# Dielectric Properties
# in LiTaO₃-CaTiO₃ Solid Solution Ceramics

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A set of solid solution ceramic synthesizing in $(1-x)LiTaO_3$-$xCaTiO_3$, $0 \leq x \leq 0.2$, family made it clear that $CaTiO_3$ component lowered their Curie temperature at 16°C/mol% up to 17%, where the solution effects were markedly changed. The more the $CaTiO_3$ concentration came, the more significant the feature of the relaxer like phase transition was. The reciprocal dielectric permittivity depended upon uniaxial pressure, showing their possibility of application for pressure sensors.

*Key Words* : Lithium Tantalite, Calcium Titanite, Dielectric Permittivity, Relaxer, Phase Transition, Gibbs Free Energy, Piezoelectric Effect

## 1. INTRODUCTION

A single crystal LiTaO₃ has been widely used as SAW devices, non-linear optical devices, pyroelectric infrared sensors and so on [1]. The experimental investigations so far studied were mainly on the single crystal LiTaO₃ because Matthias and Remeika, the first reporters of this ferroelectric material, pointed that LiTaO₃ has rather low crystal symmetry and suggested that the investigation on this material should be carried out with a single crystal but polycrystalline ceramics [2]. Nowadays the most important and the most widely used piezoelectric ceramic is lead zirconate titanate (PZT) family ceramics. However, the element, lead, containing in these ceramics has been regarded as an unacceptable· substance from the view points of environmental problem. The LiTaO₃ piezoelectric ceramics, then, has received considerable attention due to the possible substitute for PZT ceramics for signal processing. We have so far developed piezoelectric LiTaO₃ ceramics and demonstrated the successful operation of both the CMOS oscillator and the Lamb wave device using the newly developed piezoelectric ceramics [3]. In the present work, the effects of partial substitution by CaTiO₃ in the LiTaO₃ ceramics, with special interest in the composition where the solution effects changes, has been investigated in more detail, particularly on their dielectric properties.

## 2. EXPERIMENT

Starting materials of the ceramics were powder of reagent grade Li₂CO₃, Ta₂O₅, CaCO₃, and TiO₂. The required amounts of the materials together with ethanol were mixed for 24 h by zirconia balls. After drying, mixtures of these materials were calcined in an alumina crucible at 1000°C for 3 h, then crushed into powder and pressed at 10 MPa to form a pellet of 20 mm in diameter with adding a small amount of PVA solution. The pellet was sintered at

1250°C for 5 h.

The crystal phase and surface morphology of the ceramics were confirmed by XRD and FE-SEM, respectively. After grinding the ceramic into 0.5 mm, their surfaces were lapped up and electrodes were sputter-deposited by 0.1 μm-thick Ti first and 5 μm-thick Au on them, 15 mm in diameter. The dielectric properties were measured by using the impedance analyzer, HP-4192A.

The effects of uniaxial pressure on the dielectric permittivity were measured by adjusting to the desired pressure by air press. In order to detect the electrostatic capacitance, a CR oscillator circuit consisting of the timer IC, IC555, as shown in Figure 1, was devised. The oscillation frequency, $f$, in this case, is given by

$$f = \frac{1.443}{3RC} \text{ [Hz]} \tag{1}$$

where, $R$ [Ω] is the externally added resistance and $C$ [F] is the capacitance to be measured.

## 3. RESULTS AND DISSCUSION

### 3.1 XRD and SEM Studies:

Unlike the perovskite structure, the LiTaO₃ structure consists of a sequence of distorted oxygen octahedra joined by their faces along a trigonal polar c-axis. The space point group has 3 m symmetry under Curie temperature [4]. Phase identification was made by X-ray diffraction meter (Rigaku Denki, RINT 2200 V/PC-SV) using Cu-Kα radiation. Figure 2 shows the XRD patterns of the ceramics with different amount of CaTiO₃ substitution. Although the ceramics substituted by up to x=0.20 in $(1-x)LiTaO_3$-$xCaTiO_3$ system seem in the lithium niobate structure as the major phase, XRD patterns in x ≥ 0.17 seem to result a small additional peak near $2\theta = 35°$. At least up to x=0.17, the lattice constant, $a$, became larger as the substituted amount increased, while the constant, $c$, became smaller at the

corresponding conditions (Figure 3); in another word, the c/a value decreases with $CaTiO_3$ solution. The uniaxial ferroelectric crystals, in general, the spontaneous polarization lies in their c-axis direction and the larger polarization corresponds to the larger elongation in this direction. When the temperature of the ferroelectric material is lowered from its Curie temperature, the c/a value increases as typically observed in $BaTiO_3$ crystal in the tetragonal phase [5]. Therefore the XRD data suggest the decrease of their spontaneous polarization or the lowering of the Curie temperature by the $CaTiO_3$ solution.

