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IMPACT OF SINTERING TEMPERATURE ON STRUCTURAL AND DIELECTRIC PROPERTIES OF BARIUM STRONTIUM TITANATE PREPARED BY SOL-GEL METHOD

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Microstructure and dielectric properties of Barium Strontium Titanate (BST) nanopowders were prepared by sol-gel method. $Ba_{0.6}Sr_{0.4}TiO_3$ has been synthesis from raw materials which (Ba,Sr)acetate. Acetic Acid and Titanate (IV)isopropoxide. EDAX spectra showed that all components of the compound already exist. The free sintering methods was used for final densification of BST compounds. SEM showed particles size increasing with sintering temperature increased. Phase evolution for BST samples were characterized used X-ray diffraction which appeared cubic structure and showed the peaks graded to high value angles when increased sintering temperature. The measured dielectric constant of the samples was increasing with increased sintering temperature and decreasing with increased frequency.

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1. Introduction

Piezoelectric materials were an important type of functional materials. Lead-free piezoelectric, pyroelectric and ferroelectric had attracted more and more attention during recent years by reason of the toxicity of lead (1).

Ferroelectric materials are sub-groups of dielectric materials that show unique physical properties (2). These materials exhibit a change in their relative permittivity (ε) with respect to the applied field (3). Complex oxide perovskite possessing the ferroelectric property which have verity of application , as , ceramic capacitors in bulk and of thin film forms for ferroelectric random access memory , microwave phase shifter , tunable filters, varistors, oscillators, electro-optical properties to be applied to the light senser, microactuator and sensors, infrared pyroelectric sensors , transistors , microwave electronics, electro-optic modulators, etc. [4,5]

Ferroelectric material has the ability to change the direction of its internal electricity, can be spontaneously polarized and show hysteresis effects associated with the shift dielectric in response to an internal electric field. (5,6).

First perovskite type ferroelectric material developed and intensively studied ever since its discovery about 70 years ago. It has high dielectric constant and low dielectric loss, good piezoelectric, pyroelectric, and ferroelectric properties, positive temperature coefficients(7).

There are several important ferroelectric materials which were studied such as $PbTiO_3$, $Pb(MgNb)O_3$, $SrBiTaO_3$, $SrTiO_3$and $BaTiO_3$, which are the origin of (Ba, Sr) TiO_3 (8).

Barium Strontium Titanate ($Ba_{1-x}Sr_xTiO_3$) system is one materials which considerable interest to researchers and engineering in the field of electro-ceramics and microelectronics(9). $BaSrTiO_3$ is one of the most ferroelectric materials among the complex oxide perovskite It has a dielectric constant and a high charge storage capacity(10,11).

Barium titanate ($BaTiO_3$) is extensively used in a variety of capacitor device, because of its high dielectric constant but also high dispassion factor. So, to improve electric properties for

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BT compounds by used doping $SrTiO_3$ which has more structural stability, Sr^+ ions are introduced into barium titanate to substitute for Ba^{+2} ions on A sites and form $Ba_{1-x}Sr_xTiO_3$(13).

BST has been considered to be a leading candidate materials for new dielectric device by virtue of strong dielectric nonlinearity under bias electric field and linearly variable Curie temperature with the content of strontium (14).

Barium Strontium Titanate (BST) is aternary ceramic compound with the stoichiometric formula ($Ba_{1-x}Sr_xTiO_3$). It is a continuous solid solution containing $BaTiO_3$ and $SrTiO_3$ over the entire composition range (7). A number of titanate-based ferroelectric materials have been investigated in the past for tunable device applications. These ferroelectrics are used as resonators, phase shifters, filters and capacitors in communication systems(15). The molar ratio of strontium increased that introduced to A site in perovskite barium titanate matrix to replace barium atoms, the phase transition temperature of paraelectric to ferroelectric decreases(16).The phyiscal properties have been affected by various parameters such as temperture, pressure, substitution and size due to the close relationship between ferroelectric properties and crystal stucture(17). Due to the interplay of competing energies, properties can be varied significantly with a variation of concentration of Sr^+ ions (18).

In this paper, $Ba_{0.6}Sr_{0.4}TiO_3$ powders were prepared via sol-gel method. The effect of sintering temperature on microstructure and dielectric properties.

