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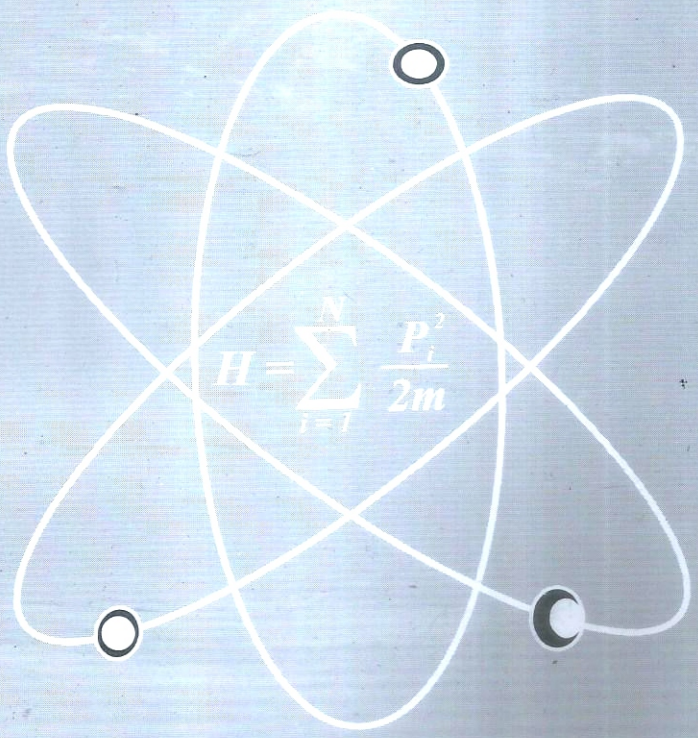

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TABLE OF CONTENTS

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SYNTHESIS, STRUCTURAL AND ELECTRICAL PROPERTIES OF NANOCRYSTALLINE BARIUM TITANATE CERAMIC USING MECHANOCHEMICAL METHOD.

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Abstract.
Barium Titanate ($BaTiO_3$ or BT) powders were synthesized by a combination of solid state and mechanochemical method. The thermal decomposition, phase formation, microstructure and electrical behavior were investigated by TG-DSC analysis, X-ray diffraction, FE-SEM measurements and Impedance Analyzer. The X-ray diffraction patterns show cubic symmetry without secondary phase. The lattice parameter a, c/a ratio and crystal size was found to be 4.0070 A˚, 1.0000 and 31.2 nm. The FE-SEM results indicated dense microstructure with an average grain size of 144.53 nm. The dielectric constant and loss of BT at room temperature were 1600 and 0.77at 40 Hz. The temperature dependence of dielectric permittivity shows that phase transition seems to be shifted towards lower room temperature with T_c observed at 90°C. The hysteresis loop was observed having a remanent polarization (Pr) and coercive field (Ec) of 0.27 Pr (μC/cm²) and 581.73 Ec (V/cm).The dielectric constants and relatively lower loss tangent values meet the current demand for device miniaturization in the electronics industry.

Keywords: Barium Titanate ceramics; high energy ball milling; XRD; FESEM; dielectric properties; ferroelectricity

1.0 Introduction.

Barium titanate ($BaTiO_3$ orBT) is one of the most basic and widely applied ferroelectric oxide materials with a perovskite- ABO_3 type crystalline structure. It is chemically and mechanically remarkably stable, and it exhibits ferroelectric properties in and above room temperature (RT).It can easily be prepared and used in the form of ceramic polycrystalline samples [1]. Due to its excellent dielectric, ferroelectric, piezoelectric, pyroelectric and optoelectric properties [2, 3], it is extensively used in multilayer ceramic capacitors (MLCC), a positive temperature coefficient of resistance (PTCR) thermistors, piezoelectric sensors, actuators and ferroelectric random access memories (FRAM) and electro-optic devices [4, 5]. There is existing demand for fabrication of fine particle, nanosized powders <100 nm to allow the production of thinner layers for MLC-s and cheaper or more reliable routes than current practice. BT nano-powders can be obtained via several routes among which: including coprecipitation [6], hydrothermal synthesis [7], sol-gel synthesis [8], alkoxide hydrolysis [9], citrate routes [10], and ultrasonic spray-pyrolysis [11] and mechanical synthesis [12] are the most important ones.

