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Ferroelectric properties of strontium bismuth titanate($SrBi_4Ti_4O_{15}$) synthesized using solution combustion technique

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Abstract. The ferroelectric properties of layer-structured Strontium Bismuth Titanate (SBT) have been investigated in this study. SBT was prepared using solution combustion technique with glycine as a fuel. Single-phase formation of the layer-structured compound of SBT with orthorhombic structure was achieved after calcinations at 800 ºC, and was confirmed by x-ray diffraction studies. Scanning electron micrograph shows that the grains exhibit a plate like morphology and possesses fine particle size. The as prepared sample exhibits ferroelectric properties with remnant polarization of 2Pr = 1.84 μC/cm^2 at coercive field 2Ec= 2.61 kV/cm and displays low dielectric loss. Its ferroelectric transition temperature (T_c) is found to be 450 ºC.

Introduction

Ferroelectric compounds, both in powder and thin film forms, have attracted considerable attention in recent years because of their potential application in non-volatile memories and as capacitors in dynamic random-access memories [1]. The most popular ferroelectric material used in memory devices is lead zirconate titanate (PZT). However, it (PZT) has drawback of being a possible environmental pollutor both during fabrication and at the stage of waste disposal, because of its toxic lead content. Thus, there is a need to develop lead free material [2] that could work as an

alternative. Strontium-based layered perovskite is currently one of the most promising candidates for new generation non-volatile ferroelectric random access memory (NvFRAM) devices. Among several Bismuth layer structure ferroelectrics (BLSF) materials, $SrBi_4Ti_4O_{15}$ (SBT) has been extensively studied by many researchers for possible applications in piezoelectric devices. Recently, lot of attention has been paid to SBT due to its high Curie temperature, low coercive field, barrier type property, large retentivity and anisotropic physical properties [3]. Various techniques have been used for the preparation of SBT. Some of the well-known methods are: pulsed laser deposition [3], polymeric precursor method [2], solid state reaction[4],ball milling [5], high-energy milling [6,7], soft chemical method [8] and sol-gel [9] synthesis. The major problems associated with these methods are either the process duration or the difficulties in achieving the desired product phase composition. Also, all these techniques require special chemicals and equipments [10].

Among the various wet chemical routes, the solution combustion technique is regarded as one of the most effective and economic methods due to its convenient processing, simple experimental set up, significant timesaving and high purity products [11]. Also, combustion technique requires lower calcinations temperature due to which volatilisation of bismuth can be minimized [12]. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides). Depending on the type of the precursors, as well as on conditions used for the process organization, the solution combustion synthesis (SCS) may occur as either volume or layer-by-layer propagating combustion mode. This process not only yields nano-size oxide materials but also allows uniform (homogeneous) grain formation in a single step [13]. Reports on the effect of solution combustion synthesis of SBT on its structure and ferroelectric properties are rare. Therefore, it is proposed to synthesize SBT powders via solution combustion technique using glycine as fuel and to investigate its ferroelectric properties. In this paper, we report a successful preparation of SBT powder through solution combustion with glycine as fuel and acetyl acetone as a chelating agent.

Experimental

Ferroelectric strontium bismuth titanate was prepared using solution combustion technique. The starting materials used in the synthesis of SBT powder were $Sr(NO_3)_2$ (Merck), $Bi(NO_3)_3.5H_2O$(Merck), Titanium Isopropoxide (Sigma Aldrich). These materials were weighed according to the stoichiometric composition of SBT. A solution of strontium nitrate and bismuth nitrate using 2-Methoxyethanol was prepared. Another solution was prepared by using an appropriate amount of Titanium isopropoxide, 2-Methoxyethanol, and acetylacetone. This Ti solution was added drop wise into Bi-Sr solution under constant stirring followed by addition of glycine as a fuel. This final mixture was stirred for 70-90 min at room temperature till a yellow viscous gel was formed. The pH of the solution was not maintained, as there was no precipitation during mixing. Then the mixture was heated at 250 ºC. First it underwent dehydration, and then at a certain stage the mixtures frothed and swelled, until large amount gases evolved, resulting an exothermic reaction with the production of flame. The whole process proved to be self-sustaining after the ignition. The resulting solid product had a foamy structure consisting of very light homogeneous flakes and was very easily crushed to give a fine powder. The obtained powder was calcined at 800 ºC for 4 hour. The calcined powder was compacted at 10 ton in a 1.0 cm diameter steel die. The white pellets of thickness 1.0 mm were fired at 1050 ºC for 4 hour.