2. Experimental

Barium Strontium Titanate powders were synthesis using the new synthesis technique . SoL-Gel method is a relatively new method for synthesizing phase pure multi-component phase material . In this method , the precursor materials , which are preferably acetate salts of metal, are made soluble in Acetic Acid .

The selected method for BST synthesis depends on some factor such as cost, low temperature and desired application.The quality of the powders affected not only synthesis route but also by starting materials used.

The raw materials were used materials to synthesis $Ba_{0.6}Sr_{0.4}TiO_3$ powders by Sol-Gel method initial from barium acetate , strontium acetate and Titanate (IV) isopropoxide as precursor.

$Ba_{0.6}Sr_{0.4}TiO_3$ nanopowders were synthesized by using Barium acetate $Ba(CH_3CHOO)_2$ (99.5% BDH Chemical-England), Strontium acetate $Sr(CH_3CHOO)_2$ (Aldrich 99%), as source of barium and strontium. Titanium (IV) isopropoxide(Aldrich, 97%) as a source titanium with 2-methoxy ethanol as if stabilizer for titanate(IV) isoproxide structure . Acetic acid CH3CHOOH (Aldrich 97%) was used as the solvent for barium acetate and strontium acetate. To obtain stoichiometric proportions aproparate wight of barium acetate and strontium acetate powder was dissolved in a sutable volume of acetic acide. The two solution separtelly stirred magnetically at 60^oC for 60 min., then mixed together to get (Ba, Sr) solution and refluxed at 110^oC for 2 h (till obtained transparent solution slightly tuned to yellow). 2-methoxy ethanol (2-4 ml) was added in Ti (IV) isopropoxide at R.T. (Ba, Sr) solution was added slowly(drop by drop) into Ti(IV) isopropoxide solution, and the pH of the product solution was adjusted in the range of 3 to 5 by adding buffering agent. Refluxing the mixture again till obtain a thick white gel. This gel was diluted by distille water and the solution was mixed by stirring on a hot plate (60^oC) with a magnetic stirrer. Finally the solutions were dried at 200°C for 2 h to separate the water completely to form amorphous powders $Ba_{0}{\cdot}_{6}Sr_{0}{\cdot}_{4}TiO_{3,}$. The amorphous powders were calcined at 700 C for 2h. The powders were ground in a mortar to obtain a fine powder. The fine powders were pressed by using a hydraulic press as a pelt at pressure equals to 10 (tons) with 1.2 cm diameter. The pellet sinttered at (900,1000, 1100 ^0C) for 3 h in atmosphere. The morphological and composition properties of the sintered pellets were performed by using field emission scanning electron microscopy (FESEM) supplemented with energy dispersive spectroscopy model (Hitachi 4700 field emission microscope).The microstructure of all sammples were recorded at R.T using x-ray powder diffractometer with $CuK_{\acute{\alpha}}$ (λ=1.5418A^0, 30 kV, 30 mA) model (Bruker, Germany) in a wide range of $2\theta= 20^o$-80^o at scanning rate 1 min^{-1}. The dielectric properties of the $Ba_{0.6}Sr_{0.4}TiO_3$

nanopowders were determine by LCR meter with variation frequency (1 KHz-200 KHz) at 0.5 V from R.T ^{0}C to 250 ^{0}C.

3. Result

Fig. (1) shows the EDX spectra of $Ba_{0.6}Sr_{0.4}TiO_3$ power which sintered at different temperature. It is clear that the elements Ba, Sr, Ti and O was detected in all spectra, and there is no other elemets which means that the pure BST phase was dominant phase, and no impurties were existed . The composition ratios (Ba/Sr) of the as-prepared powders were confirmed using the microarea EDS analysis. Stoichiometric ratios of the main metallic compounds of BST are shown in table (1) as mass or atomic percentage.

