

The Overview of The Electrical Properties of Barium Titanate

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Abstract: - The perovskite family includes many titanates used in various electroceramic applications, for example, electronic, electro-optical, and electromechanical applications of ceramics. Barium titanate, perovskite structure, is a common ferroelectric material with a high dielectric constant, widely utilized to manufacture electronic components such as multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices. Pure barium titanate is an insulator whereas upon doping it transforms into a semiconductor. Besides PTCR properties, semiconductor barium titanate is used in the sensor applications. The ferroelectricity observed in barium titanate is utilized in memory applications, i.e RAMs. The pyroelectricity and piezoelectricity are also used in the passive infrared detectors and Sonars (Sound Navigation and Ranging). In the present study, various electrical properties of barium titanate based ceramics were explained and examples of the relevant applications were given.

Keywords: - Barium titanate, semiconductor, ferroelectricity, piezoelectricity.

I. INTRODUCTION

One of the most interesting application of BaTiO_3 is as semiconductor with positive temperature coefficient of resistivity (PTCR). Dopant additions are needful to the host titanate composition to achieve PTCR property enhancement. It is possible to use some trivalent rare earth elements for substitution and to produce semiconducting behavior in the perovskite lattice. Similarly, pentavalent dopants (Sb, Nb, Ta) can also produce semiconduction by substitution at Ti^{4+} lattice sites[1].

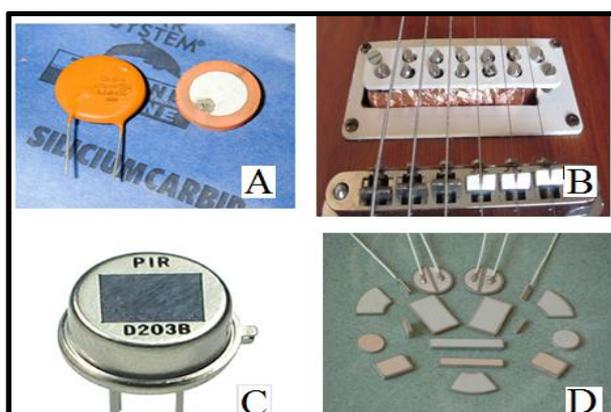


Figure 1 A. Ferroelectric capacitor[2], B. Piezoelectric electronic guitar pick up[3], C.Passive infrared sensor[4] and D. PTC elements[5].

BaTiO_3 is well known as fundamental ferroelectric perovskite oxide and is often used in multilayer ceramic capacitors due to high dielectric constant and low loss characteristics as shown in Fig.1. Despite its relative low Curie temperature and piezoelectric properties inferior to those of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, lead-free BaTiO_3 remains attractive for environmental reasons[6]. BaTiO_3 has become one of the most important electroceramic

materials among all the ferroelectric materials. BaTiO₃-based ferroelectrics transform from paraelectric phase to ferroelectric phase at Curie temperature (T_c 130°C). This transformation normally causes a complicated stress system in this ferroelectric material, and then results in a generation of internal stresses at room temperature which significantly affect properties of BaTiO₃[7]. Also, the BaTiO₃ based normal ferroelectrics are strong candidates for field induced piezoelectric transducers due to their large polarizations, large permittivity and the large induced strains achievable in these materials[8]. Infrared detection employing ferroelectric sensing elements as pyroelectrics was demonstrated over 40 years ago. Since that time, there have been a host of studies describing ferroelectric-based pyroelectric detectors. The most commercially successful pyroelectric technology to date has utilized barium strontium titanate (BST) materials[9].

II. BARIUM TITANATE AS A SEMICONDUCTOR

II. I Donor Doping Of BaTiO₃

In a stoichiometric solid solution the extra positive charge of a donor center can be compensated by a cation vacancy or an anion interstitial



(1) maintains a perfect cation sublattice, while the anion sublattice is perfect in (2). A shift from the stoichiometric solid solution with its compensation by a lattice defect, to a non-stoichiometric solid solution with compensation by an electronic defect, requires an interaction with the ambient atmosphere. The stoichiometric solution may gain or lose oxygen at oxygen activities greater than or less than, in equilibrium with the stoichiometric composition. In this way, The compensating lattice defect is eliminated and is replaced by electrons in the case of donor dopants [10].

When La³⁺ replaces Ba²⁺ on the A-site (La is too large to replace Ti on the B-site), charge imbalance is created which must be compensated by either cation vacancies on the A- or B- site (ionic compensation), or by electrons (electronic compensation) as in (3)-(5).