Mechanochemical activation technique is one of the most outstanding processes for the synthesis of advanced materials and is closely related to different structural changes such as phase transitions, generations of strains, dislocation, crystal lattice deformation or morph structural modifications, all brought about by mechanical energy involved in the milling process. In the case of conventional solid state reaction, the phases formed at the reactant

surfaces growth by diffusion of thermally activated atoms through the interfaces and this mass transport needs high temperatures and high energy consumption in order to complete the reaction and formation of the compound. In the case of intensive milling, the contact area between the reactant particles increases by continuous particle comminuting, thus creating new fresh surfaces through which the diffusion and mass transport take place easier. Moreover, the particles undergo a mechanical treatment by which the impact energy may become comparable to the energy of the crystal lattice thus allowing an easier movement of the atoms involved in the formation of the new phases.

Therefore one can assume that the fine and ultrafine powders become mechanically activated and the chemical reactions between them are stimulated to take place at lower temperature during mechanochemical synthesis without any extra heat. Unfortunately, the nature of this extremely high activity is not yet fully understood and efforts are made by the scientific community to go deeper in the understanding of this phenomenon. This paper reports on powder synthesis, structural and electrical properties of Barium titanate sintered samples obtained from solid state and mechanochemical method. The thermal decomposition, crystallinity, microstructure and electrical properties are respectively, investigated by TG-DSC analysis, X-ray diffraction (XRD), FESEM and impedance analyzer measurements.

2.0 Materials and Method

2.1 Synthesis of Barium titanate (BT)

Barium titanate (BT) was prepared fromhigh-purity (99.9%) analytical reagent (AR) grade of$BaCO_3$ and TiO_2. Stoichiometric amounts of the oxides were weighed according to nominal composition and ball-mixed for 12 hrs.in alcohol.The slurry was dried in an oven at 90°C for 24hrs and calcined in an alumina crucible at 1050°C for 4 hrs.in the air to yield $BaTiO_3$ Powder.5g of the calcined powders were ball milled in an isopropyl alcohol as wetting medium using SPEX 8000 Mixer/Mills functionally described as shaker mills or high-energy ball mills, the Mixer/Mills shake containers back and forth approximately 1080 cycles per minute (60 Hz model) with was carried out at room temperature for 7 hrs.The milling was stopped for 15 min after every 60 minutes of milling to cool down the system. The slurry was put in an oven and dried at 90^0 C for 24 hrs.The milled powder was compacted at 5 Ton to make pellets of size 10 mm in diameter and 1 mm in thickness using polyvinyl alcohol (PVA) as a binder. After burning off the binder (PVA), the pellets were sintered in a programmable furnace at temperatures of 1190^0 C for 2hr in alumina crucibles.

2.2 Characterization

The DSC and TG analysis of the BT sample was carried out using differential scanning calorimetric and thermogravimetric analysis by heating the sample from 30°C to 1200°C. TG-DSC curves were recorded with a thermo analyzer Brand Metler Toledo, Model number TGA/DSC HT. The heating was carried out in air from room temperature to 1200°C at a heating rate of *10k/min*, using a-Al_2O_3 as a reference. Phase identification of calcined and sintered powders was identified by using X-ray diffractometer with monochromatic Cu$K\alpha$ radiation (λ = 1·54178 Å) under *40kV/30mA*- over a 2θ angle from 20°to 80° at a scanning rate of 2 degrees per min. The experimental density of the samples was calculated using Electronic Densimeter MD-3005 ALFAMIRAGE. The Experimental densities (ρ_{exp}) of the mechanochemically sintered BTceramics were measured using Archimedes' principle [13].