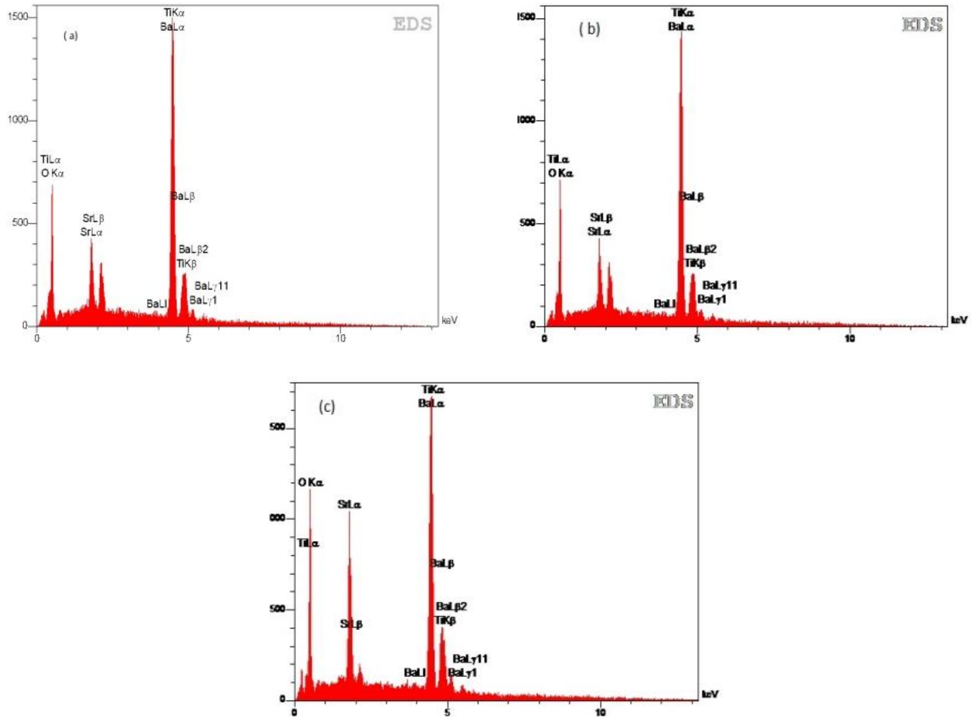

Fig. 1. EDX pattern of $Ba_{1-x}Sr_xTiO_3$ Powders with different x values.
(a) x=0.4(900 ^{0}C) (b)= x=0.4 (1000 ^{0}C) (c)= x=0.4(11).

From below Table 1, it can be seen that the ratio achieve best components at 1000 C and barium decreasing when increased sintering temperature may be attribute to increase activity Strontium with increased sintering temperature.

Table 1. The theoretical and experimental values of the element content in $Ba_{0.6}Sr_{0.4}TiO_3$ *compound.*

x	Elements	Line	Theo.values W%	Exp.values W%	Theo.Values A%	Exp. Values A%
900 ^{0}C	O	K_a	22.50	26.84	60.00	65.33
	Ti	K_a	22.44	24.12	20.00	19.61
	Sr	L_a	16.43	7.13	8.00	3.17
	Ba	L_a	38.63	41.92	12.00	11.89
1000 ^{0}C	O	K_a	22.50	25.10	60.00	63.89
	Ti	K_a	22.44	19.39	20.00	16.48
	Sr	L_a	16.43	18.81	8.00	8.74
	Ba	L_a	38.63	36.70	12.00	10.88
1100 ^{0}C	O	K_a	22.50	26.56	60.00	64.65
	Ti	K_a	22.44	21.60	20.00	17.56
	Sr	L_a	16.43	19.19	8.00	8.53
	Ba	L_a	38.63	32.69	12.00	9.26

Fig. (2) shows SEM micrograph of the surface morphologies of the $Ba_{0.6}Sr_{0.4}TiO_3$ powders calcined at 700 ^{0}C and sintered at (900, 1000, 1100 ^{o}C) for 3 hrs . It is seen that sintering temperature has obvious effect on the grain size, which indicates that the grain size increases with the rise of sintering temperature.

This is occur due to that the small particle tend merge with each other to become larger ones when sintering temperature increased. The synthesis parameters such as initial concentration and reaction time (stirrer and reflux time) have a great influence on the size of nanostructure of $Ba_{0.6}Sr_{0.4}TiO_3$. By controlling on these parameters the particles size change to be (24 ,49.23,79.80,105.42 nm) corresponding to temperatures rise (700 ^{0}C, 900 C, 1000 ^{0}C , 1100 ^{0}C), respectively. It is clear that the particles size of BST increasing with increased sintering temperature due to change densification and reduced porosity. This result agree with the results of S. Hu *et al* (1), and Yanling et. al (2).