Ionic compensation ([3] and [4]) should have negligible effect on the room temperature conductivity due to the immobility of cation vacancies; La doped BaTiO₃ compensated in this way should, therefore, remain insulating. In contrast, electronic compensation ([5]) should cause a substantial increase in conductivity, in which the number of carriers equals the La concentration[11].

Fig.2. indicates the effect of donor concentration (La³⁺) on the electrical conductivity and grain size of BaTiO₃. As the donor concentration increases initially the conductivity increases up to 0.15% of La³⁺ and then decreases up to 0.3% of La³⁺. The high conductivity region is where the electronic compensation dominates, after a critical donor concentration, cation vacancy compensation dominates and electrical conductivity decreases. Up to 0.3% of La³⁺, the grain size of BaTiO₃ is not affected by donor concentration being 25 μm, however, above 0.3% of La³⁺, grain size decreases to 5μm.

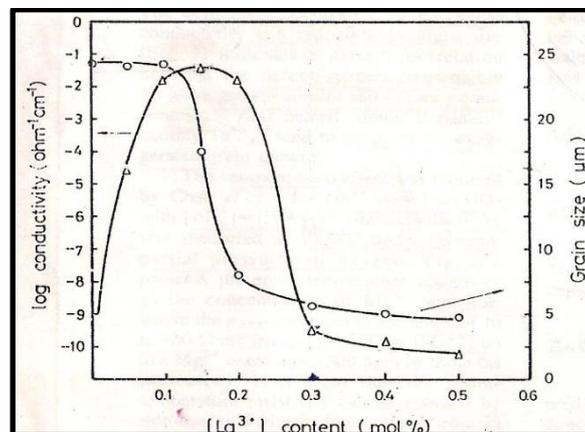


Figure 2 Schematic of donor concentration influence on room temperature electrical conductivity and grain size[10].

Donor dopant incorporation is achieved by either electronic compensation at low concentrations or vacancy compensation at high concentrations. High concentrations of segregating donors at grain boundaries inhibits grain growth. At small concentrations, donor incorporation by electronic compensation explains the high conductivity. As the average dopant concentration increases, the local donor concentration at the grain boundary increases rapidly due to segregation. The donor incorporation at the grain boundary shifts from electronic to vacancy compensation, resulting in the formation of highly resistive layers and also, grain size decreases due to significant dopant drag on the boundary mobility[12].

Poly-crystalline n-type semiconducting barium titanate (BaTiO_3) exhibits a behaviour known as the positive temperature coefficient of resistivity (PTCR) effect. The electrical resistivity of n-type semiconducting barium titanate increases by several orders of magnitude near the ferroelectric Curie temperature (120°C)[13]. At the Curie temperature, barium titanate undergoes ferroelectric to paraelectric transition[14]. This behaviour is indicated in Fig. 3 [15]. It has also been reported that single crystals of barium titanate exhibit negative temperature coefficient of resistivity (NTCR) properties.

