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ENTROPY VARIATION IN 0.85(NaO.5BiO.5TiO$_3$)-0.15(SrTiO$_3$) RELAXOR FERROELECTRIC MATERIAL

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ABSTRACT

Ferroelectric to paraelectric phase transitions are associated with an electrocaloric effect (ECE), an entropy change of ferroelectric material during application or withdrawal of electric field. Under low electric fields, electrocaloric effects (ECEs) accompanied with the ferroelectric to paraelectric phase transition is due to order or disordered dipoles. The dipole-ordered state can be enhanced by decreasing temperature or enhancing applied electric field. Hence, the entropy drops and the ferroelectric material releases heat during application of field, while the entropy rises and the material absorbs heat during withdrawal of field. Generally ECE process occurs near Curie temperature. In the present study, electrocaloric properties of 0.85(Na0.5Bi0.5TiO$_3$)-0.15(SrTiO$_3$) ceramic prepared by sol–gel method are presented. Polarization vs electric field measurement was done for the sample in temperature region 30^{0}C -125^{0}C. Strain vs electric field (S-E) loops were derived from the hysteresis loops. Electrostrictive coefficient (Q) value is obtained from piezoelectric measurement. S-E curves are butterfly like in shape. The value of the elctroetocaloric effect has been determined from PE loop studies at different temperatures. From these studies many features of ECE, including the changes of entropy are extracted.

Key words: NBT, ST, Entropy change, Electrocaloric effect.

INTRODUCTION

The electrocaloric (EC) effect is a change in the temperature of a material upon the application or withdrawal of an electric field [1]. It generated great interest in the 1960s to 1970s but has not been exploited commercially because the reported EC effects were small. EC effect has many commercial applications [2]. In Practical applications the heat absorption capacity is higher for bulk materials which should be seriously consider [3,4]. Complex phase transitions exist in NBT based ceramics, so it is expected that a large ECE may exist in these materials [5].

Lead free ferroelectric materials are becoming promising candidates for cooling applications. Ferroelectric and conducting properties of NBT based ceramics are studied by many researchers [6-9]. But in the present work, including these ferroelectric and conducting properties we made an attempt to understand the elctrocaloric effect of NBT-ST composite .

Materials and methods:

NBT, ST samples are synthesized using Sol gel method. To prepare NBT, the stoichiometric proportion of $NaNO_3$ (SD fine 99.5%), $Bi(NO_3)_3$ (SD fine 99.5%), Ti (100 mesh, Aldrich 99.7%), H_2O_2 (30%, SD fine) and Ammonia solution (25% AR grade, SD fine) are taken. Initially the required proportions of constituents are dissolved in water. The Ti metal powder is added to a solution containing 70ml of H_2O_2 and 30ml of Ammonia at 0°C. Under constant stirring yellow gel is obtained after 12h. Then this solution is added to the previously prepared aqueous solution of Na and Bi nitrates in appropriate quantities. Then the citric acid is added to this solution in the molar ratio of 2:1 so that citrate is formed. The P^H of the resultant solution is adjusted between 6 to 7 by adding Ammonia and the solution is heated. After 48 hrs, thick viscous liquid is obtained. At this stage ethylene glycol is added in the molar ratio1:1.2 of the citric acid to the ethylene glycol. The mixture is heated at 180°C for 5-6hrs. A black precursor solid is obtained. The precursor powder obtained is ground and calcined at various temperatures required for the phase formation. For the preparation of $SrTiO_3$,the initial compounds are $Sr(NO_3)_2$ (SD fine 99.5%),Ti(100 mesh Aldrich 99.7%), H_2O_2(30% SD fine) and Ammonia solution(25%AR grade SD fine) taken the remaining procedure for preparation is similar as NBT.