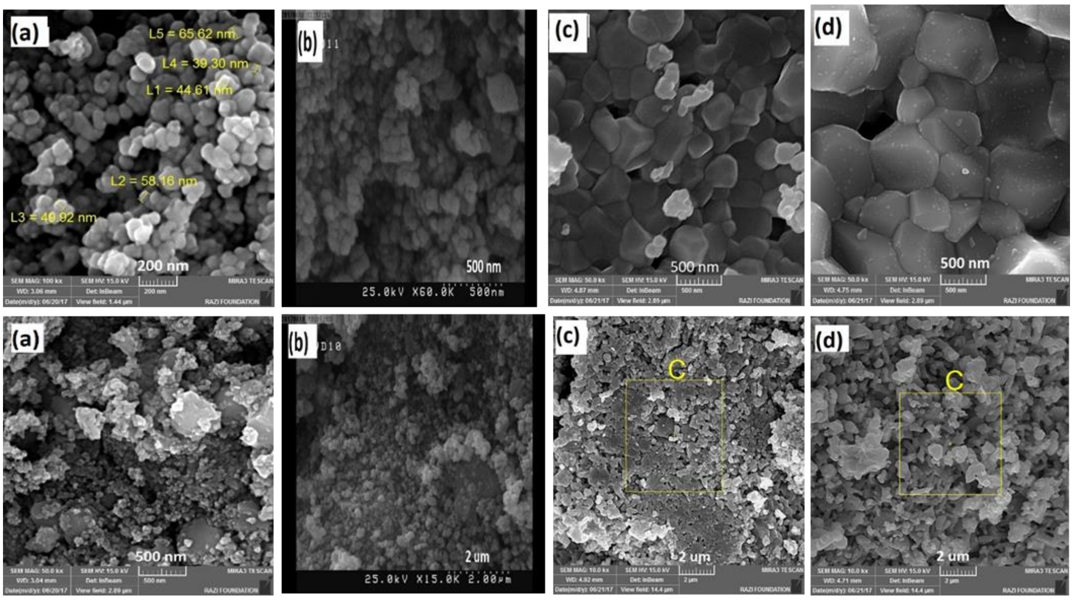

Fig. 2. Field emission scanning electron microscopy (FESEM) images for $Ba_{\,0.6}Sr_{0.4}TiO_3$
(a) 700 0C (b) 900 0C (c) 1000 0C (d) 1100 0C.

Fig. (3) shows the XRD diffraction patterns of $Ba_{0.6}Sr_{0.4}TiO_3$ sintering at different temperature. Firslty, it seen that compound calcined at (700 ^{0}C) and sintering at (900, 1000, 1100 ^{0}C) are polycrystalline phases with perovskite structure and there is evidence intermediate phases. It is clear that implies Sr^+ ions have entered the unit cell maintaining the perovskite structure of solid solution.

The XRD pattern shows many peaks Correspond to (100), (110), (111), (200), (210), (211) and (220) planes. These peaks are related to cubic BST phase, and the peaks perfectly match with pdf card no. (00-034-0411), with Pm3m space group (221) and lattice constant a=3.965A.

The peaks were evidence as a secondary phase besides the peaks of BST phase, which appeared at (2θ=24.21,26.8^0) and (28.8^0) belong to intermediate oxycarbonates such as $Ba_2Ti_2O_5CO_3$, and (Ba, Sr)$Ti_2O_5CO_3$ (7,19). The most probable crystalline impurity are Sr_2TiO_4, $SrTiO_{10}$, Sr_3 Ti_2O_7 almost appear at 44.6^o (2,18) respectively .

It is clear that the Intensity of peaks has been increased with increasing sintering temperature that is explained effect of sintering temperature on crystalline completed which turn on disappeared intermediate phases.

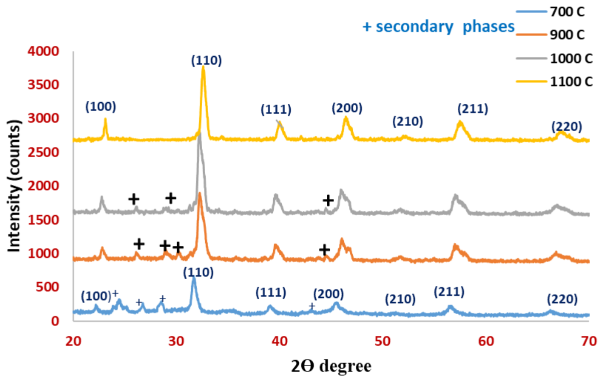

Fig. 3. XRD patterns of $Ba_{0.6}Sr_{0.4}TiO_3$ powders with various sintering temperatures.