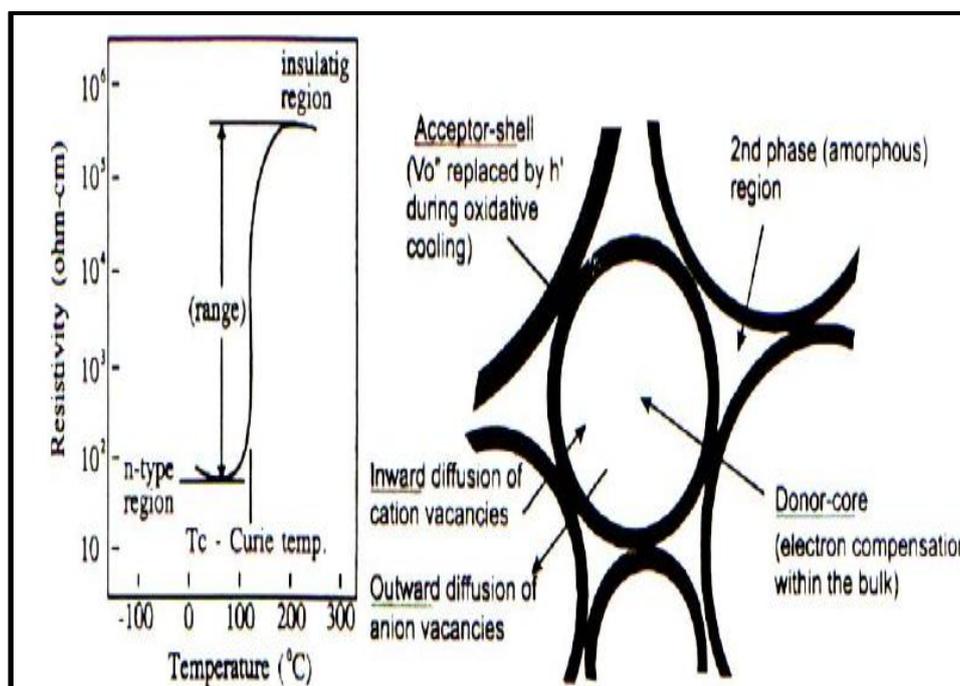


Figure 3 Electrical resistivity for typical PTCR device and schematic presentation of defect chemistry responsible for PTCR effect [16].

Sintering under O_2 atmosphere affects not only barrier height but the resistance and capacitance of grain boundaries. The effect is due to variation of the adsorbed gases at the grain boundaries. The diffusion coefficient of oxygen at grain boundary is much higher than that in bulk, which implies that there is a gradient of adsorbed oxygen density in the surface of the grain. Sintering under O_2 atmosphere results in increasing number of oxygen acceptors at the grain boundary and increase in resistance. The barrier height also increases with sintering[17]. These PTC materials prepared from doped semiconducting BaTiO_3 ceramics can be used in various kinds of electronic circuitry as a switching device or as a constant temperature heater. Other important application of a PTC thermistor is the measurement/detection/control of temperature or parameters related to temperature. These PTC materials are known to have the highest temperature coefficient of resistance among all sensor materials available [16].

III. FERROELECTRIC PROPERTIES OF BARIUM TITANATE

Amongst other ferroelectric materials, barium titanate (BaTiO_3) is a useful and technologically important material owing to its ferroelectric behavior at and above room temperature (T_c 393°K), and having polarization (P_s) values several orders higher than the potassium dihydrogen phosphate-type ferroelectrics[18]. In order to improve the electrical reliability of barium titanate, nano-sized second phases were incorporated into matrix. Dielectric constant, ϵ_r was 3279, which increased with additive and dielectric loss, $\tan \delta$ remained constant. BaTiO_3 ceramic showed a slim ferroelectric loop with 4.55 kV/cm of E_c , $3.72 \mu\text{C/cm}^2$ of P_r and 0.59 of

loop squareness (R_{sq})[7]. In an attempt to improve the dielectric properties, microwave sintering was used. As a result, ϵ_r and $\tan \delta$ were measured as 2500 and 0.03, respectively. The sharpness of the P–E hysteresis loop indicates the better homogeneity and crystallinity of the prepared system. P_r and E_c are $6 \mu\text{C}/\text{cm}^2$ and 1.45 kV/cm, respectively[8]. Al doped and undoped barium titanate indicated P_r of 11.4 and $5 \mu\text{C}/\text{cm}^2$ and E_c of 4 and 3.1 kV/cm. The dielectric constant increased and dielectric loss factor decreased by doping. However, Curie transition shifted to lower temperature (from 121 to 113°C) [19].

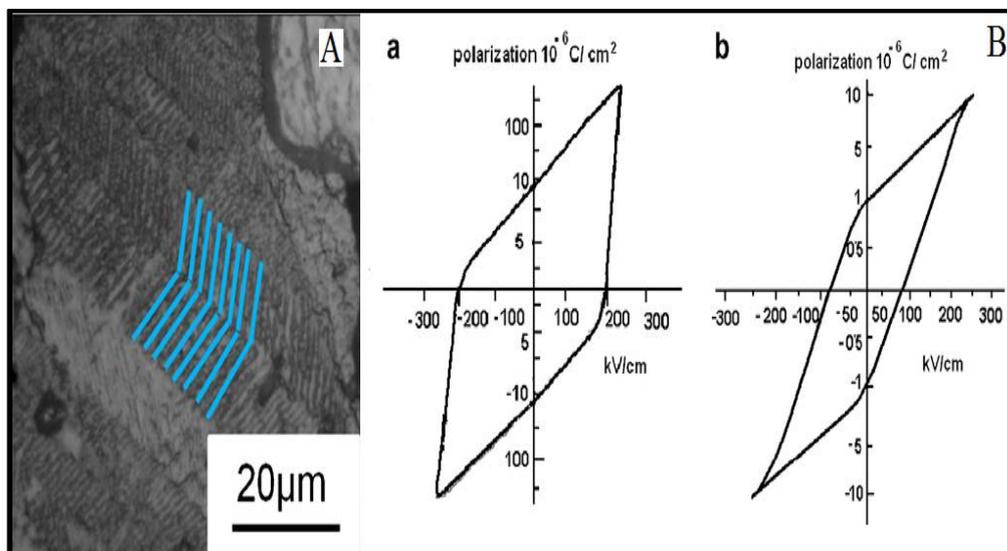


Figure 4 A. Ferroelectric domain pattern of BaTiO₃[20] and B. Hysteresis loop of a. pellet form and dispersed[18].