Photo 1 shows SEM images observed by Hitachi FE-SEM, S-4100, with 25 kV acceleration voltage. According to our experiences, it is very difficult to obtain densely sintered $A^I B^V O_3$ ($A^I$: alkaline metal, $B^V$: five valence metal) bodies by ordinary sintering. Pure $LiTaO_3$ ceramic always has coarse structure as can be seen from Photo 1 (a), while solid solutions in x≧0.1 (Figure 2 (c)~(d)) have very small porosity; that is the solid solution does not only affect on electrical properties discussed below, but also is very effective on the sintering behavior. Thin ceramic
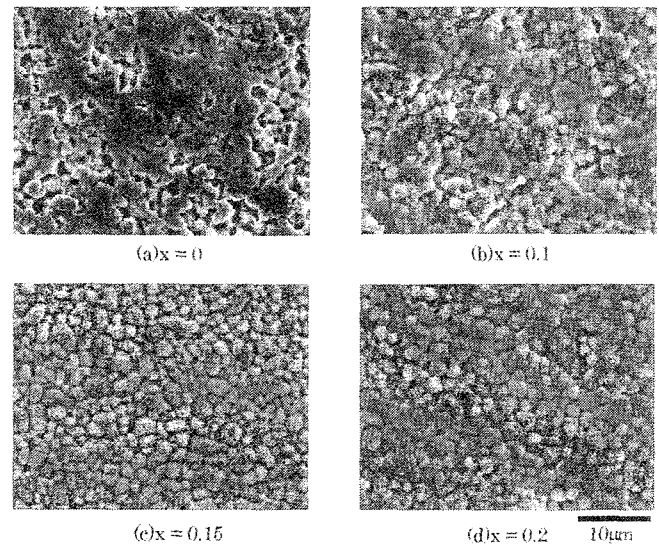


(a)x = 0    (b)x = 0.1

(c)x = 0.15    (d)x = 0.2    10μm

Photo 1    SEM images of (1-x)LiTaO₃-xCaTiO₃ ceramics.
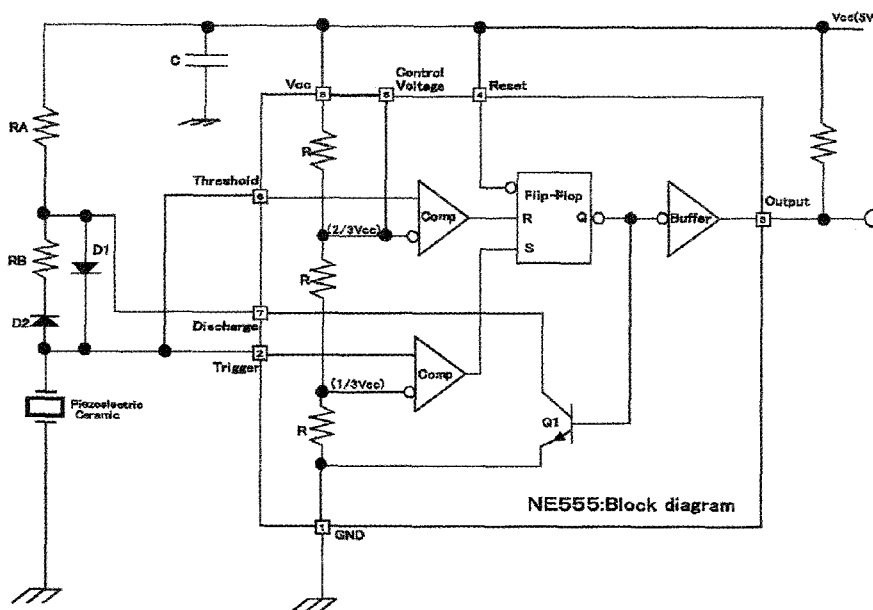


