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Influence of Sintering Temperature on Ferroelectric $Ba_{0.7}Sr_{0.3}TiO_3$ Microstructure, Grain Size, and Electrical Properties

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Abstract: Barium strontium titanate is a ferroelectric material that is currently attracting much attention because it has high dielectric constant, low dissipation factor, tunable dielectric constant at microwave frequencies, and low-leakage current.The Ba0.7Sr0.3TiO3 compound studied in the present paper was synthesised using sol-gel method. The ferroelectric Ba0.7Sr0.3TiO3 was prepared using the sol-gel method, with barium and strontium acetate as a source for Ba and Sr as well as Ti(IV) isopropoxide as a source for Ti. The solvent used in this paper was acetic acid whereas 2-methoxyethanol has was used a stabiliser for Ti (IV) isopropoxide. Moreover, the effect of changing the electrical properties, the nanocrystal structure, and the particle size of ferroelectric Ba0.7Sr0.3TiO3 on its sintering temperature phase was investigated. The XRD results showed that sintering Ba0.7Sr0.3TiO3 at 900, °C 1000 °C, and 1100 °C occurred in a tetragonal phase. The sintering temperature affected the lattice constant and tetragonality of the material, where increasing sintering temperature decreased the tetragonality and the lattice constant. The dielectric properties of Ba0.7Sr0.3TiO3 sintered at 1100 °C were superior to that of the ferroelectric sample sintered at 1000 °C. The Curie temperature occurred at (28–32) °C when the dielectric constant was plotted as a function of temperature.
Keywords: ferroic materials; ferroelectric materials; barium strontium titanate; Curie temperature.

1 Introduction

Ferroic materials consist of ferromagnetic and ferroelectric materials [1]. Ferroelectric, pyroelectric, and piezoelectric materials have electric polarisation properties [2]. These materials appear significant changes in temperature and electric field when exposed to an external force such as mechanical stress because they are already insulating materials and the external force changes their charging centres. So that the distance between the negative pole and the positive pole becomes very small; Thus, forming a 'dipole moment' and is formed ferroelectric, pyroelectric, and piezoelectric effects. The crystallographic structure of the material is closely related to the phenomena of piezoelectricity, pyroelectricity, and ferroelectricity [3]. Ferroelectrics are materials that exhibit spontaneous polarisation over a certain temperature range. They are a Special type of pyroelectrics belongs to piezoelectrics. All these classes are formed of dielectric materials. Ferroelectric materials can be defined as dielectric materials with spontaneous polarization that can be reversed by an electric field and still retain polarisation even when removed from the external electric field [2,4].
solutions of $SnCl_2.2H_2O$ [2] and $SnCl_4.5H_2O$ [3] at relatively higher temperatures. The formation of nano crystalline SnS_2 thin film reported by [4,21] and SnS_2 nano wires [30] using other than spray pyrolysis preparation method. In the present study, it is intended to prepare and characterize light sensitive SnS_2 thin film on the glass substrate with lower thermal energy and spray pyrolysis method using the precursor solutions of $SnCl_2.2H_2O$ and thiourea.

The essential features of this material, namely their dielectric nonlinearity when applied with a bias electric field. Moreover, they materials display pronounced behaviour when their ratio of ions is manipulated to obtain a linearly adjustable Curie temperature [5].
Perovskite structure (ABO_3), A, B atoms have different

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valance electrons and different sizes or radii of atoms as shown in Fig. (1) [2]. More features can be seen in the perovskite structure with Barium Strontium Titanate (BST) compounds such as substituting one atom A from B or vice versa. hence,when replacing one ion with another ion, the properties of the compound such as conductivity or dielectric constant, etc. will change [5]. "The Curie temperature is the temperature at which the maximum dielectric constant occurs and the value after this degree will change polar materials to non-polar materials (ferroelectric–paraelectric)" [6].

BST belongs to the (ABO_3) perovskite family of crystal structures (ABX_3) and possesses similar crystalline properties to that of general perovskites with a cubic nature and with the chemical formula $Ba_x Sr_{1-x}TiO_3$ [7].

The BST perovskite structure allows its transition from the ferroelectric phase to the paraelectric phase with a change in the Curie temperature. These conditions have posed significant challenges in creating new materials and technologies [8].