The prepared sample was analyzed for the presence of phases using X-ray diffractometer (Rikagu-Miniflex 2) equipped with Cu Kα. Surface morphology of both powder & sintered pellets were examined using scanning electron microscope (JEOL/EO version-1, JSM-6390). Gold plating was done on both surfaces of sintered pellets for ohmic contacts. Ferroelectric properties such as the remnant polarization (2Pr) and the coercive field (2Ec) of the material were determined with the help of automatic P-E loop tracer (Marine India Pvt. Ltd.). Dielectric measurements such as dielectric constant and dielectric loss were carried out as a function of temperature from 50 ºC to 550 ºC over the frequency range 1 kHz to 1 MHz using impedance analyzer (Wayne Kerr 6500B).

Results and discussion

XRD analysis. The X-ray diffraction pattern of SBT (calcined) sample recorded by using Cu K_α radiation is shown in Fig. 1(c). The sharp peaks indicate the crystalline nature of the particles. It is seen that all the peaks match well with the standard JCPDS card No: 43-0973 as shown in Fig. 1(a). No other secondary phases are seen. As seen from the Fig. 1(b), the combusted powder without calcination possesses amorphous nature, also some secondary phases are seen , which disappear and complete crystallinity is reached only after calcination at 800 ºC for 4 hour.

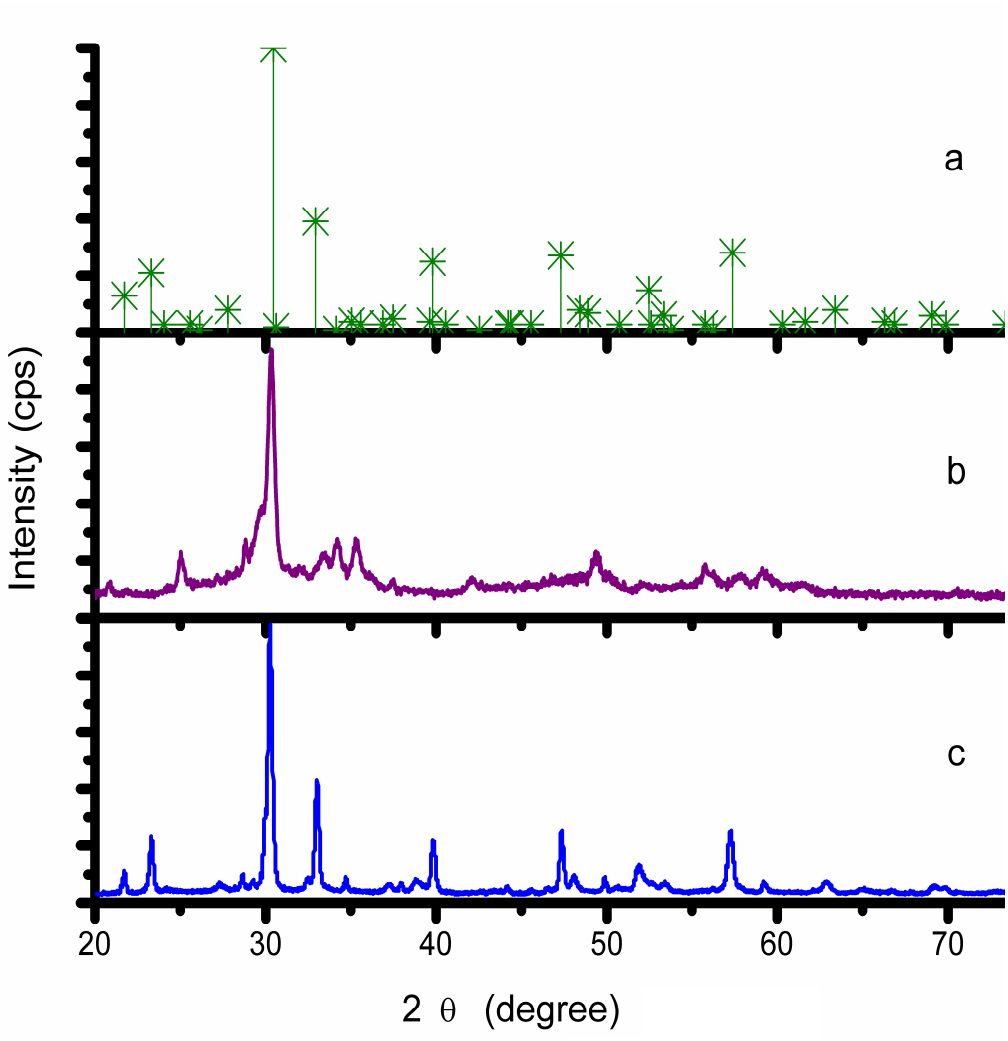
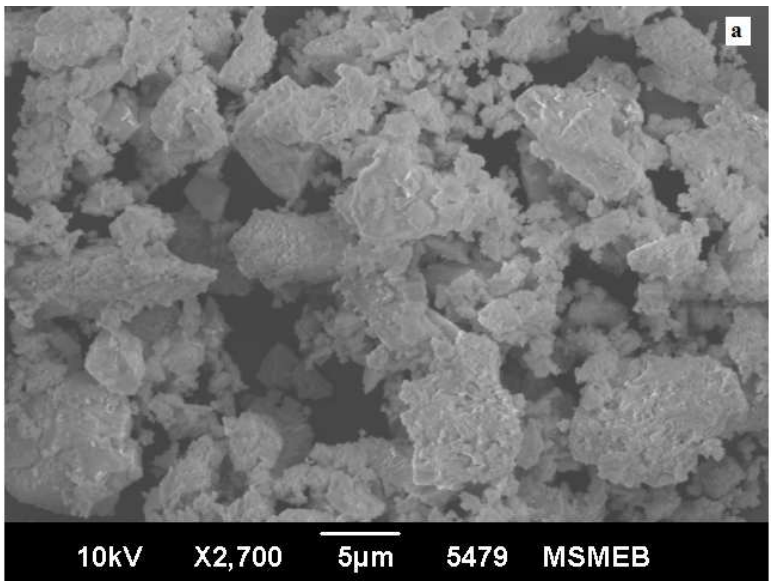


