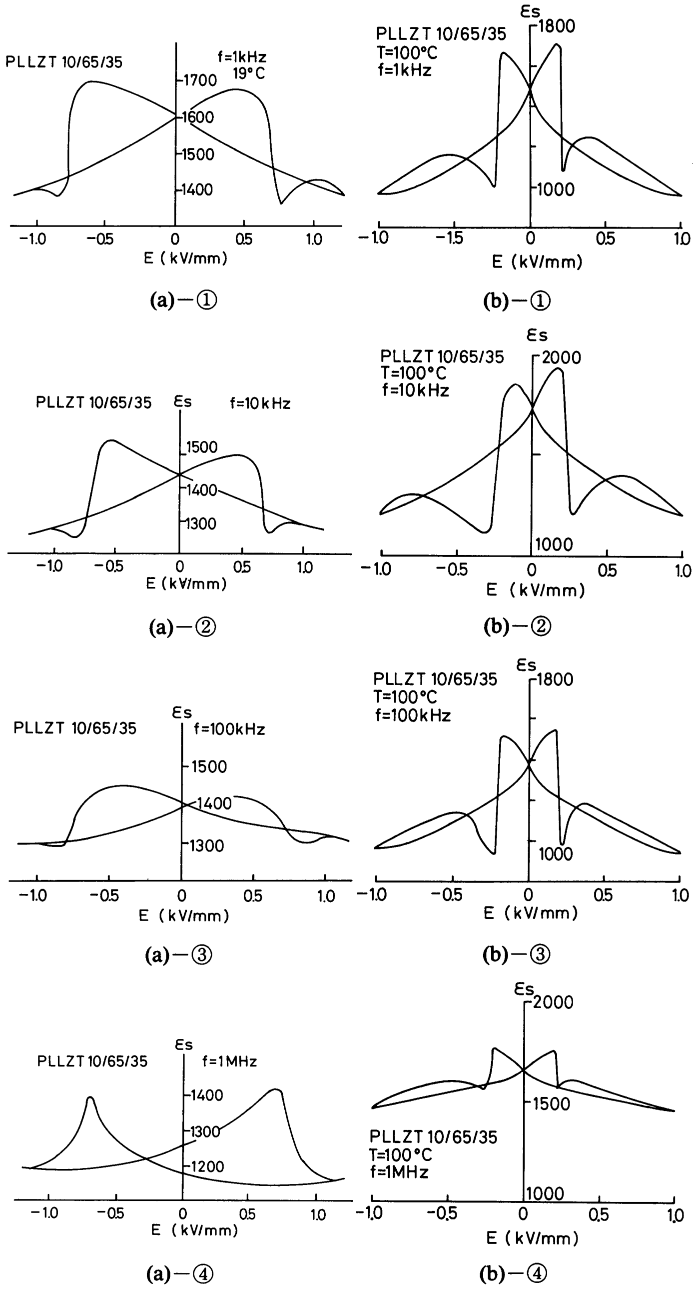

Fig. 3. (a) The d.c bias and frequency dependence of dielectric constant for PLLZT10/65/35 ceramics at 19°C.
(b) The d.c bias and frequency dependence of dielectric constant for PLLZT10/65/35 ceramics at 100°C.

almost frequencies independent with the range 1-100 kHz. As a measuring frequency of 1 MHz, the peaks at *N* and *J* almost disappear.

Owing to reverse the biasing field, two laerge dielectric anomaries appear right and left side symmetrically.

(c) The dielectric peak observed at 100°C appears more sharply than one at room temperature. Because it seems that the results of coercive field of ferroelectric ceramics decreases with increasing temperature. The electric field which occurs the dielectric peak shifts the lower direction, owing to increasing higher temperature.

The dielectric constant of poled PLLZT10/53/47 ceramics increase more 26% than its value at vergin state and one of poled PLLZT10/40/60 composition decreases less than about 15% than its at vergin state, respectively. This experimental results can be explained following that the re-orientation of 90° domain rotating and 180° domain switching.

(i) Vergin state ($A \longrightarrow E$)

The dielectric constant anomalies have been no influenced by 180° domain switching from point A to E. In the vergin state, dielectric behavior indicated by *D* in the figure, was determined by cooparation both of 90° rotative domain and inverse piezoelectric effect.

(ii) Depolarization process ($E \longrightarrow F$)

As depolarizing process from point *E* to *F*, the increasing of dielectric constant is influenced by 90° domain ratation in ceramics, mainly.

(iii) Polarization-reversal process ($F \longrightarrow K$)

The reversal of 180° and 90° re-rotation domains play their respective parts in changing the dielectric constants under the biasing field from point *F* to *K*. It seems that laerge dielectric anomarry at point *G* consist with interactions of both 180° reversal and first 90° domain ratation and the dielectric behavior of point *J* corresponds to second 90° domain rotation. The valley of dielectric constant near the point *I* consists with "domain clamping effect" observed at $BaTiO_3$ single crystal reported by M. E. Drougard and D. R. Young. The dielectric distributions concerned with 180° reversal and 90° rotation occurs remarkably at 1, 10, and 100 kHz measuring frequencies, but the dielectric peak at point *J* disappears at 1 MHz, because this effect can be explained that the relaxation frequency of 90° domain is smaller than 1 MHz.

(vi) Total dielectric constant.

A schematic picture of d.c bias dependence of dielectric constant is shown in Fig. 5. The ferroelectric ceramics are composed of both 180° and 90° domains in tetragonal phase and 180°, 109° and 71° domains in trigonal phase respectively. In order to simplify the calculation, the ceramics is considered as a mixture of two phases corresponding to the 180° and 90° domains. By applying Fig. (1), where ε_1 and ε_2 are dielectric constants of the 180°C and 90° domains, respectively and v_1 and v_2 are thier relative volume fractions, the total dielectric constant ε is calculated.