$$\rho_{exp} = \frac{M_a \rho_w}{M_a - M_w} \quad (1)$$

Where $M_a$and $M_w$are respectively the weight in gram of the pellet measured in air and in water. Theoretical density (ρ_{th}) of the sample was calculated from the molecular weight of the samples and its lattice parameter.

$$\rho_{th} = \frac{Z.M.u}{V} \quad (2)$$

were Z is the number of atom per unit cell, M is the molar mass of the composition in g/mol, u the atomic mass unit of $1.66057.10^{-27}$ kg and V the volume of the unit cell in g/m^3.The percentage porosity was calculated using the formula:

$$\%\ porosity = \frac{(\rho_{th} - \rho_{exp})}{\rho_{th}} \times 100 \quad (3)$$

The morphological studies of the sintered sample were carried out using field emission scanning electron microscopy (FE-SEM) (JEOL 7600F) operated at 15kV.The average crystallite size t of BT ceramic was calculated from the full width at half maximum of the (110) diffraction peaks using Scherer formula [14]:

$$t = \frac{0.9\lambda}{\beta cos\theta}, \quad (4)$$

where 0.9 is the crystalline shape factor, λ is the X-ray wavelength *(1·54178 Å)*,$\beta = (\beta_M^2 - \beta_S^2)^{\frac{1}{2}}$ is the full width at half maximum (FWHM), β_M andβ_S are the measured peak broadening and instrumental broadening in radian, respectively, and θ is the Bragg angle in radian corresponding to the peak. The dielectric measurement was carried out for the sintered sample using Agilent 4294 A Impedance Analyzer in the frequency and temperature range of 40Hz – 1MHz and 30-400 ^{0}C, respectively. The polarization-electric field (P–E) hysteresis characteristics of the samples were determined using a Precision LC material analyzer (Radiant, U.S.A).