The calcined powders are mixed in molar ratio as required for synthesizing composite materials and it is ground for 6 hours to obtain a homogeneous mixture. The mixture obtained is pressed into pellets of about 10 mm diameter and 2 mm thickness using a hydraulic press. About 2% of Poly vinyl alcohol (PVA) binder is added during the process of pelletization. The pellets are sintered in the temperature range of 1160-1190°C (depending on the composition) for 5h for densification. The sintered samples are annealed at 800°C for 4h. These samples are electroded with silver paint on both sides for electrical contact. From here after, the composites $0.85(Na_{0.5}Bi_{0.5}TiO_3)$-$0.15(SrTiO_3)$ are named as NBST.

Polarization of the samples is observed by using custom built automatic P-E loop tracer of Marine India ltd. working at 50Hz frequency. The measurement is carried out from room temperature to 125°C at an inter val of 25ºC, with constant heating rate of 5°C/min.

Results and Discussion:

P-E loops:

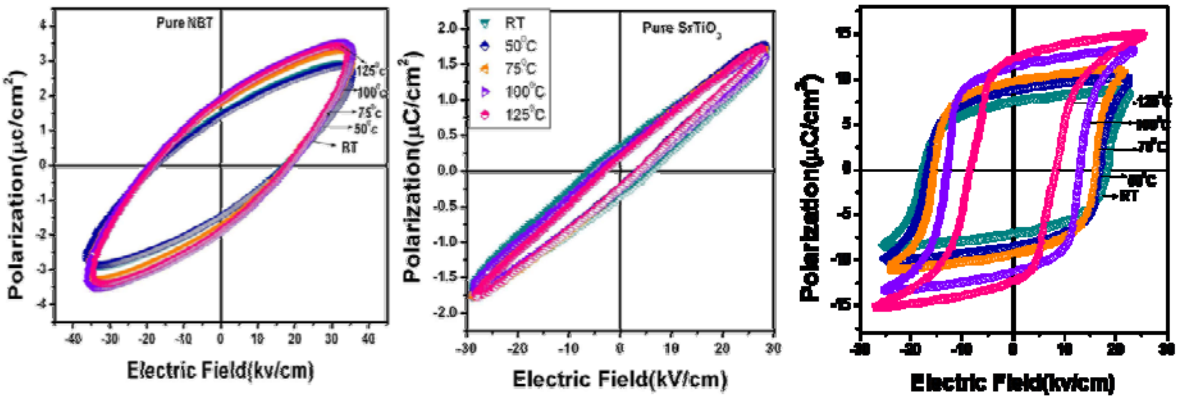

Figure 1. Variation of P-E lo ops for NBT,ST and NBST samples at different temperatures.

Fig 1 shows the polarization lo ops for NBT, ST and NBST ceramics at differ ent temperatures. No saturated ferroelectric loops are observed for pure NBT and pure ST. NBT is having high conductivity [10] and ST is a paraelectric in nature [11]. These natures ma y responsible for absence of saturated loops in NBT and ST. NBST composite show a typical ferroelectric behavior. ST addition in NBT l eads to decrease the conductivity and enhanced the ferroelectric and polarizing nature of the s ample. ST ions in NBT are highly polarizable in nature and facilitate the ferroelectric prop erties in NBST sample. In the studied composition, with the addition of ST to NBT, both coercive field (Ec) and remnant polarization (Pr) decreased and the values are listed in the Table 1.

Table.1: Variation of remnant po larization and coercive field values with temper ature

$T(^0C)$	P_r (μC/cm^2)	E_c (kV/cm)
30	7.295	17.922
50	8.129	17.234
75	9.490	15.879
100	11.342	12.958
125	12.272	8.327

S - E curves:

Electrostriction is a general property of all dielectric materials but it is significantly large in ferroelectrics just above the Curie temperature Tc, where an electric field can induce energetically unstable ferroelectric phase. In relaxor ferroelectrics, the electrostrictive strain can be kept at a relatively high level in a wide temperature range, because of the diffused phase transition. Strain values are calculated from polarization by considering the equation $S=QP^2$ [12] where S is strain, Q is electrostrictive coefficient and P is maximum polarization. Q value obtained from the relation d33 /(2εε0Ps). where d33 is the piezoelectric coefficient, ε is the dielectric constantat room temperature, ε0 is the permittivity of free space and Ps is the spontaneous polarization. The curves are plotted between S and E. The S vs E for composites show butterfly shape loops and i s shown in Figure 2.