This work provides insight into ferroelectric materials, namely a sub-group of piezoelectric materials focusing on perovskite structures such as $BaTiO_3$, $SrTiO_3$ and $BaSrTiO_3$. The preparation method, the crystalline structure, and other conditions such as sintering, etc., influence the dielectric properties of the ferroelectric materials. Barium Strontium Titanate (BST) with the general formula $BaSrTiO_3$ is a solid solution of $BaTiO_3$(BTO) and $SrTiO_3$ (STO) [9].

BST belongs to the perovskite family of materials with the general formula ABO_3. The structure of BST is similar to that of $BaTiO_3$ [10]. In BST, the A site is occupied by(Ba) atoms and (Sr) atoms. The Ba^{2+} and Sr^{2+} ions occupy the angular point seats of the unit cell corners while Ti^{4+}.

occupies the centre of the unit cell. The O^{2-} ions occupy the face centres of the unit cell [11].

transition temperature, T_C, the material will exist in cubic paraelectric form while below T_c, the material exhibits a tetragonal ferroelectric state. The lattice parameter and T_c depend on the Ba: Sr ratio [13].

The solid solution composition of ferroelectric barium titanate ($BaTiO_3$) and paraelectric $SrTiO_3$, $BaSrTiO_3$ (BST) possess the best dielectric constant and have a relatively low loss over a wide range of frequencies, a low leakage current and large electric field tenability [11,14].

Understanding this application requires comprehending the growth structure of the high-quality thin film and equivalent bulk materials. Barium Strontium Titanate (BST) compounds has been very attractive materials throughout the last ten years [15]. BST compounds are increasingly used in new and important applications such as piezoelectric sensors, dynamic random dielectric access memory (DRAM), microwave phase shifter voltage-controlled oscillators, infrared detectors, frequency limiters, transformers, micro-electrical mechanical switches, resonators, pulse shaping and sharping applications, and tunable Lange-couplers [16]. The main features of BST are its lead-free material (non-hazardous), pyroelectric properties, and high dielectric ferroelectric properties.

It can also be produced via the processing of metal alkoxides and the hydrothermal growth of fine powders [17].

The sol-gel method is known as a green chemistry method for preparing metal oxides with high-porosity. This material is attractive to use in applications such as ceramic precursors, insulators, and catalyst supports. This method allows the mixing metal oxides where mixing two or more phases can be controlled on both nanometer and molecular scales. Such systems comprise metal oxide/silicon oxide composites that are desirable for a variety of transition and main group metals [17, 18].

BST compounds have a high dielectric constant and a low dissipation factor, they are used in a variety of capacitors.

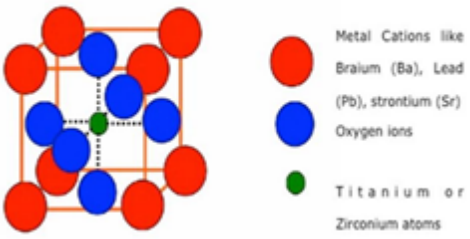

Fig. 1: Perovskite structure [2].

BST can either exist as a tetragonal or cubic structure ($BaTiO_3$ is ferroelectric at room temperature whereas $SrTiO_3$ is paraelectric) depending on the Ba: Sr ratio and temperature [12]. At temperatures above the phase

The manufacture of material oxides is affected by several parameters of the sol-gel method.

Previous related studied have shown that sintering temperature influences the electric properties

microstructure, the Curie temperature of BaSrTiO3-based ceramics. Previous related studied have revealed that sintering temperature influences the electric properties, the microstructure, and the Curie temperature of BaTiO3-based ceramics [19]. When the sintering temperature increased, the density of the ferroelectric samples proportionately changed depending on the nanometer sintering kinetics of BaSrTiO3 ceramics [20]. However, insufficient information is available on the effects temperature of sintering on the dielectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$. Consequently, $Ba_{0.7}Sr_{0.3}TiO_3$ was prepared in this paper using the conventional sol-gel method. The effects of sintering temperature on the microstructure and the dielectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ were then investigated in detail [21].

2 Experimental Details

The sol gel method, which is one of widely used techniques for preparing some oxide materials (such as ferroelectric materials $BaSrTiO_3$) is used in this work. This work used the sol-gel method to produce nanoparticles. In this method, the processing temperature and size of the particles were reduced so that better physicochemical properties could be achieved compared to using bulk counterparts. The starting materials and the synthesis route affect the quality of the material powders.