It is found that the diffraction peaks of Ba $_{0.6}$Sr $_{0.4}$$TiO_3$ shift to higher angle with the rise of sintering temperature. This shifted indicates the interatomic space of the BST decrease with the increase of sintering temperature which affected by increased particles size.

Table 2. Structural parameters viz. 2θ values, inter-planar spacing, miller indices, and phase of $Ba_{0.6}Sr_{0.4}TiO_3$ powders sintering at different temperature.

2 Theta 700 ^{0}C	2 Theta 900 0C	2 Theta 1000 0C	2 Theta 1100 0C	d-theo. Theortical	d-Exp. 700 ^{0}C	d-Exp 900 ^{0}C	d-Exp 1000 ^{0}C	d-Exp 1100 ^{0}C	Hkl
22.2649	22.8314	22.9701	23.0539	3.96600	3.9695	3.9611	3.8686	3.8547	(100)
31.6933	32.2933	32.4398	32.724	2.80600	2.8209	2.7931	2.7577	2.7344	(110)
39.1389	39.705	39.7661	39.9482	2.29000	2.2963	2.2940	2.26401	2.2971	(111)
45.5324	46.0585	46.218	46.4429	1.982300	1.9855	1.9852	1.9526	1.9506	(200)
51.5213	51.7641	51.8438	52.224	1.773500	1.7723	1.7685	1.7621	1.7501	(210)
56.72	57.0246	57.234	57.4899	1.61950	1.6216	1.6137	1.6083	1.6017	(211)
66.5136	66.8374	66.97	67.18	1.4023	1.4046	1.3977	1.3961	1.3923	(220)

Fig. 4 shows the plotted between dielectric via log frequency constant and dielectric loss factor, it exhibited the electric field dependence of the dielectric constant for resultant BST powders at different sintering temperature.

The dielectric constant and dielectric loss factor of BST depended on the physical properties and the fabrication process of BST compounds. The effect of degree crystallization on dielectric properties, there was an increase in dielectric constant with increasing sintering temperature due to better crystallinity and increase in grain size with a rise sintering temperature.

The variation in the value of the dielectric constant has been carried out at diverse temperature (1000. 1100 ^{0}C) attributed to the grain size, crystallinity, and porosity of BST compound. At lower sintering temperature poor crystallinity and smaller grain size of the samples induced the dielectric constant (ε) reduction.

The frequency dependence of dielectric properties in $Ba_{0.6}Sr_{0.4}TiO_3$ sintering at various sintering temperature, illustrated that the dielectric constant of $Ba_{0.6}Sr_{0.4}$TiO3 sintering at (1000, 1100 ^{0}C) decrease as frequency increase attributed to different types of polarization mechanisms. Space charge polarization and dipole polarization gradually cannot catch up with change of electric field as frequency increases, which make dielectric constant decrease.

As frequency increase, the dissipation factor of $Ba_{0.6}Sr_{0.4}TiO_3$ sintering at (1000, 1100 ^{0}C) decreases continuously, and dissipation factor of samples sintering at 1100 ^{0}C greater than samples sintering at 1000 ^{0}C which means hat behavior belong to increase sintering temperature increases the vibration of crystal atoms around its equilibrium position, since resistive loss component of dissipation factor is directly proportional to leakage current so the energy is dissipated such as heat.