Figure 1    Timer oscillation circuit for measuring mechanical stress.
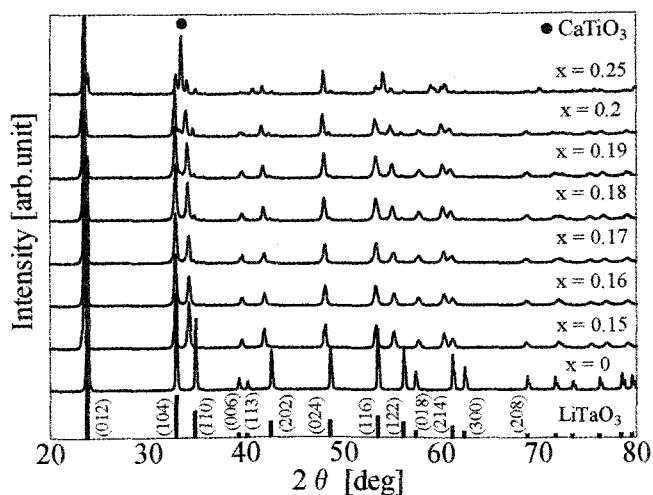


Figure 2    XRD patterns of (1-x)LiTaO₃-xCaTiO₃ ceramics.
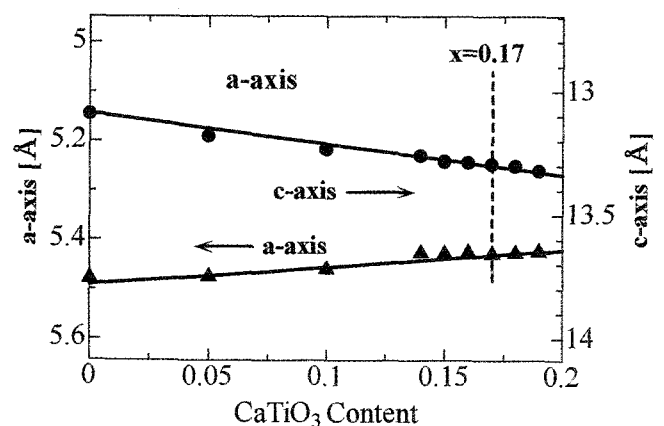


Figure 3    Lattice constants as a function of CaTiO₃ content in (1-x)LiTaO₃-xCaTiO₃ ceramics.

plates of these dense solid solutions were semitransparent.

## 3.2 Temperature Dependence of Dielectric Properties:

Figure 4 shows dielectric characteristics of the ceramics with various compositions. The Curie temperature has been lowered with increased amount of $CaTiO_3$, with an approximate rate of $16°C/mol\%$ up to 17%. The phase transition becomes smeared considerably with the substitution, suggesting the diffused phase transition. The dielectric loss tangent begins to increase at a temperature corresponding to the phase transition. Since the loss tangent increment at higher temperatures is regarded as the increased ionic conduction, the ion which contributes to the ferroelectric interaction may become free from such restriction in the paraelectric phase.

## 4. Relaxer Like Phase Transition

The dielectric characteristics in these ceramics depend on the measuring frequency; the dielectric constant of $0.83LiTaO_3$-$0.17CaTiO_3$ is lowered at higher frequencies (Figure 5) as often observed in the complexly substituted composites. It is known that the typical relaxer material shows the peak temperature $T_m$, defined by the dielectric maximum, shifts to a higher temperature and at the same time the peak dielectric constant is lowered with the
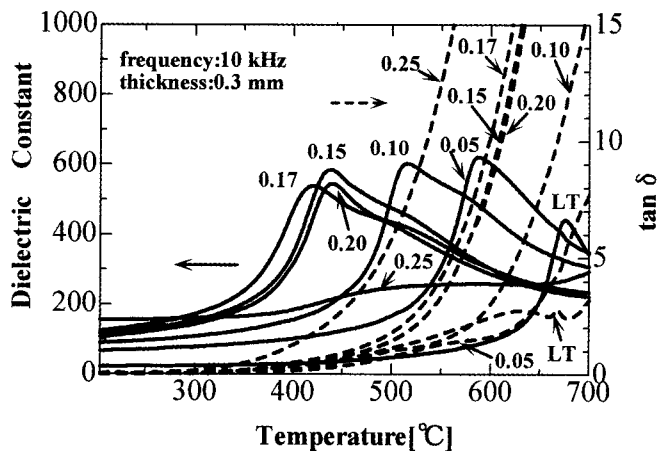