Ferroelectric $Ba_{0.7}Sr_{0.3}TiO_3$ was prepared via sol-gel. "The starting raw materials were high-purity Barium acetate (BDH Chemicals England, 99.95%), Strontium acetate (Sigma Aldrich, 99.9%), and Ti (IV) isopropoxide (97% Sigma Aldrich) as sources of barium, strontium, and titanate, respectively. Acetic acid (Merck 99.8%) was used as solvent and 2-methoxy ethanol was used as a stabiliser for Ti (IV) isopropoxide".

An appropriate weight of strontium acetate (0.034 mol) and barium acetate (0.08 mol) powder were dissolved in a suitable volume of acetic acid (10 ml and 5 ml), respectively. Each solution was separately stirred for 60 min at 60 °C and then mixed to make up the (Ba, Sr) solution. This solution was refluxed in a reflux system (Hotmintal (110 V), three-necked flask, reflux condenser) and the temperature of the solution at 110 °C was adjusted as shown in Fig. (2).

The solution was refluxed at 110 °C for 2 h (until the transparent solution slightly turned yellow). Then, 2-methoxy ethanol (2–4 ml) was added as a stabiliser to maintain the crystalline structure of Ti-isopropoxide at room temperature. The (Ba, Sr) solution was filled in a burette and added slowly (drop by drop) in the second solution (Ti(IV)). The final solution was then adjusted to a pH range of pH3.5 to pH5. The solution was refluxed again in the reflux system until the solution turned into a white gel. Deionising water was used to dilute the solution gel and then a hot plate stirrer was used to stir the solution at 60 °C for one hour (1 h). The final solution was dried at 200 °C for 2 hours to separate the water completely and then again at 700 °C. The powders were calcined for a limited period (2 hours). A mortar and pestle were used to obtain a fine powder. The BST nano-powder and fine powder were compacted in a cylindrical steel model with a (120 mm) internal diameter. The process was used to press the powder into a pellet shape to reduce the vacancies and porosity between the particles and shrinkage in size by packing the particles close to each other. The final average dimension was (120 mm) diameter, thickness of (2.5–3.0 mm), and pressure below (250–300 MPa). All samples were sintered at different temperatures (900, 1000, 1100 °C) in an ambient atmosphere. The ferroelectric samples were examined via XRD (Bruker, Germany) with Cu K_α (40 kV and 30 mA). The grain size and particle size of the ferroelectric sample were examined using Scanning Electron Microscope (FESEM, S-4700, Hitachi) and the electric properties were measureed using an impedance analyser, LCR.

3 Results and Discussion

Figure (3) shows the Energy Dispersive Spectroscopy (EDS) of bulk BST ($Ba_{0.7}Sr_{0.3}TiO_3$). Table (1) indicated the ratios of metallic compounds of BST as mass or atomic percentages. The stoichiometric composition of Titanium and Oxygen remained approximately close to 1:3 for most of the samples. The stoichiometric composition of strontium and barium changed in line with the change in the value of x.

The XRD pattern of the $Ba_{0.7}Sr_{0.3}TiO_3$ phase showed polycrystalline phases, perovskite tetragonal phase with reflection angle planes [" (100), (101), (111), (200), (201), (211), (202), (221), (301)"] planes. The phase exhibited the space group P4mm with (3.9771, 3.9883 Å for a, c) respectively. All those peaks matched PDF card no. (00-044-0093).

Figure (4) shows the polycrystalline structure of ferroelectric $Ba_{0.7}Sr_{0.3}TiO_3$ and the X-ray diffraction patterns of $Ba_{0.7}Sr_{0.3}TiO_3$ sintered at different temperature.

It can be observed that ferroelectric $Ba_{0.7}Sr_{0.}3TiO3$ sintered at 1100 °C. There was no evidence of any additional phase, "Ferroelectric $Ba_{0.7}Sr_{0.3}TiO_3$ sintered at 900 °C and 1000 °C showed two weak diffraction peaks as a secondary phase (+, +) besides the peaks of the BST phase, which appeared at (2θ = 24.21°, 26.8°) and (28.8°) belonging to the intermediate oxycarbonates such as $Ba_2Ti_2O_5CO_3$, and (Ba,Sr) $Ti_2O_5CO_3$"[19]. The most probable crystalline impurity was attributed to Sr_2TiO_4, $SrTiO_{10}$, Sr_3 Ti_2O_7, which almost appeared at 44.6°.