The effect of sintering temperature on the ferroelectric properties was also investigated. When the sintering temperature was raised, Curie transition shifted to higher temperature (125°C). The improved densification resulted in the reduction of cavities, thereby the dielectric constant increased. E_c and E_c are $10.2 \mu\text{C}/\text{cm}^2$ and 6.4 kV/cm, respectively. The remanent polarization, P_r first increased and then decreased with sintering temperature while coercive field, E_c increased continuously. However, oxygen vacancies were easier created at high sintering temperature, which strengthen the pinning effect to the ferroelectric domain as in Fig.4.A under an electric field, thereby inducing a continuous increase of the E_c and a decline of the P_r [20].

Nano-sized barium titanate was synthesized by solid state reaction. A 100% c-oriented system gives a square loop, whereas the loop for randomly oriented grains is likely to be tilted. The hysteresis loops obtained for this study is shown in Fig.4.B. The hysteresis loop is found to be wide and stretched in the case of barium titanate nanopowders used in the form of a pellet. In contrast, the polymer-dispersed BaTiO₃ nanoparticle system showed a relatively narrow loop, with long tails at the ends. The remanent polarization (P_r) was found to be 10 times larger in the case of a compact nanoparticle system ($10 \mu\text{C}/\text{cm}^2$) compared to the dispersed nanoparticles ($1 \mu\text{C}/\text{cm}^2$). It is already known that a single-crystal BaTiO₃ system could show a P_r as large as $26 \mu\text{C}/\text{cm}^2$. The coercive fields were found to be 200 and 70 kV/cm, respectively[18].

IV. PIEZOELECTRIC PROPERTIES OF BARIUM TITANATE

The BaTiO₃ based normal ferroelectrics are strong candidates for field induced piezoelectric transducers due to their large polarizations, large permittivity and the large induced strains achievable in these materials[8]. The synthesis of BaTiO₃ by conventional solid-state reaction and oxalate coprecipitation route was carried out. The properties of the ceramics from the coprecipitation process are very good and superior to those usually published especially for the d_{33} piezoelectric coefficient. The quasi-linear relation found between d_{33} and ϵ_r corresponds to a g_{33} value of $14 \times 10^{-3} \text{ Vm}/\text{N}$. In the relationship, $g_{33} = d_{33} / \epsilon_{r33}$; g_{33} is the piezoelectric voltage constant (Vm / N) is the induced electric field in direction 3 (parallel to direction in which ceramic element is polarized) per unit stress applied in direction 3, d_{33} is the piezoelectric coefficient and ϵ_{r33} is the relative permittivity of ceramic material. This is the permittivity for dielectric displacement and electric field in direction 3 (parallel to direction in which ceramic element is polarized). BaTiO₃ ceramics prepared from chemical process shows dielectric and piezoelectric coefficients superior to those of other lead free materials. The piezoelectric d_{33} coefficient shows a very good stability up to $3 \times 10^5 \text{ V}/\text{m}$. The piezoelectric d_{33} constant is more than 260 pC/N at

around 25°C. This value is largely higher than usually published ones for barium titanate ceramics: classically room temperature ϵ_r (1kHz) and d_{33} values are respectively around 1700 and 190 pC/N[6]. Fig.5 shows the development of strain vs. electric field (S–E) butterfly loop with a max. strain 0.13% at 25 kV/cm electric field, which confirms the piezoelectric nature of the microwave sintered BaTiO₃ samples. Piezoelectric coefficient, d_{33} , has also been calculated from converse piezoelectric effect, i.e. by using the slope of the S–E plot in the higher field region, using the relation $d_{33} = \Delta\text{Strain \%} / \Delta\text{electric field}$ at higher side. The d_{33} piezoelectric coefficient calculated from the slope of S–E plot is found to be 335 pm/V. The very high value of d_{33} piezoelectric coefficient in microwave sintered BaTiO₃ samples suggests the importance of this system for piezoelectric applications. From P–E hysteresis loop of microwave sintered BaTiO₃ samples, the coercive field (E_c) of microwave sintered BaTiO₃ samples is 1.45 kV/cm. The decrease of E_c in BaTiO₃ ceramics hints towards the easy poling process and improvement in the piezoelectric properties[8].