Figure 4   Dependence of dielectric constant and tan $\delta$ on temperature for $(1-x)LiTaO_3$-$xCaTiO_3$ ceramics.
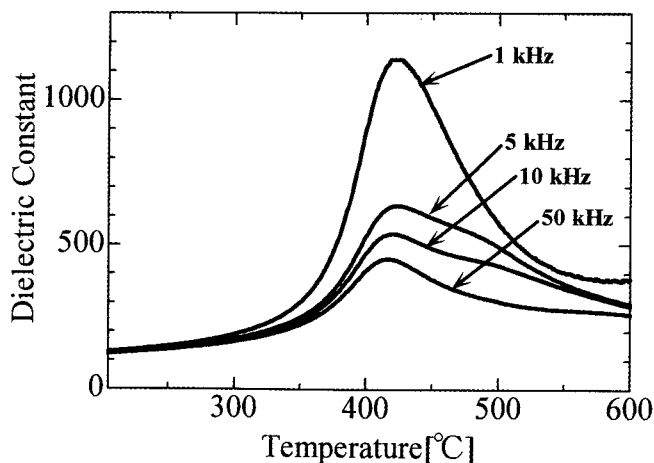


Figure 5   Dependence of dielectric constant on frequency for 0.83 $LiTaO_3$-0.17 $CaTiO_3$ ceramic.

increased frequency [6-7]. As for the peak value of the dielectric constant, it is significantly lowered by the higher frequency, coinciding with the feature of the relaxer material.

The temperature dependence of a usual relaxer material deviates from the Curie-Weiss law above the Curie temperature and instead follows the relation [6],

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T-T_m)^2}{C} \qquad (2)$$

where $\varepsilon$ and $\varepsilon_m$ are the dielectric constants at temperatures $T$ and $T_m$, respectively, and $C$ is the constant. In order to check the feature of the relation in our solid solution system, the same data in Figure 5 were plotted $(T-T_m)^2 - 1/\varepsilon$ plane as in Figure 6. In the figure, the abscissa indicates square of the temperature difference between the measured and dielectric-peak temperatures, while the ordinate shows the relative reciprocal dielectric constant normalized so as to 100% for the peak temperature. The reciprocal dielectric constant $1/\varepsilon$ seems to be fundamentally proportional to $(T-T_m)^2$. On the other side, we have noticed that the peak temperature $T_m$ is not markedly affected by the measuring frequency different from typical relaxer materials. Since the relaxer characteristics are regarded as a kind of meso-scopic phenomena, which assumes the distribution of the Curie temperature within the material [8], the present solid solution system may suggest a feature of inhomogeneous distribution of the solute, $CaTiO_3$.

## 5. Piezo-Dielectric Properties

Since there exists an interaction between dielectric and elastic energies in ferroelectrics, the dielectric permittivity of those materials usually depends upon the elastic stress. We call the phenomenon as the piezo-dielectric effect for convenience. Prior to the measurement, the ceramics were poled through the dc voltage application. The treatment started at $450°C$ with 1.0 $A/cm^2$ of the dc electric current and lowered the temperature keeping the current constant. Since the ceramic resistivity increases with lowering the temperature, the voltage applied to the ceramic becomes larger during the cooling process. After the electric voltage attained to 500 V/mm, then the electric field were kept constant until room temperature. The observed data were
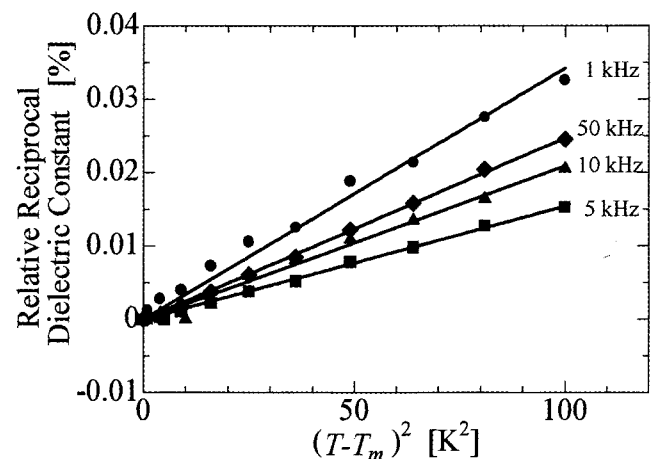