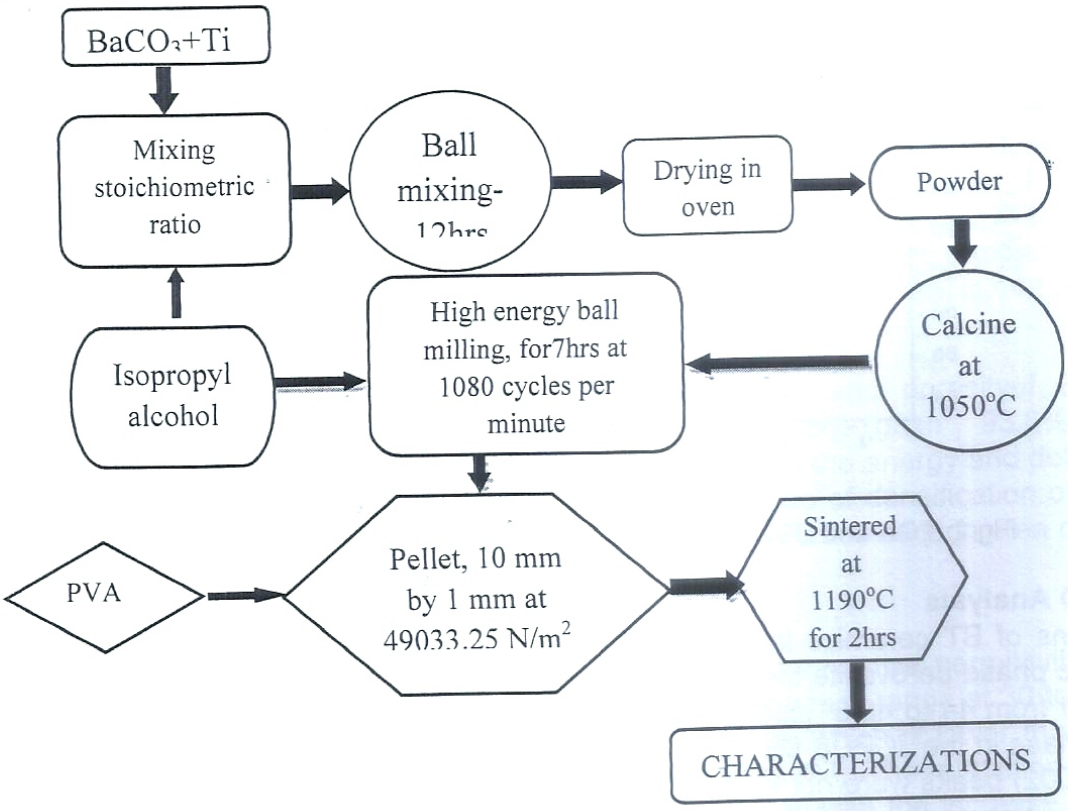

Fig. 1. A Flowchart of the synthesis of BT using a combination of solid state reaction and high-energy ball milling.

3.0 Results and discussion

3.1 TG-DSC Analysis

The TG and DSC plots are shown in the Fig.2. Here temperature is taken at X-axis and mass loss (TGA) and heat flow (DSC) in the Y axis. The TGA curve shows total weight loss of 15.51% in two steps. The first step a major weight loss (15.50%) in the temperature range of 602-831°Cis attributed to the decomposition of $BaCO_3$,similar weight loss is observed by other workers [15]. The second weight loss (0.0047%) in the temperature range of 831-933 is attributed to the formation of $BaTiO_3$ and the release of CO_2[16]according to the reaction:

$$\longrightarrow \quad BaCO_3+TiO_2BaTiO_3+CO_2 \qquad (5)$$

Above 933°C, no substantial weight loss is observed. The weight loss of 15.50% observed experimentally is in agreement with the theoretical weight loss (15.87%) calculated according to the reaction (1).

In the DSC curve, two endothermic peaks have been recorded. The first endothermic peak at ~831°C corresponds to the physical transformation of precursors. The second endothermic peak at ~916°C corresponds to the formation of $BaTiO_3$ according tochemical equation 1. From DSC curve, the first exothermic at ~940°C is due to the formation of CO_2 molecules [17]. When the temperature is higher than 933°C, the weight of the $BaTiO_3$ powder no longer decreased, which hints about the calcination temperature of $BaTiO_2$to be above 933°C.