Fig.1. XRD pattern of Bismuth Titanate powder (a) Reference JCPDS data file no 43-0973 (b) after combustion without calcinations and (c) after calcination at 800 °C

SEM analysis. The scanning electron microscope (SEM) images that describe the surface morphology of the calcined powder and the sintered ceramic of SBT are shown in Fig.2a and 2b respectively. Fig.2(a) shows that the particles do not display any definite shape. A great number of agglomerates can be seen in the powder which is typical of combustion synthesis products [14]. The milling in agate mortar before compacting and sintering was adopted in order to break the agglomerates. Fig 2(b) shows that the grains of SBT pellets exhibit a plate like morphology. It was also found from the SEM micrograph that the grains of different sizes are homogeneously distributed. Similar grain morphology was observed in SBT prepared by other methods. It is known that plate-like grain formation is a typical characteristic of bismuth layer structured ferroelectrics (BLSFs) because they have highly anisotropic crystal structure [15]. The sintered surface shows dense structure.



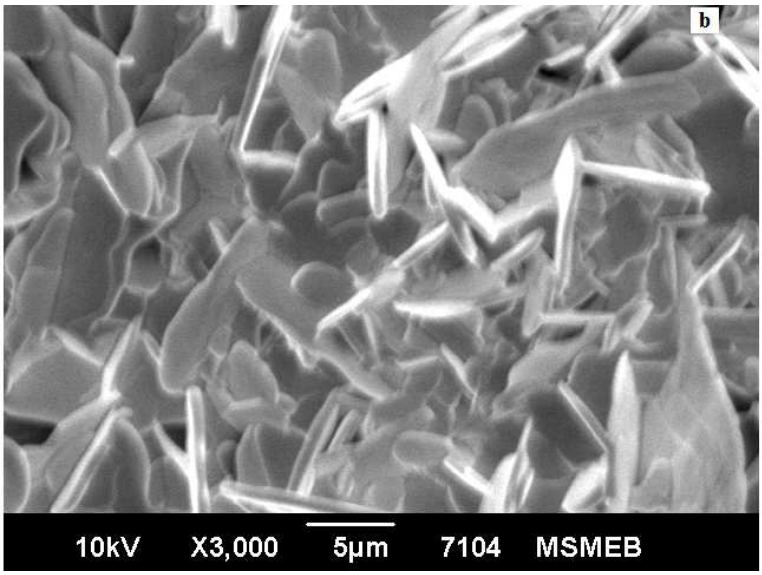


Fig. 2.a. SEM micrographs of calcined $SrBi_4Ti_4O_{15}$ sample, **b.** SEM Micrographs of SBT pallets sintered for 5 hours at 1050 °C.