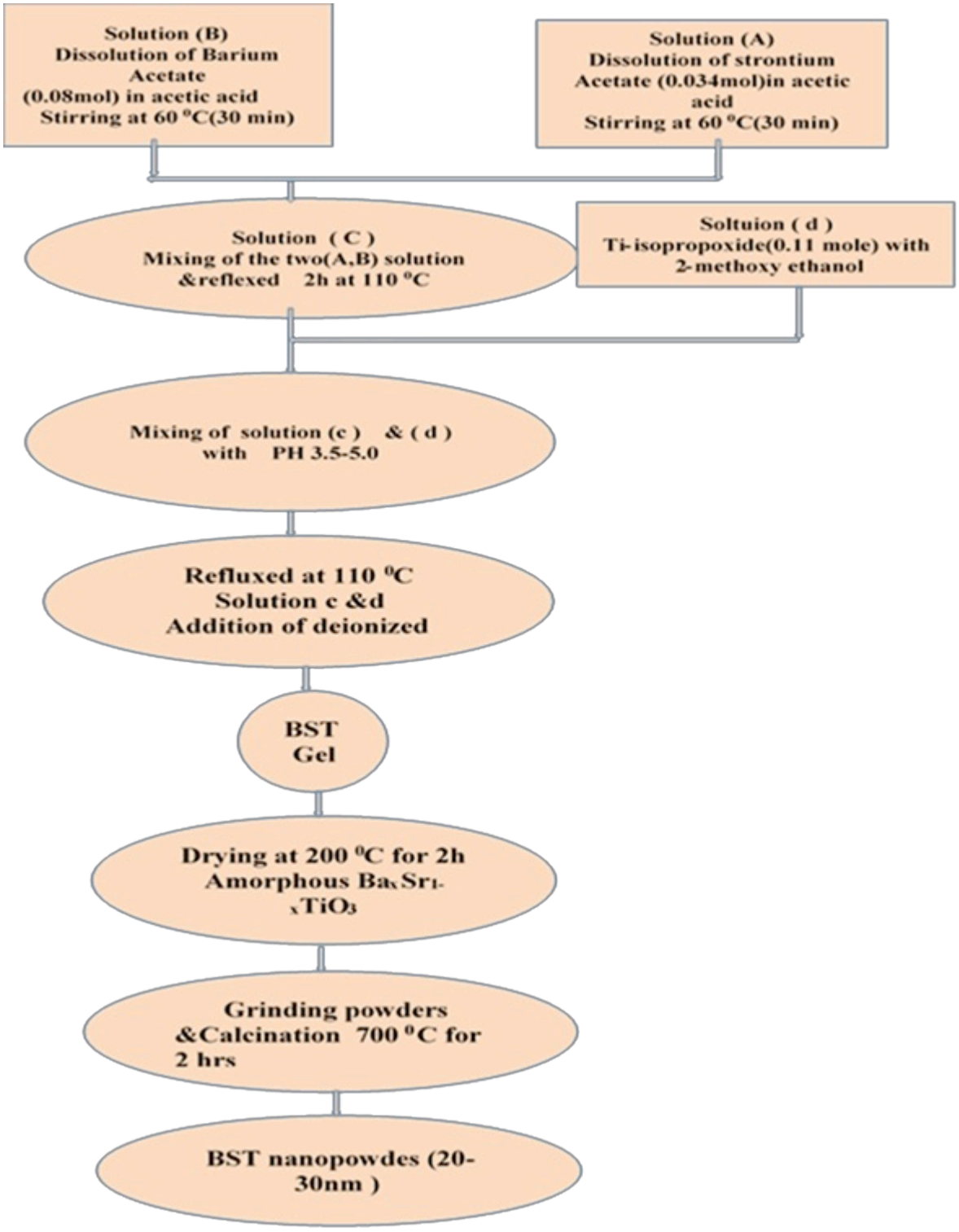

Fig. 2: Flow chart preparation of BST by the Sol-Gel method.

Table 1: The standard and experimental values of the elements $Ba_{0.7}Sr_{03}TiO_3$ compounds.