From the experimental results, it is deduced that there exists an interaction between the 180° and 90° domains. When the bias field is decreases, the 90° domains are not rotated to a direction perpendicular to the field direction, as long as most of the 180° domains are alinged with the field. This is due to the internal field created by the ordered 180° domains. When the most of the 180° domains are several process, this internal field becomes low enough to allow this 90° domain rotation. Hence, in considering the field dependence of the dielectric constant,

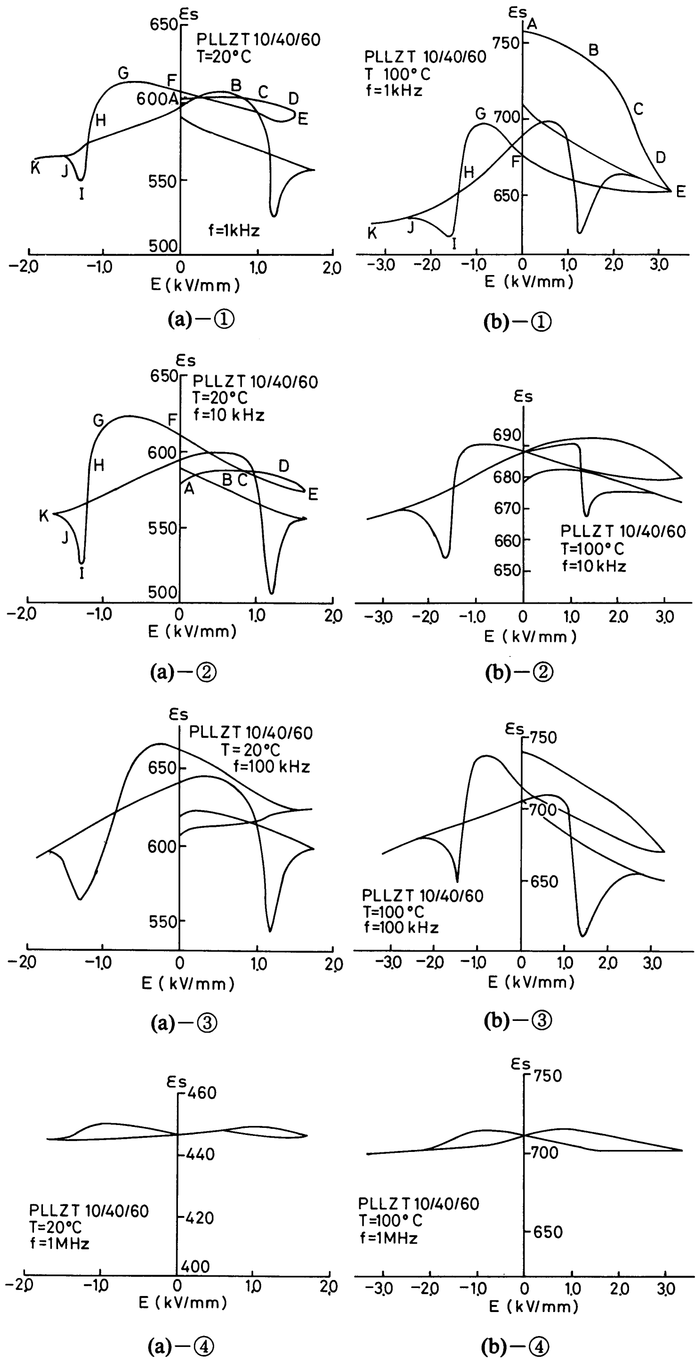

Fig. 4. (a) The d.c bias and frequency dependence of dielectric constant for PLLZT10/40/60 ceramics at 19°C.
(b) The d.c bias and frequency dependence of dielectric constant for PLLZT10/40/60 ceramics at 100°C

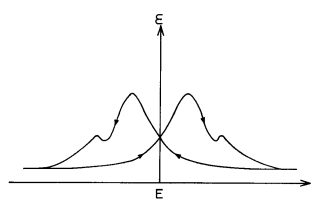

Fig. 5. Schematic description of the total dielectric constant vs d.c electric field.

the first peak due to 90° domains coincides with the one due to 180° domains, giving one big peak. When the field is increased further, the second 90°C rotation occurs, causing the appearance of the other peak in the dielectric constant.

$$\varepsilon = v_1 \varepsilon_1 + v_2 \varepsilon_2 \tag{1}$$

§4. Conclusions.

D.C bias and frequency dependence of PZT family ceramic compositions can be explained by schematic model on re-orientations of 180° and 90° domains qualitatively. Hereafter, we must be determined the best optimum poling conditions quantitatively, owing to applying the piezoelectric, ultrasonic and ligth functional devices.

References

1) A. F. Devonshire: Philos. Mag. Suppl. **3** (1954) 85.
2) H. Diamond: J. Appl. Phys. **32** (1961) 909.
3) J. Janta: J. Phys. Soc. Japan. Suppl. **28** (1970) 340.
4) M. Marutake and T. Ikeda: J. Phys. Soc. Japan. **12** (1953) 233.
5) N. Uchida and T. Ikeda: Jap. J. Appl. Phys. **4** (1965) 867.
6) M. E. Drougard and D. R. Young: Phys. Rev. **94** (1954) 1561.
7) N. Bar-Chaim, M. Brunstein, J. Gruberg and A. Seidman: J. Appl. Phys. **45** (1974) 2398.