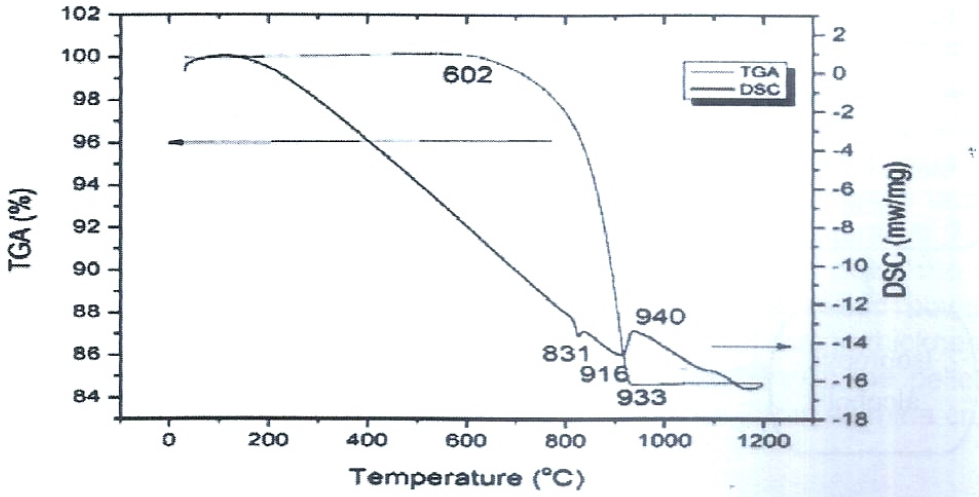

Fig 2. TGA and DSC plot of conventionally heated dried $BaTiO_3$ powder

3.2 XRD Analysis

XRD patterns of BT ceramics in the range of $2\theta$are shown in Fig. 3. The XRD pattern shows cubic phase perovskite structure. The enlarged XRD patterns of the ceramics in the range of 2θ from 44 to 46.5° clearly show that the crystal structure of BT was assigned to the cubic phase in the JCPDS file no 96-150-7758 and space group *Pm -3 m*, because the (200) and (002) peaks were not split [18] as reported by other workers [19, 20]. In general, at room temperature (25-30°C) bulk barium titanate exists in ferroelectric phase, however, due to microstructural size effect nanocrystals of barium titanate are stable in cubic phase [21[.The calculated crystallite size of 31.2 nm for BT is similarto the one of 32nm obtained by [22]. Lattice constants of BT ceramic were calculated from the XRD spectra tobe $a=b=c=4.0070$ which gives c/a ratio of 1.000. The crystal cell volumes for and BT weredetermined to be 64.34 $Å^3$.

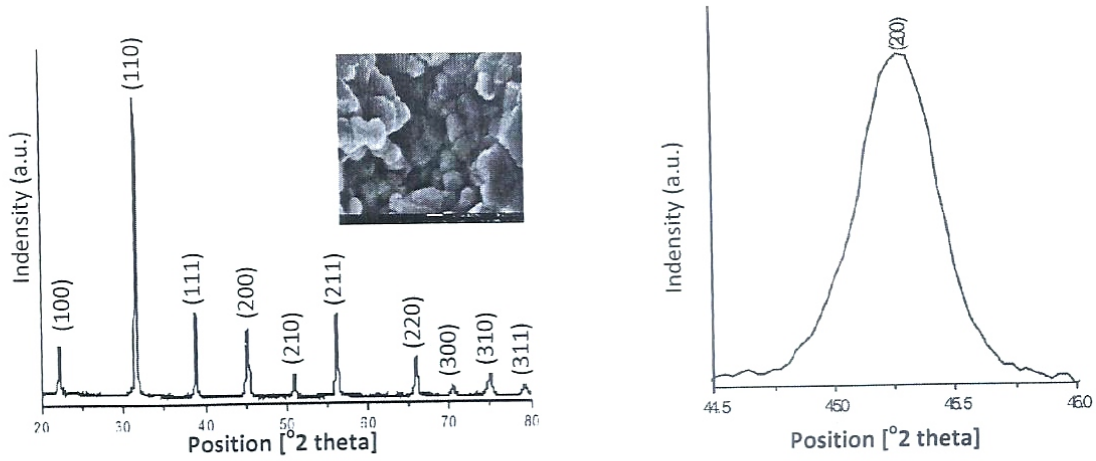

Fig. 3. Room temperature XRD Patterns and inset FESEM micrograph at × 100000 magnification of nanocrystalline BT ceramics sintered at 1190°C

Using the conventional solid-state reaction of $BaCO_3$-TiO_2, the temperature for synthesizing the BT single phase was higher than 1200°C [23]. Here, the temperature (960°C) at which the BT single phase was obtained is significantly lower than that required by the conventional solid-state reaction process. The low formation temperature for BT is believed to be beneficial from the refined powders as a result of HBM [24].

3.3 Surface Morphology

The inset of Fig. 3 shows the typical FESEM micrographs of BT ceramics sintered at 1190°C for 2 hrs. It can be seen that the sintered ceramic sample are dense and have varying microstructures with the little presence of voids. The presence of voids in the FESEM images indicate that the pellets have a certain amount of porosity. The grain size and grain boundary are observed very clearly in the non-agglomerated region. The average grain size of BT ceramic is determined by using quadrant technique [25] is 142.07 nm.

3.4 Density and porosity measurement

The calculated theoretical, experimental, relative density and porosityof BT ceramic obtained from equation 1, 2, and 3 are 6.02 g/cm3, 5.369 g/cm^3, 93.6% and 6.3% respectively. It has been reported that porosity can dissipate the energy and deteriorate the dielectric properties of a material [26].It indicates the degree of densification of a ceramic. Porosity decreases strength because pores reduce the true cross-section area of a member and also pores act as stress-concentrating notches.