X	Element	Line	Standard value	Exp. Value	Standard value	Exp. Value
0.3	O	K_α	22.14	20.3	60.00	59.32
	Ti	K_α	22.08	16.29	20.00	15.89
	Sr	L_α	13.34	16.58	4.60	8.85
	Ba	L_α	42.44	46.83	15.40	15.94

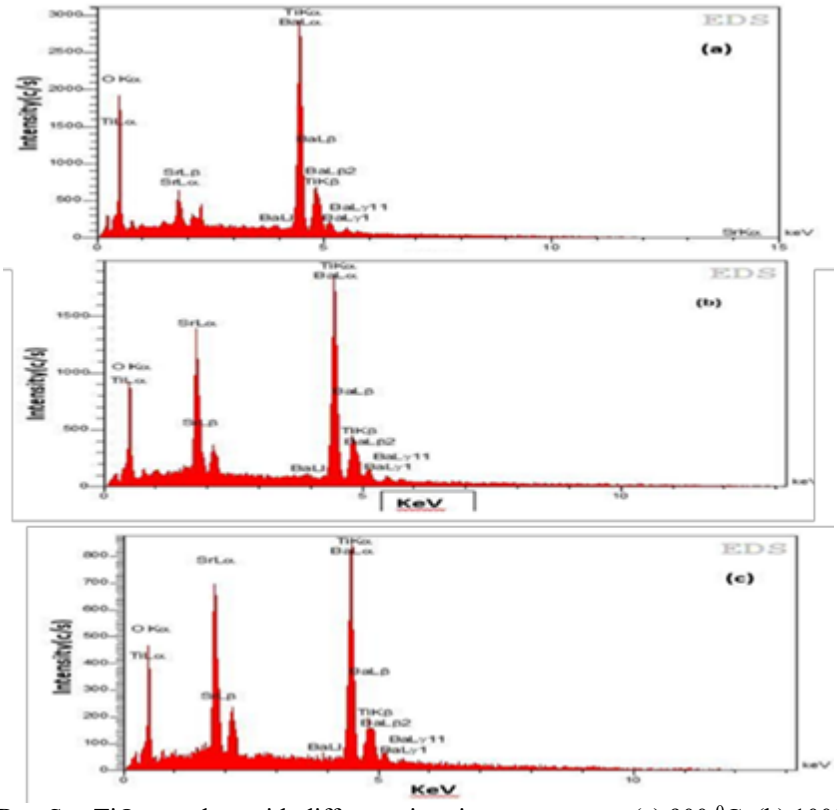

Fig. 3: EDS pattern $Ba_{0.7}Sr_{0.3}TiO_3$ powders with different sintering temperature (a) 900 ^{0}C (b) 1000 ^{0}C (C) 1100 ^{0}C.

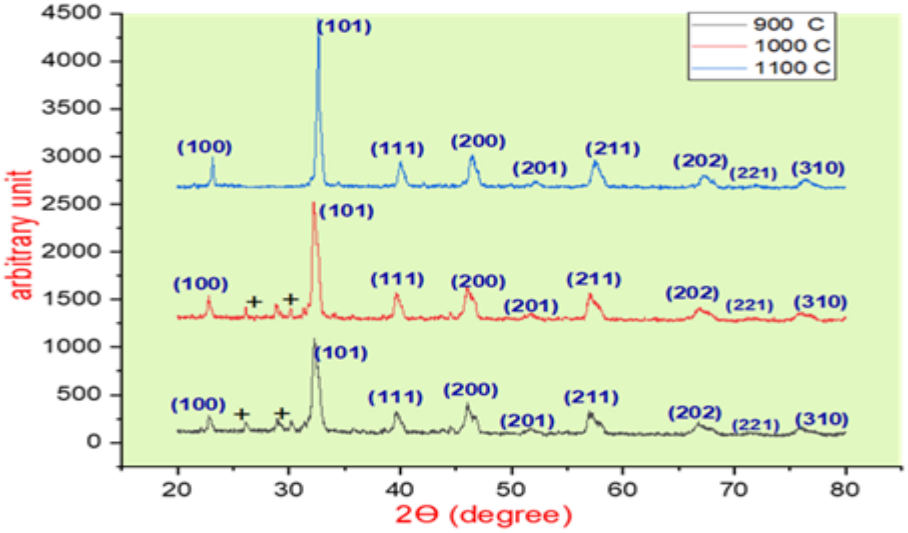

Fig.4: XRD patterns of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics sintered at different temperate.