Dielectric Properties. Fig. 3 displays dielectric constant (ε) as a function of temperature of the as prepared sample measured in a frequency range 1 kHz to 1 MHz. As expected, a maximum of dielectric constant (ε) related to the ferroelectric– paraelectric transition is observed at the Curie Temperature T_c = 450 ºC. The ferroelectric transition temperature, which determines the working temperature range of the as prepared sample , is well within the reported results that is around 500 °C [4,15]. Apart from this peak there is a slight hump seen at around 200 °C. This has been reported by earlier researchers as well and is attributed to phenomena such as structural distortions [16], space charge relaxation [17], and oxygen vacancy movement [18]. The temperature corresponding to this hump in the low temperature range is called as 'depolarization temperature' (T_d), which indicates the stability of ferroelectric domains [19]. The depolarization temperature also corresponds to the ferroelectric to antiferroelectric transition as the specimen is depolarized and loses its piezoelectric activity over this temperature [20]. Further, the transition temperature is found to be almost the same for different frequencies, which indicates that SBT belongs to the category of normal ferroelectric but not a relaxor ferroelectric [8].

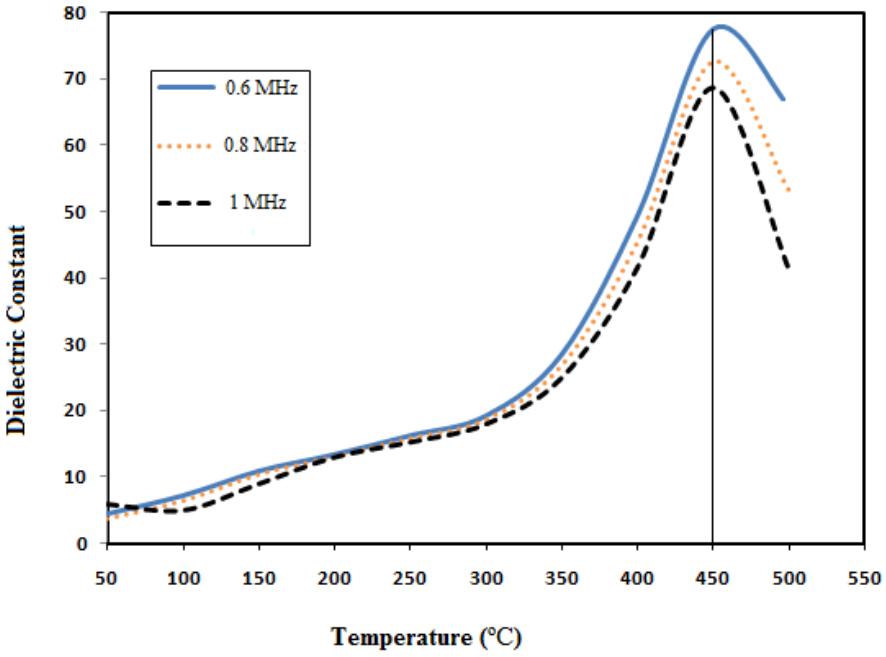


Fig. 3. Variation of dielectric constant with temperature at various frequencies.

Fig. 4 depicts the variation of dielectric loss as a function of temperature. Even in this dielectric loss Vs Temperature curve two depressions are seen - one around the depolarization temperature and the other around the ferroelectric transition temperature. Beyond T_c there is an increase in the dielectric loss. It can be seen that the loss in the sample is very less, that is almost zero, up to the stage of ferroelectric to paraelectric transition temperature (T_c), but beyond T_c, an increase in dielectric loss can be seen which is attributed to the structural changes in the sample after the phase transition.