Figure 6   Dependence of reciprocal dielectric constant on temperature represented as $1/\varepsilon - (T-T_m)^2$ relation on 0.83 $LiTaO_3$-0.17 $CaTiO_3$ ceramic.

represented as in a form of the reciprocal dielectric permittivity on the applied elastic stress and normalized so that the value becomes unity at 0 MPa pressure (Figure 7). From the figure, we can see in all the ceramics that the reciprocal permittivity, $\beta$, increases with increasing amount of the elastic stress, $X$, and, among them, the solid solution ceramic with 17% $CaTiO_3$ has the maximum sensitivity.

The thermodynamic potential convenient for the discussion on the elastic stress effect is the elastic Gibbs free energy, which is expressed as a function of independent variables of temperature, stress and dielectric flux density [9]. Assuming the spontaneous polarization exists along with a certain direction of crystal axis and the applied electric field is restricted to this direction, we can write the stress free energy, $G_1$, as the polynomial by using only one dielectric flux density component, $D_i = D$,

$$G_1 = G_{10} - \frac{1}{2} \beta^X D^2 + \frac{1}{4} \gamma^X D^4 \qquad (3)$$

where $G_{10}$ is the energy at the non-polar phase and we terminate the polynomial up to $D^4$ for simplification. The coefficient of the second term, $\beta^X$, is in general temperature-dependent but we mainly consider the case in a ferroelectric phase sufficiently lower than the Curie temperature. The coefficient of the last term, $\gamma^X$, should be the positive value.

Differentiating the elastic Gibbs free energy with respect to $D$ at the constant temperature and stress, the dielectric equation of state comes

$$E = \frac{\partial G_1}{\partial D} = -\beta^X D + \gamma^X D^3 \qquad (4)$$

where $E$ is the electric field. In the $D$-$E$ relation of ferroelectrics, we find the operating point without external biasing field exists at

$$D = \sqrt{\frac{\beta^X}{\gamma}} \qquad (5)$$

Upon application of the mechanical stress $X$, additional dielectric flux density is induced through piezoelectric strain coefficient, $d_{33}$. Then the operating point $D_0$ of the ordinate shifts into

$$D = \sqrt{\frac{\beta^X}{\gamma^X}} \left( 1 + \sqrt{\frac{\gamma^X}{\beta^X}} d_{33} X \right) \qquad (6)$$
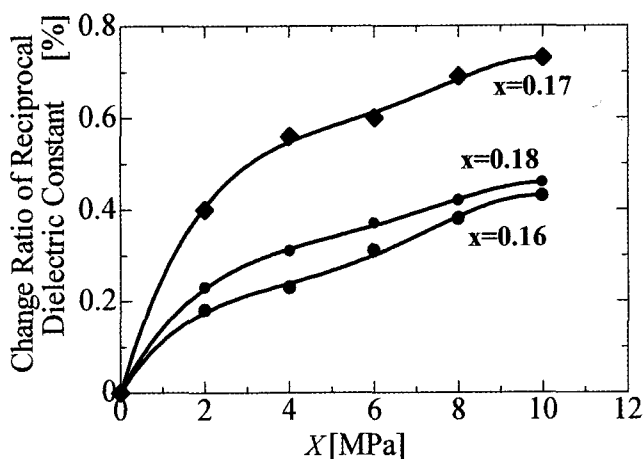
where the relation

$$1 >> \sqrt{\frac{\gamma^X}{\beta^X}} d_{33} X$$

is usually held.

On the other hand, we can now easily deduce isothermal reciprocal permittivity upon stress application by differentiating Eq. (4) with respect to $D$,

$$\beta = \frac{\partial^2 G_1}{\partial D^2} = -\beta^X + 3 \gamma^X D^2 \qquad (7)$$

Since the dielectric flux density $D$ under the elastic stress has derived as in Eq. (6), the reciprocal permittivity can be approximately written as

$$\beta \approx 2\beta^X + 6\sqrt{\beta^X \gamma^X} d_{33} X \qquad (8)$$

Although this is merely a rough approximation for small $X$ value, we can see that the reciprocal permittivity increases with increase of the applied stress through the shift of the operating point on $D$-$E$ curve. The observed result in Figure 7 corresponds to the tendency that the derived equation suggests. We can also see from the equation that the piezoelectric strain coefficient, $d_{33}$, affects the property or the solid solution ceramic $0.83LiTaO_3$-$0.17CaTiO_3$ should has the highest piezoelectric activity.