The effect of different cation radius (Sr^{+} ion 1.13 Å, Ba^{+} ion 1.35 Å) made the peaks shift toward higher 2θ angles when the concentration of strontium ions increased as shown in Tabel (2).

Fig. (5) shows, when the temperature of sintering increased, the lattice constant decreased and tetragonality decreased with increasing sintering temperature.At a temperature of sintering of 1100 °C, the tetragonality was close to 1, showing that $Ba_{0.7}Sr_{0.3}TiO_3$ gradually changed from tetragonal to pseudo-cubic phase with increased sintering temperature.

According to Fig. (6), the calculated grain size of $Ba_{0.7}Sr_{0.3}TiO_3$ sintered at (900, 1000, &1100 °C) was 73.38 nm, 193.378 nm, and 278.45 nm, respectively. The ImageJ program (1.51j8) showed that the particle size increased with increased sintering temperature.

The change in the dielectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ based on the various sintering temperatures is presented in Fig. (7). First, it was found that the dielectric constant of $Ba_{0.7}Sr_{0.3}TiO_3$ sintered at (1000–1100) °C decreased as the frequency increased, because of different polarisation mechanisms (electronic, atomic or ionic, orientation, dipolar and space charge polarisation), which affected the total polarisation. At low frequencies, all types of polarisation were affected by increased frequencies. Some types of polarisation could not catch up with the relaxed time of the frequencies while others disappeared when the frequencies increased.The physical properties of $Ba_{0.7}Sr_{0.3}TiO_3$ compound greatly affect the value of its permittivity and loss factor. The sintering temperature affects the degree of crystallisation, which, in turn, affects the values of the dielectric constant and dissipation factor. Compared to its

dielectric constant, the porosity, crystallinity, and particle size of the BST compound were significantly affected by the changing temperatures (1000 °C, 1100 °C).

The dissipation factor of $Ba_{0.7}Sr_{0.3}TiO_3$ sintering at (1000 °C, 1100 °C) decreased with increasing temperature of sintering, as exhibited in Fig. (7). The dissipation factor of the sample at (1000 °C) was greater than the sample at (1100 °C), which is the stabilised sample, when the sintering temperature increased, because of reduced porosity and higher density.

Fig. 7 also illustrates the dielectric properties as a function of different frequencies (1 kHz, 20 kHz, &100 kHz) and temperature. The dielectric constant initially increased till critical temperature i.e. the Curie temperature, where the maximum dielectric constant was achieved. Then, $Ba_{0.7}Sr_{0.3}TiO_3$ is a tetragonal structure within the Curie temperature range of (28–30) °C.

"Above the transition temperature, the decrease in the dielectric constant occurs because of the increased thermal oscillation of the molecules and the increased degree of disorder of the dipoles" [17]

Table 2: Structural parameters viz. angle values, Miller indices, inter-planar spacing for the phase of $Ba_{0.7}Sr_{0.3}TiO_3$ powders.

2Θ (degree) at 900 ^{0}C	2Θ (degree) at 1000 ^{0}C	2Θ (degree) at 1100 ^{0}C	d-standard (Å)	d -Exp. (Å) at 900 ^{0}C	d -Exp. (Å) at 1000 ^{0}C	d -Exp. (Å) at 1100 ^{0}C	hkl
22.3363	22.6523	22.9745	3.96600	3.9611	3.8686	3.8547	(100)
31.7481	32.4398	32.724	2.80600	2.7931	2.7577	2.7344	(101)
39.1642	39.7661	39.9482	2.29000	2.2940	2.26401	2.2971	(111)
45.5621	46.218	46.4429	1.982300	1.9852	1.9526	1.9506	(200)
51.3012	51.8438	52.224	1.773500	1.7685	1.7621	1.7501	(201)
56.6100	57.234	57.4899	1.61950	1.6137	1.6083	1.6017	(211)
66.3281	66.97	67.18	1.4023	1.3977	1.3961	1.3923	(202)
70.9431	71.3118	71.3897	1.3213	1.3221	1.3218	1.3202	(221)
75.3203	75.8211	76.123	1.2537	1.2598	1.2566	1.25401	(310)