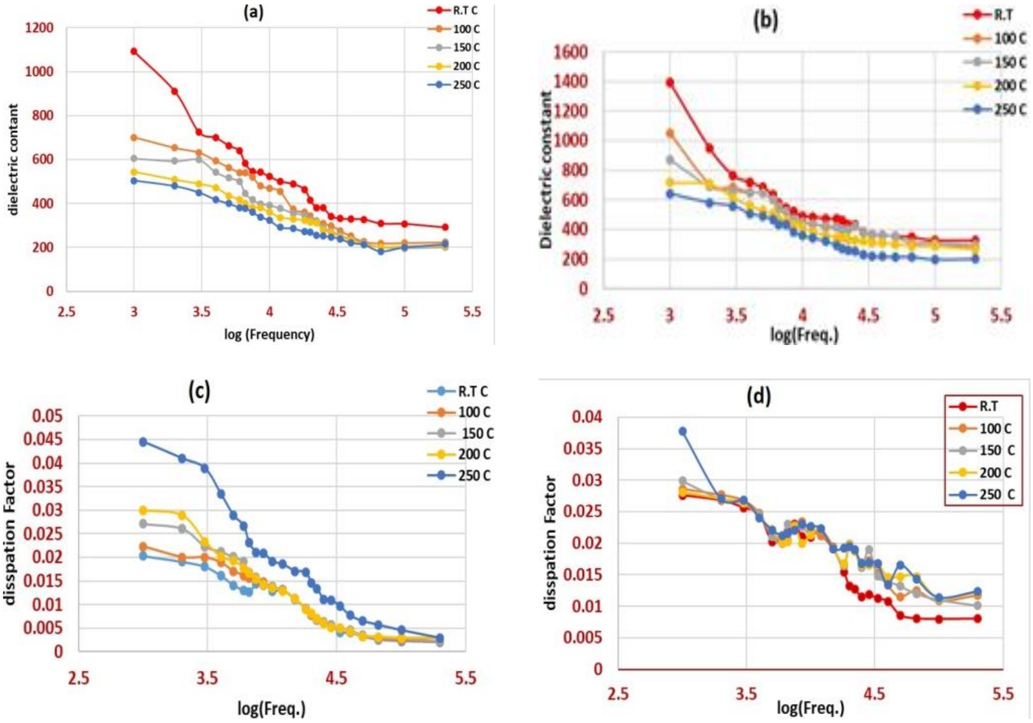

Fig. 4. Frequency dependence of dielectric properties [dielectric constant(a&b), (c,d) dissipation loss factor) for $Ba_{0.6}Sr_{0.4}TiO_3$ at different sintering temperature.

Fig. 5 illustrated the dielectric properties were studied as function of temperature and different frequency (1 KHz, 20 KHz, 100 KHz), the real part of the permittivity ε) and dissipation loss factor (tanδ) for $Ba_{0.6}Sr_{0.4}TiO_3$. The dielectric constant decreasing with increased temperature and dissipation factor increase. Some parameters lead to this phenomena, the increase of the sintering temperature leads to a higher order structure crystalline. $Ba_{0.6}Sr_{0.4}TiO_3$ is cubic structure then Curie Temperature may be zero or less than. Above transition temperature, the decrease in the dielectric constant is due to increase of thermal oscillation of the molecules &increase of degree of disorder of dipoles[18].