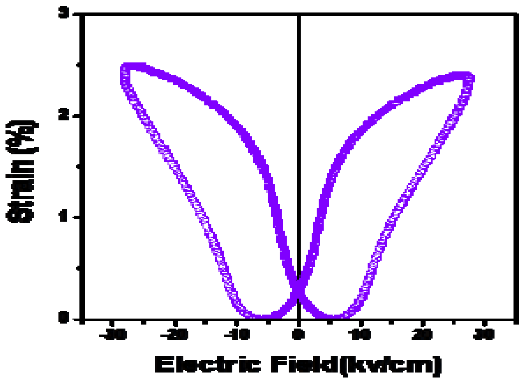

Figure 2: Strain vs ele ctric field loop for NBST sample at room temperature

Entropy change:

Entropy variation of the sample obtained by the theoretical calculations using the equation 1 and 2 are shown in Figure 3. The polarization data obtained from PE loop measurement used to find the entropy variation in NBST composite. Generally entropy variation will occur at the transition temperature. The present NBST sample exhibited ferroelectric to antiferroelectric transition near 160°C. Near this transition temperature dipoles are orients from order state to disorder state.

$$P = (\frac{P_i - P_f}{2})[\tanh(A(T_c - T))] + BT + C \text{ ....(1)}$$

$$\Delta S^E = (-A(\frac{P_i - P_f}{2})\sec h^2(A(T_c - T)) + B)\Delta E \text{ ....(2)}$$

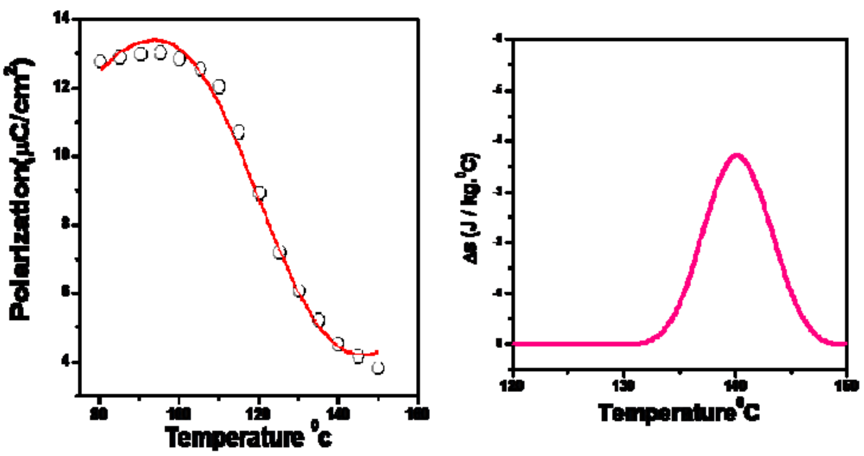

Figure 3: (a) Polarization variat ion of NBST sample with temperature, (b) Entropy variation of NBST sample

For present sample maximum en tropy change observed in the Figure 3b is arou nd 140°C. At this temperature applied field causes changes in spontaneous polarization leads to change in the alignment of dipoles. Change i n entropy causes change in the heat capacity from the sample leading to the cooling effect. This cooling effect finds applications in refrigeratioon process.

Table.2: Variation of remnant polarization and coercive field values with temperature

A	B	C	Q (m^4/C^2)
0.03906	0.20134	15.36213	0.10

Conclusion:

The sol gel method was found to be an advantageous method to produce NBST piezoelectric ceramics. From PE loops, it is concluded that the NBST sample exhibited saturated ferroelectric loops and the remnant polarization is increased with temperature and coercive field is decreased as the temperature is increased. The piezoelectric constant attains for the NBST sample is 64 pC/N. The electrostrictive coefficient value found for the sample is good when compare to lead based samples. Entropy variation in the sample obtained near ferroelectric to antiferroelctric transition temperature. The results of entropy yield cooling applications.

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