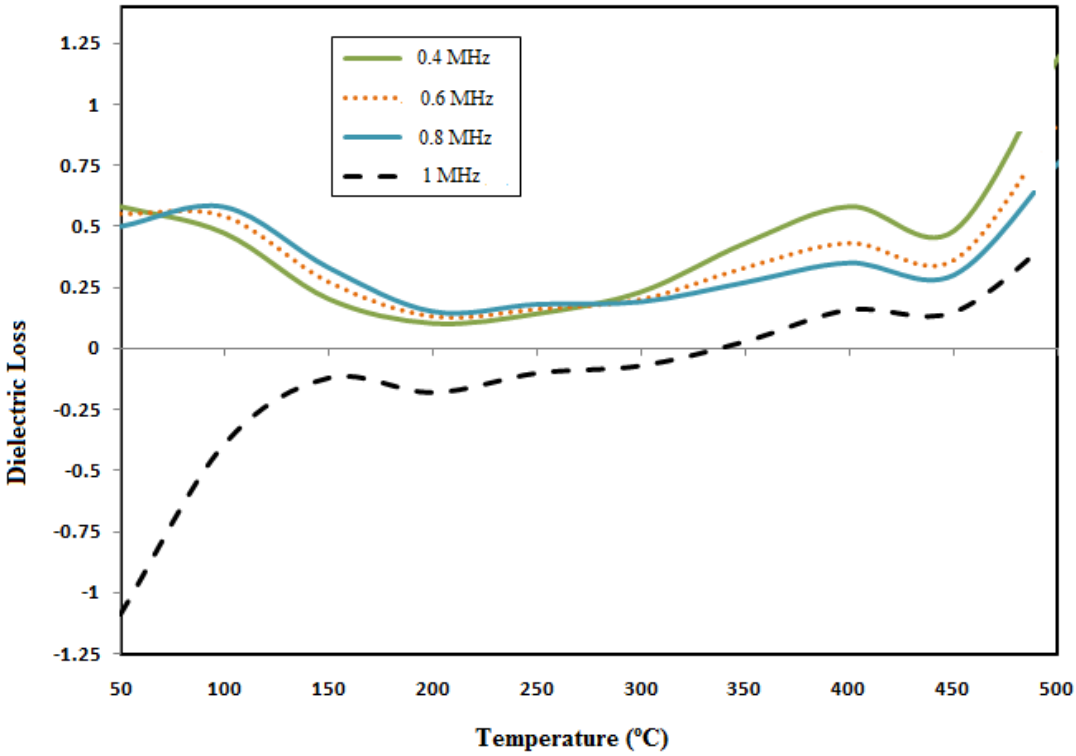


Fig. 4. Variation of dielectric loss with temperature at different frequencies.

Impedance Analysis. Fig. 5 displays the variation of impedance (Z) with frequency at different temperatures and shows that the Z value increases initially, reaches the maximum value ('Z_p'- peak value) and then decreases with frequency for all temperatures. This Z_p value decreases with increasing temperature denotes the increase in capacitance and decrease in resistance of the material indicating increase in conductivity [4]. During the preparation of this compound it is sintered at 1050^0C. So, there is a possibility for loss of oxygen thus creating vacancies as per thermal equilibrium conditions. When the samples are cooled to room temperature, oxygen re-enters the lattice, but may not totally compensate for the loss of oxygen during sintering. The entry of oxygen is compensated only on the surface while the interior of the sample has oxygen vacancy. The oxygen loss is denoted as per Kroger-Vink reaction [24].

$$O_o^x \leftrightarrow \tfrac{1}{2} O_2^{"} + V_o^{"} + 2e^{'}$$

Where e' represents the electron and V_o'' represents the oxygen vacancy. So the conductivity of the samples can therefore be associated with the mobility of oxygen vacancies [12].