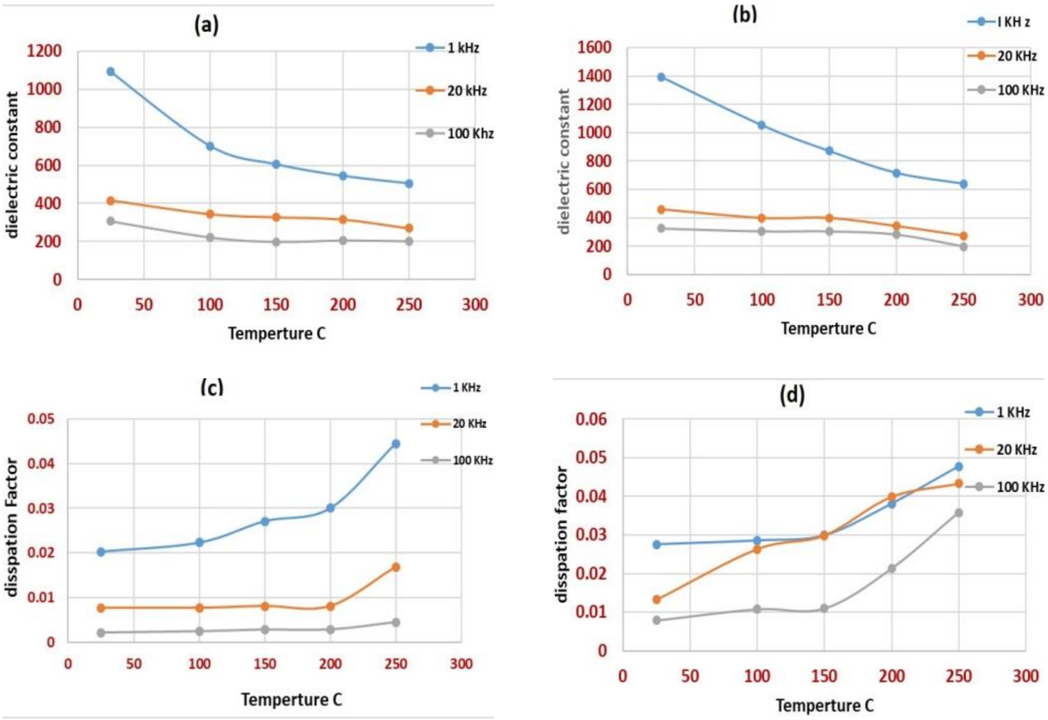

Fig. 5. Temperature dependence of the dielectric constant (a&b) and dielectric loss(c&d) for $Ba_{0.6}Sr_{0.4}TiO_3$ with sintering at 1000, 11000 ^{0}C.

4. Conclusions

$Ba_{0.6}Sr_{0.4}TiO_3$ compound was prepared by sol-gel method used the acetate of barium and strontium, and titanate (IV) isopropoxide. Actic acid used such as solvent and 2-methoxy Ethanol used like stabilizer for isoproxide. The effect of sintering temperature on microstructure ,dielectric constant and dielectric loss have been investigated.

Various grain size ranging from (24 t0 105.42 nm) was detected by scanning electronic macroscopy and it observed increasing grain size with the rise of sintering temperature. XRD results show $Ba_{0.6}Sr_{0.4}TiO_3$ sintering at different temperature belong to cubic perovskite structure with Pm3m space group (221) and lattice constant a=3.965A. And interatomic space decreased with increased sintering temperature which attribute to increasing grain size. Dielectric constant and dielectric loss increasing with increased sintering temperature but decreasing with increased frequency and measured temperature.

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References

[1] S. Hu et al., J. Mater. Sci. Mater. Electron. **28**(13), 9322 (2017).
[2] U. Gleissner et al., Ceram. - Silikaty **60**(1), 1 (2016).
[3] N. K. Woong, J. Appl. Phys., **53**, no. Japanese 9 (2014).
[4] L. N. Ioachim, M. I. Toacson, Rom. J. Inf. Sci. Technol. **10**, 347 (2007).
[5] H. H. Mulyadi, W. Rika, Sulidah, IOP Conf. Ser. earth Env. Sci. 54 012094, **54** 10.1088/1755-1315/54/1/012094, 1 (2017).
[6] M. E. Azim Araghi, N. Shaban, M. Bahar, Mater. Sci. **34**(1), 63 (2016).

[7] G. S. Kathait, V. Rohilla, P. Thapliyal, D. Biswas, S. Singh, (IJLTEMAS, **VI**(Vi), 75 (2017).

[8] B. Sr, J. Zhang, J. Zhai, X. Chou, X. Yao, Mater. Chem. Phys. **111**, 409 (2008).

[9] R. Waster C. Pitham, D. Henning, Int. J. Appl. Ceram. Technol. **2**, 1.14 (2005).

[10] M. . B. A.Loachim, M. I. Toacsan, IJLTEMAS Int. J. Latest Technol. Eng. **VI**(VI), 2278 (2017).

[11] K. Kageyama, T. Hosokura, T. Nakaiso, H. Takagi, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **57**(10), 2198 (2010).

[12] A. Selmi, O. Khaldi, M. Mascot, F. Jomni, J. C. Carru, J. Mater. Sci. Mater. Electron. **27**(11), 11299 (2016).

[13] Uk. P. Reports, SpeciPaul O'Brien, University of Manchester, Nanoscience **1**: Nanostructures through Chemistry, vol. DOI: 10.10. 2013.

[14] G. S. Kathait, V. Rohilla, P. Thapliyal, D. Biswas, S. Singh, IJLTEMAS **VI**(Vi), 75 (2017).

[15] P. M. Kshirsagar, P. P. Khirade, D. N. Bhoyar, S. J. Shukla, K. M. Jadhav, Ijiset **4**(2), 5 (2017).

[16] V. Somani, S. J. Kalita, J. Electroceram, 57 (2007).

[17] U. Adem, Phd Thesis, Middellast Tech. Univ., no. December, p. 96, 2003.

[18] T. . L. L. H. A.El ghandouri, S. Sayouri, J. Mater. Env. Sci. **8**(s), 4945 (2017).