3.5 Dielectric properties

Fig. 4 shows the frequency dependence of the real part of relative permittivity (ε') for BT nanocrystalline ceramic sample in the 40 Hz – 1 MHz frequency range at 30 to 150°C. The highest value of ε' (1600) is obtained at room temperature which is lower than that of the sample prepared by conventional solid state reaction route [27]. The relaxation frequency is about 3000 Hz for BT at 90°C. It is noted that ε' decreases with the increase in frequency and temperature as observed by other workers [28]. The decrease of ε' with increase of frequency arises from the fact that because of inertia, the polarization does not occur instantaneously with the application of the electric field. The delay in response towards the applied alternating electric field leads to decrease in dielectric constant. It is observed that the values of ε' at all temperatures is higher at low frequencies. This is because at lower

frequencies, all four types' mechanism of polarization (atomic, electronic, dipolar, space charge) contributes to the total polarization of the material. With the increase in frequency, the dipoles with large relaxation times cease to respond with the applied frequency and hence decrease in the dielectric constant is caused. This type of frequency dependence dielectric behavior is found in many ferroelectric materials [29, 30]. A low dispersion of ε' is observed at 70°C, 110°C, 130°C, and 150°C which becomes frequency independent beyond 100 Hz. At higher frequencies, due to the lack of the ability of dipoles to follow the fast alternation of an applied field, the dielectric constant remains constant [31]. However, the constant arises due to the electronic polarization at higher frequencies. With an increase of the frequency, the ionic and orientation polarizabilities descend, and their contribution finally becomes insignificant.

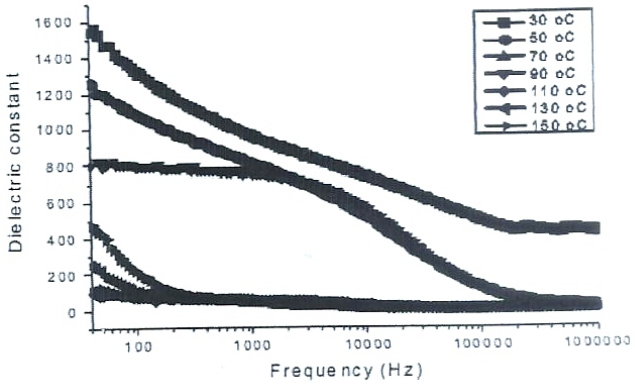

Fig. 4. Frequency dependences of dielectric constant at various temperature of BT nanocrystalline ceramic.

Fig. 5 shows the frequency dependences of dielectric loss of nanocrystalline BT ceramic at various temperature. The tan δ of BT shows dispersion at low frequencies with low loss at 30, 50 and 90°C and then decreased sharply with increasing frequency. Thereafter it remains almost constant over the entire frequency range. At 110-150°C, there is dispersion at low frequency with the presence of two relaxation peaks. The peaks observed at low and higher frequency range shift toward high frequency region with increase in temperature, the tan δ decreases with increase in frequency. This indicates the relaxation to be thermally activated [32]. The lowest and highest loss of BT are 0.096 and 1.62 at 90°C and 110°C respectively. Eventually, at all temperature and at higher frequencies, the dielectric losses are reduced, a stanδ is associated with the dissipation of energy in dielectric systems.

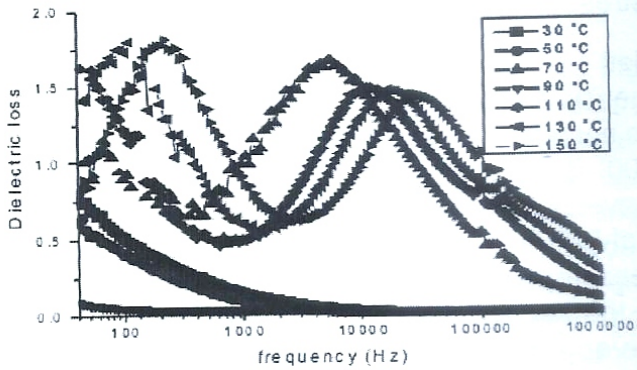

Fig. 5. Frequency dependences of dielectric loss at room temperature of BT nanocrystalline ceramic