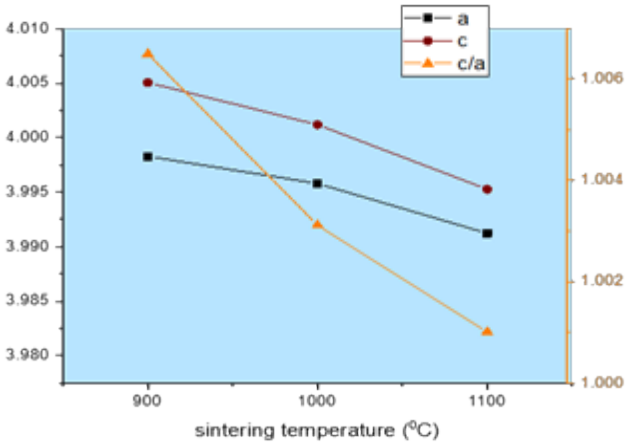

Fig.5: Sintering temperature dependences of lattice constant and tetragonality in $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics.

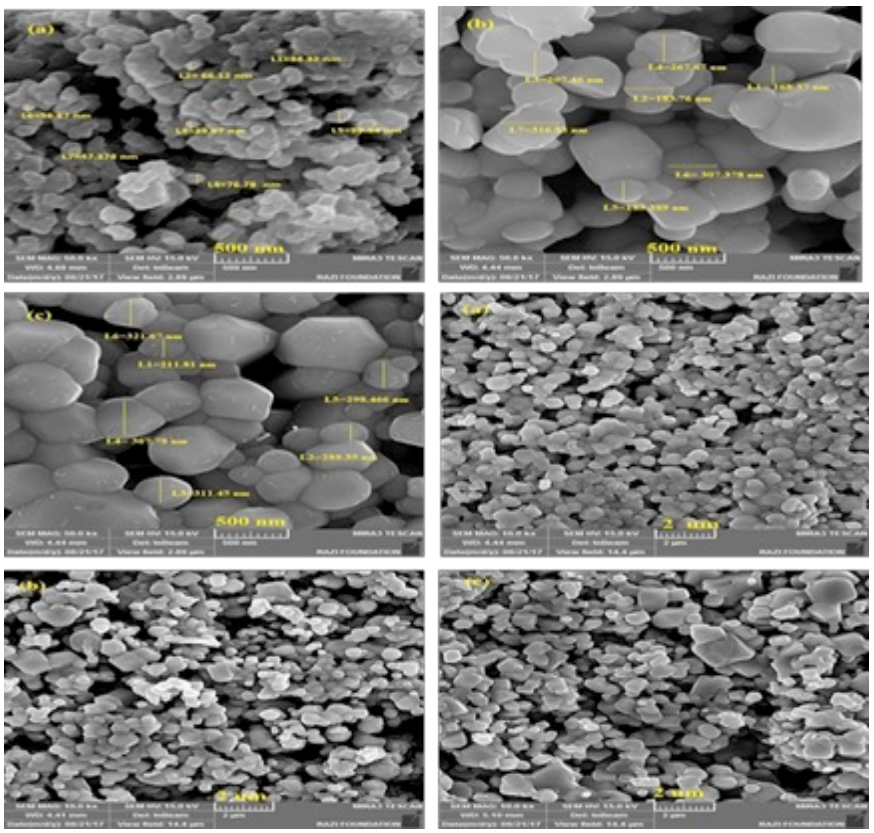

Fig.6: FESEM micrograph of Ferroelectric $Ba_{0.7}Sr_{0.3}TiO_3$ sintered at various temperatures (a) 900 °C, (b) 1000 °C, (c) 1100 °C.