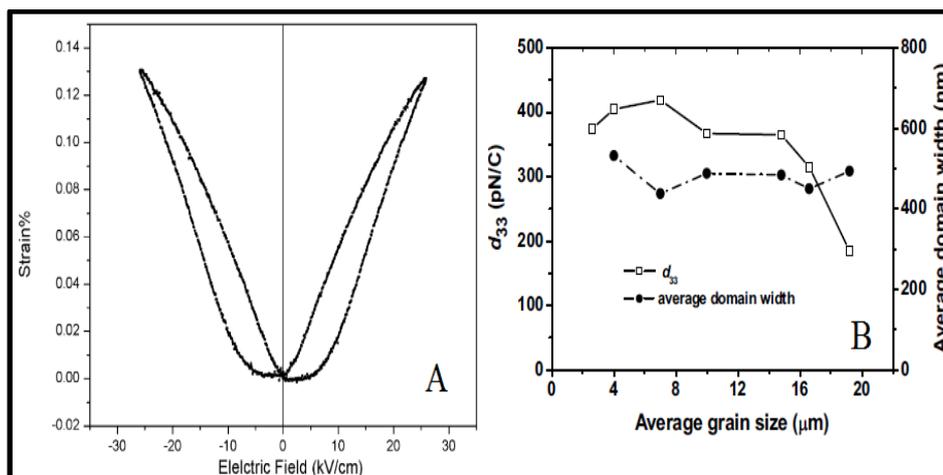


Figure 5 A. Strain vs. bipolar electric field loop of BaTiO₃ samples[8] and B. Changes in d_{33} and the domain width with the grain size[12].

After Al doping, d_{33} piezoelectric coefficient increased from 75 to 135 pC/N. The planar electromechanical coupling factor (k_p) also increased by Al doping. Since d_{33} and k_p are proportional to P_r , large remanent polarization resulted in high piezoelectric properties. Strains of 0.085 and 0.042% were obtained for Al doped and pure samples. The planar electromechanical coupling factor (k_p) was 1.86 and 1.53 for pure and Al doped samples [19]. The effect of sintering temperature on the piezoelectric properties was also examined. Besides the high relative density and moderate grain size, the sample sintered at 1190°C is closer to the phase transition between tetragonal symmetry and orthorhombic one, which provides a favorable condition for easier motion of domain and thus gives rise to high piezoelectric properties. This may be the main reason for the excellent piezoelectric properties of the sample sintered at 1190°C[20].

The piezoelectric constant d_{33} increased significantly at room temperature with the reduction of the average grain size and reached the maxima (338 pC/N) at 0.94 μm . The average 90 domain width decreases monotonically with grain size. Both the 90 domain wall density and the area dimension of domain wall are considered as important factors that greatly influence the d_{33} value. The piezoelectric effect in perovskite-type ferroelectric ceramics is known to be greatly influenced by the movement of the 90 domain walls. The domain walls of small area dimension will respond more actively to the external electrical or stress signal. Consequently, those BaTiO₃ ceramics with smaller grain size showed higher d_{33} values[21]. BaTiO₃ ceramics with excellent piezoelectric properties of d_{33} 419 pC/N and k_p 0.453 have been successfully obtained using ordinary BaCO₃ and TiO₂ powders. d_{33} increases with the decrease in grain size and the domain width in the poled BaTiO₃ ceramics is nearly independent of grain size. The d_{33} change with grain size has been explained by the area change in the domain walls[22].

V. PYROELECTRIC PROPERTIES OF BARIUM TITANATE

A common figure-of-merit for pyroelectrics is $\text{FOM} = p/c (K \cdot \tan\delta)^{1/2}$. p is the pyroelectric charge coefficient, c the specific heat, and $\tan\delta$ the dielectric loss tangent. Maximizing the performance of a material then involves selecting a ceramic with a high pyroelectric coefficient and low specific heat, dielectric constant, and dielectric loss factor[23].