We have noticed from the temperature characteristics of the dielectric constant, that the Curie temperature is lowered with increase of $CaTiO_3$ amount until 17%, while further amount of $CaTiO_3$ no more lowers the temperature but brings about deformed characteristic curve. That is to say, the situation of the solid solution system is markedly changed at 17% $CaTiO_3$ content. In the most widely used piezoelectric ceramics, PZT or $PbZr_{1-x}O_3$-$PbTi_xO_3$, the improved piezoelectric activity is observed near the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral phases in the solid solutions [10]. More recently, on the way to develop a new lead-free piezoelectric ceramic, Yasuyoshi Saito et. al. investigated the other type of piezoelectric active MPB between a different pair of crystal structures and found a new MPB composition between the perovskite-type and pseudo-ilmenite-type structures [11]. They explain such mechanism from the view point of the hybridization of ionic and covalent bonding of the solid solution system. Since the present study has also treated on the solid solution system between end members of pseudo-ilmenite-type and perovskite-type structures, similar mechanism may occur near 17% $CaTiO_3$ content in our solution system.

## 4. CONCLUSIONS

The effects of the solute in $(1-x)LiTaO_3$-$xCaTiO_3$, $0 \leq x \leq 0.2$, family ceramics were found duplex, that is, not only to modify their electrical properties but also to improve the sintering behavior. The rate of lowering the Curie temperature by the solute $CaTiO_3$ component was at $16°C/mol$ up to 17%, where the solution effects were markedly changed. The feature of the relaxer like phase transition became significant when the $CaTiO_3$ concentration increased. The reciprocal dielectric constant depended upon the uni-axial pressure and the observed sensitivity was lead to the maximum at the composition of 17% $CaTiO_3$.



Figure 7  Piezo-Dielectric effect at room temperature as a function of stress $X$ on $(1-x)LiTaO_3$-$xCaTiO_3$ ceramics.

Naoyuki ENDO et. al.

## References

[1] M. Lines and A.Glass (1977), "*Principles and Applications of Ferroelectrics and Related Materials*," pp.559-604, Clarendon Press, Oxford.

[2] Matthias and Remeika (1949), "Ferroelectricity in the Ilmenite Structure, "*Phys. Rev.*, 76, pp.1886-1887.

[3] T. Fukami, T. Yokouchi, N. Bamba, B. Elouadi and K. Toda (2002), "Piezoelectric Properties in $LiTaO_3$-$CaTiO_3$ Solid Solution Ceramics.", *Ferroelectrics*, 273, pp.265-370.

[4] K-Hellwege and A. M. Hellwege (1981), "Ferroelectronics and Related Substances" *LANDOLT-BÖRNSTEIN* III/16a, Springer-Verlag Berlin, Heidelberg, New York, p157.

[5] H. F. Kay and P. Vousden (1949), "Symmetry Changes in Barium Titanate at Low Temperatures and Their Relation to Its Ferroelectric Properties", *Phil. Mag.*, 40, pp.1019-40.

[6] V. Kirillov and V. Isupov (1973), "Relaxation Polarization of $PbMg_{1/3}Nb_{2/30}O_3$ (PMN)- a Ferroelectric with a diffused Phase Transition," *Ferroelectrics*, 5, pp.3-9.

[7] S. Chattopadhyay, P. Ayyub, V. K. Palkar and M. Multani (1995), "Size-induced diffuse phase transition in the nanocrystalline ferroelectric $PbTiO_3$," *Phys. Rev.*, B52, pp.13117-83.

[8] G. A. Smolenskii, V. A. Isupov, A. I. Agranovskaya and S. N. Popov (1961), "Ferroelecrics with diffuse phase transitions," *Sov. Phys. Solid State*, 2, pp.2584-94.

[9] A. F. Devonshire (1949), "Theory of Barium Titanate," *Phil. Mag.* 40, pp.1040-1079.

[10] B. Jaffe, W. R. Cook, Jr., and H. Jaffe (1971), "*Piezoelectric Ceramics*", pp.135-183, Academic Press.

[11] Y. Saito, H. Takao, T. Tani, T. Monoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura (2004), " Lead-free piezoceramics," *Nature*, 432, pp.84-87.