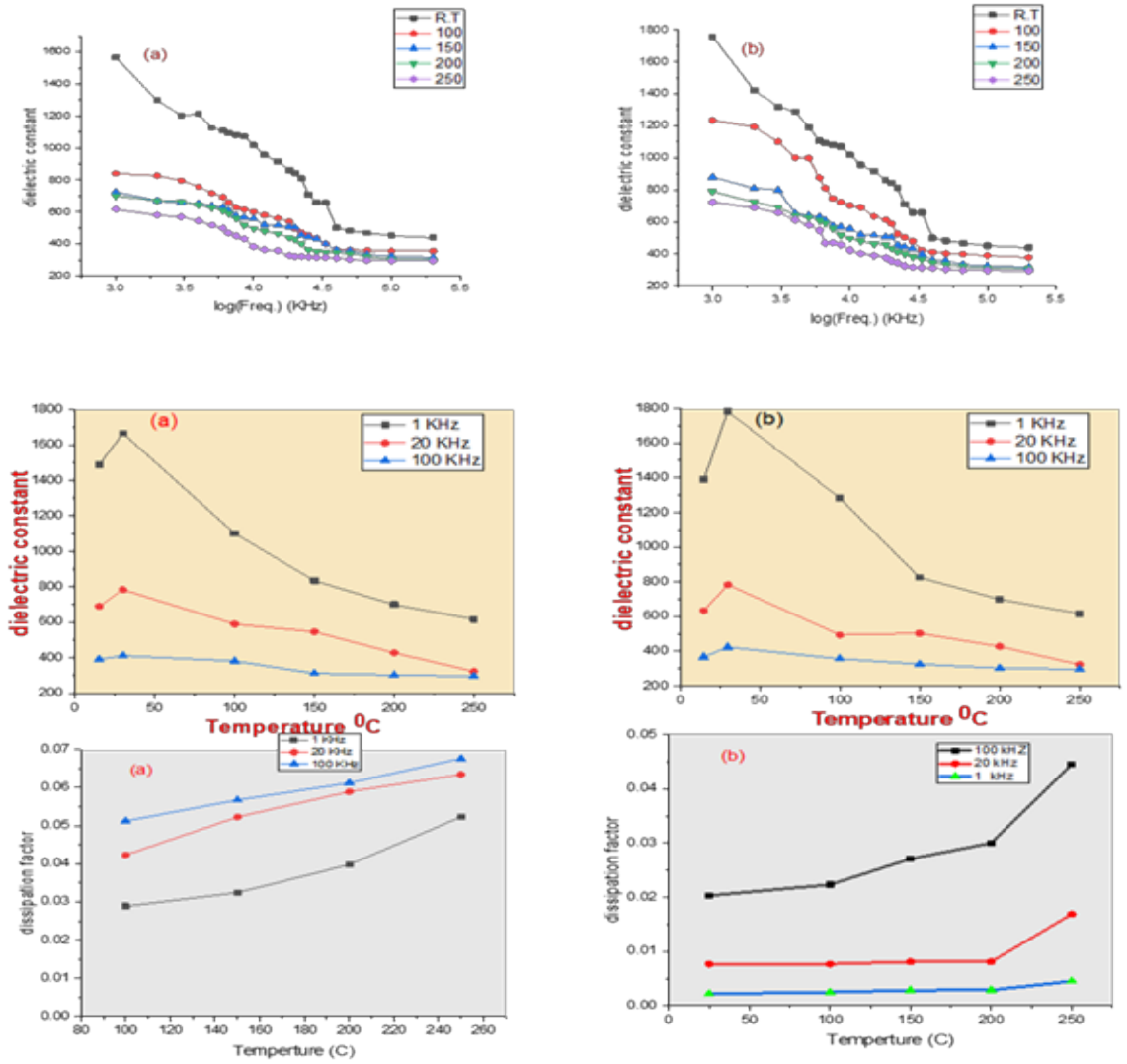

Fig.7: the dielectric constant as a function for frequency and temperature and dissipation factor as a function temperature.

4 Conclusions

$Ba_{0.7}Sr_{0.3}TiO_3$ compound which was synthesized using the sol-gel method composed of strontium, barium acetate, and titanate (IV) isopropoxide. The solvent used was Acetic acid and the stabiliser for the isoproxide structure was 2-methoxy ethanol. Moreover,the effect of different sintering temperature on the nanoparticles, dielectric, and dissipation factor of $Ba_{0.7}Sr_{0.3}TiO_3$ was investigated.

SEM was used to define the size of the particles. The results showed that the particle sizes varied (73.38 nm, 193.378 nm, and 278.45 nm) with varying sintering temperatures. In addition, the increasing temperature of sintering led to increased particles size.

The XRD pattern showed a tetragonal perovskite structure for the $Ba_{0.7}Sr_{0.3}TiO_3$ compound with a lattice Constant (a = 3.9771 Å) and P4 mm space group (221).

The d-spacing decreased when the sintering temperature increased because of a change in particle size. Increasing the sintering temperature led to an increased dielectric constant but decreasing it caused increased frequency and temperature.

Availability of data material: Data will not be shared because they can promote designing a better photonic sensor with high-quality factor and sensitivity.

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