The variation of the dielectric constant ε' and dielectric loss (tan δ)as a function of temperature for nanocrystalline BT ceramic sample measured from room temperature to 150°C at a different frequency is shown in Fig. 6 and 7 respectively. The ε' at all temperature decrease from 30°C to 70°C and then increases sharply at 90°C and afterward falls to the lowest level at 110°C thus indicating a *ferroelectric–paraelectric phase transition* $T_c$at 90°C.It is clear that the $T_c$is shifted to a lower value than the one of conventionally sintered BT (T_c 120°C), which is similar to that obtained by others workers [33]. The ε' peaks at T_c decrease with increase of frequency (Fig. 5) and is associated to a minimumof the losses (Fig. 6). It is clear that the maximum ε' of BT is less than the one obtained in CuO-modified BTSZ ceramics synthesized using solid-state method [34]. The low value of the ε' of BT sintered by HBM should be attributed to two factors, grain size in nanometer range and distortion of crystal lattice caused by HBM. As the grain boundaries increase the grain size decrease and the grain boundary exhibited the polarization of grain boundary may be little or even none. Uchino et al. [19] suggested that with decreasing grain size, T_c was shifted downward through room temperature, eventually tending toward 0 K at some critical particle size.

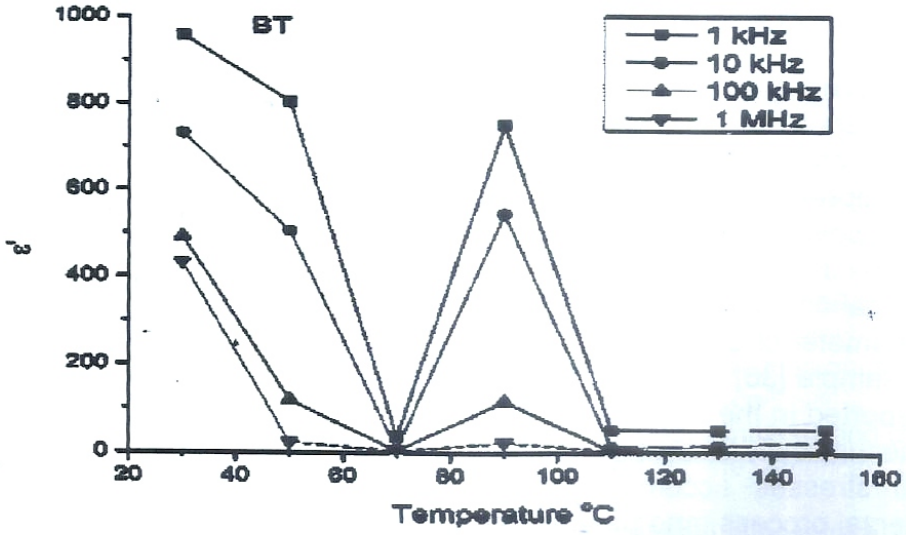

Fig. 6. Temperature dependences of dielectric constant at room temperature of BT nanocrystalline ceramic.

Fig. 7 display the frequency dependence of dielectric loss (tan δ) of the BT at various frequencies. Similar to the behavior of dielectric constant with frequency, the dielectric loss increases with increasing temperature. This indicates the thermally activated nature of the dielectric relaxation of the system. This sharp increase of dielectric loss in the high-temperature region for BT may be attributed to the increased mobility of charge carriers arising from defects or vacancies in the sample [35]. The maximum ε' and tan δ obtained at room temperature and T_c are 957.7, 750.7 and 0.50, 0.048 at 1 kHz respectively.