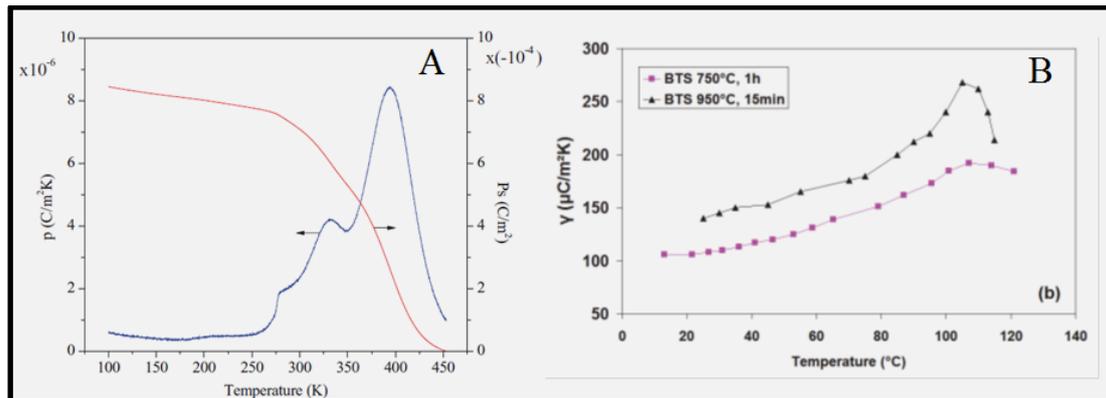


Figure 6 A. Polarization P_s and pyroelectric coefficient vs. temperature[24] and B. pyroelectric coefficient vs. temperature[25].

HA-40 wt% BaTiO₃ and HA-60 wt% BaTiO₃ composites were produced and pyroelectric properties were measured. The room temperature pyroelectric coefficients for both the compositions are 2.35 and 21 $\mu\text{C}/\text{m}^2\text{K}$, respectively. The pyroelectric coefficient was calculated from the pyroelectric current by $p = i/A \cdot (dT/dt)$ where p is the pyroelectric coefficient, i is the pyroelectric current, A is the electrode area, and (dT/dt) is the heating rate. For H6B4, the pyroelectric coefficient reaches its maximum value, 8.6 $\mu\text{C}/\text{m}^2\text{K}$ at temperature of 393°K. This temperature corresponds to the maximum polarization change and phase transition. With further increase in temperature, the polarization decreases rapidly and finally, attains a small value. For H4B6, the phase transitions at 380° K and 270° K are clearly evident, where the peak value of the pyroelectric coefficients are 85 $\mu\text{C}/\text{m}^2\text{K}$ and 29 $\mu\text{C}/\text{m}^2\text{K}$, respectively[24]. In another study, the change in surface charge is given simply by $\Delta Q = A \cdot \Delta P_s$ where A is the area and ΔP_s is the change in spontaneous (or induced) polarization due to a temperature change, ΔT_p . This formula is often normalized to produce an intrinsic quantity, called the pyroelectric coefficient, defined as $p = \Delta Q/A \cdot \Delta T_p = \Delta P_s/\Delta T_p$ [9]. In another study, the evolution of the pyroelectric coefficient as a function of temperature for two BaTiO₃ films doped with Tin (BTS), annealed at 750 °C during 1 h and at 950 °C 15 min. The pyroelectric coefficient varies linearly temperature. For the BTS film annealed at 950°C for 15 min, it increases from 140 $\mu\text{C}/\text{m}^2\text{K}$ at 25°C to 240 $\mu\text{C}/\text{m}^2\text{K}$ at 100°C. The pyroelectric properties confirms that the dielectric and the ferroelectric properties are much better with an annealed at 950°C than at 750°C. For the two BTS films the pyroelectric coefficient reaches a maximum for a temperature of 105°C which corresponds to the ferroelectric to paraelectric transition[25].

VI. CONCLUSION

Initially the discovery of the high dielectric constant and later that the discovery of the enhancement of the dielectric constant by the ferroelectricity of barium titanate ceramics led to utilization of ABO₃ crystals as ferroelectrics. The electrical poling of barium titanate provided the complete alignment of all the domains in the ceramic as in the single crystals. The relatively low Curie temperature (120°C) of barium titanate restricts its usage in high power transducers. Also the electromechanical coupling factor, k_p of barium titanate is low (i.e., 0.35) with regards to other piezoelectric materials. However, barium titanate based ferroelectrics are strong candidates due to its large polarization, high permittivity and large strain. Being a lead free ferroelectric ceramic, BaTiO₃ is an environmentally friendly material, thus making it a good candidate for various applications. Despite a low piezoelectric constant d_{33} of 191 pC/N, the piezoelectric properties are considered to be closely related to both grain and domain sizes.

VII. ACKNOWLEDGEMENTS

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