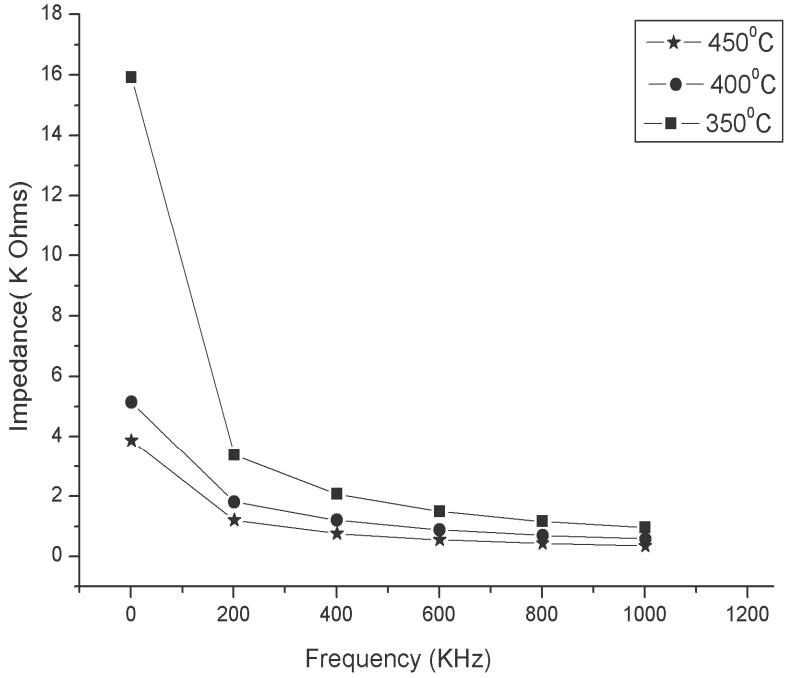


Fig. 5. Variation of impedance with frequency at different temperatures.

P-E Hysteresis Loop. Fig. 6 shows the ferroelectric hysteresis loop of the as prepared SBT pellet under an applied electric field of 8 KV/cm in a silicon oil bath at room temperature. The hysterises loop is saturated and the remnant polarization ($2P_r$) of the sample is found to be 1.84 μC/cm^2 and the coercive field ($2E_c$) is 2.61 kV/cm. Low remnant polarization is typical of layered structure, which is attributed to higher conductivity of the sample due to movement of oxygen vacancies created during the sintering process [21]. The value of remnant polarisation of the as prepared SBT was less than the reported results found by the other researchers, which may be improved by poling the sample.

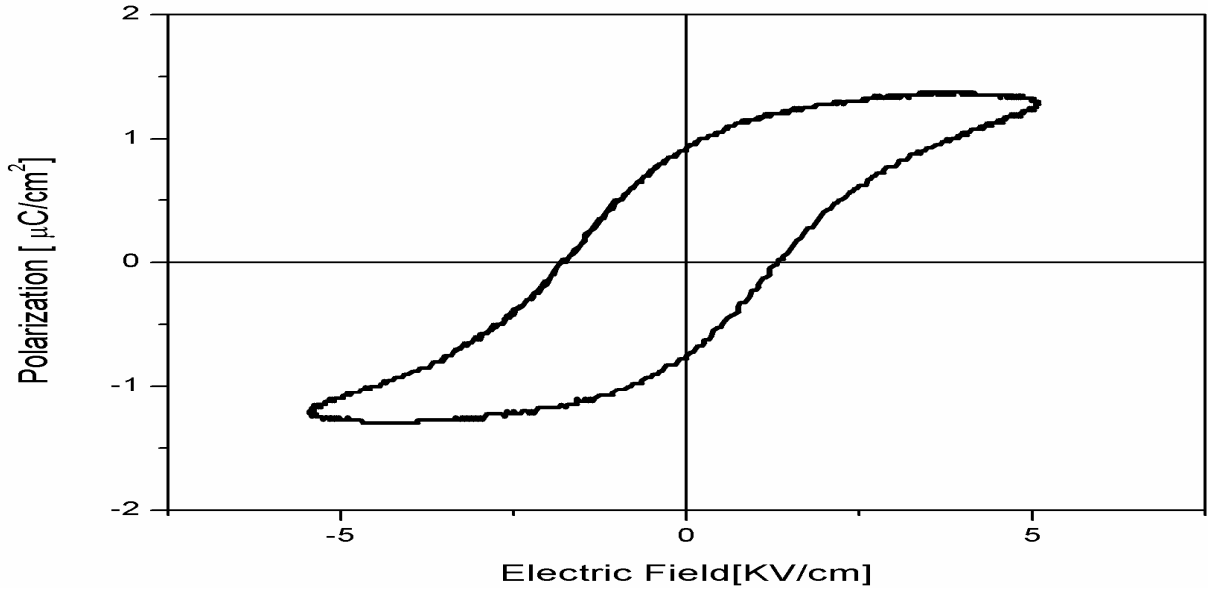


Fig.6. P-E Loop of the as prepared pellet of SBT.

Conclusions

SBT powder can be successfully prepared by the solution combustion technique with glycine as fuel in a short duration. Complete phase formation and crystallinity was attained only after calcinations at 800 °C. Low remnant polarization of the sample was attributed to high conductivity due to oxygen vacancy movement. Variation of dielectric loss was also studied as a function of temperature.

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