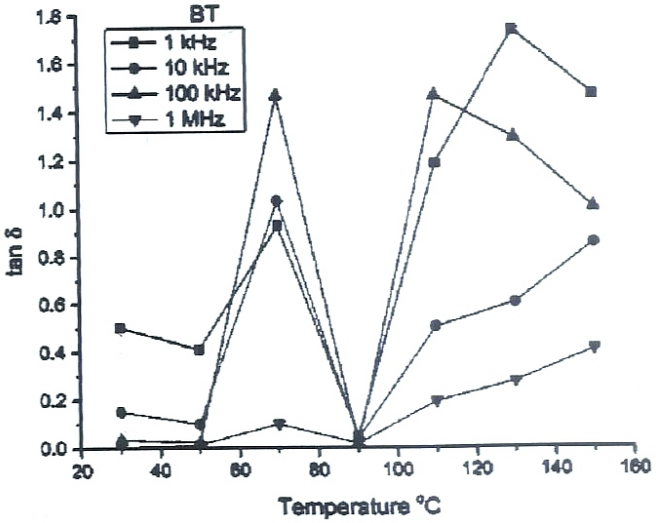

Fig. 7. Temperature dependences of dielectric loss at room temperature of BT nanocrystalline ceramic

3.6 Ferroelectric properties

The polarization versus electric field (P-E) hysteresis loops of BT ceramic measured at room temperature and 1 kHz is shown in Fig.8. The values of remanent polarization, coercivity, and saturated polarization are *0.27 μC/cm², 581.73 V/cm, and 1.93 μC/cm²* respectively. The polarization hysteresis loop is not fully saturated which might be as a result of leakage current. Residual dipole reorientation causes the difference between maximum polarization at the saturation and the remanent polarization [17]. The performance parameter of BT is very close to that of the reported value (*Ps* of 2.0 μC/cm²) for the ceramic sample [36] and lower than the one obtained having the same composition [37]. It is well reported in the literature that with the decrease in grain size, E_c increases as each grain is mechanically clamped by its surrounding. This clamping effect, in addition to the mechanical stresses accompanying 90° domain rotations, tends to impede the polarization reversal process, and hence, apparently increasesE_c.

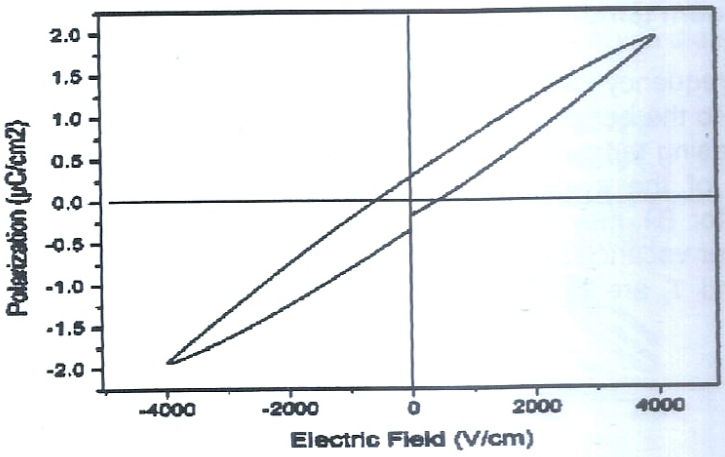

Fig. 8. P-E hysteresis loop of BT nanocrystalline ceramics.

4.0 Conclusion

BT nanocrystalline powder with average crystallite sizes of 31.2 nm and grain size of 142.53 nm was produced by combination of solid state and high-energy ball milling. Thermal analysis of the milled powder confirms that the optimum calcination temperature is 933°C. X-ray analysis shows that the compound has a cubic crystal structure at room temperature. Dielectric properties of sample have been studied in the temperature range between 30 - 150°C and frequency range 40 Hz - 1 MHz. The maximum ε' and tan δ obtained at room temperature and ferroelectric transition temperature T_c are 957.7, 750.7 and 0.50, 0.048 at 1 kHz respectively. The remnant polarization (*Pr*) and coercive field (*Ec*) of BT were found to be 0.27 μC/cm^{2}and 581.73 V/cm respectivelyTherefore, lead-free BT might be useful for multilayer ceramic capacitor and for practical applications.

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