

Synthesis and CHARACTERIZATION of BaTiO_3 High-K NANOMATERIAL

Aditya N. Khare ¹, Abhishek Sharma ²

¹Nanotechnology, Gyan Ganga college of Technology, Jabalpur, M.P. INDIA

²Electronics and Communication engg, Gyan Ganga College of Technology, Jabalpur

Abstrat

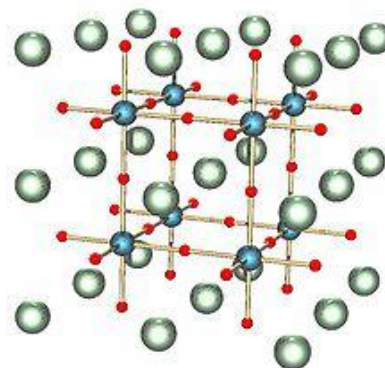
Synthesis of Cubic barium titanate(BaTiO_3) powder by heating barium titanyloxalatehydrate (BTO) precursor in microwave heating system in air at 600c . Heating BTO in microwave 700c yielded tetragonal form of BaTiO_3 Experiments repeated in silicon carbide furnace showed that BaTiO_3 was formed. The product obtained was cubic.

1. Introduction

BaTiO_3 is ceramic materials with high dielectric constants. However, the high dielectric constant in BaTiO_3 is due to a ferroelectric transition Barium titanate (BaTiO_3), a high-tech material used for the manufacture of capacitors and sensors is the first of the ceramic type ferroelectrics to be discovered and has been most extensively studied (McQuarrie 1955). Doped BaTiO_3 is a strategic material used in different electro ceramic Devices. Barium titanate, perovskite structure, is a common ferroelectric material with a high dielectric constant, widely utilized to manufacture electronic components such as multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices. Because of the people's demands and needs dielectric (essentially nonconducting) characteristics of ceramics materials are increasing rapidly. At the same time people are attempting to reduce the size of all communication devices as small and as light as possible. Due to this trend, high

dielectric constant materials such as barium titanate nowadays become more and more important in ceramics materials[1].The perovskite- like structure, named after the CaTiO_3 perovskite mineral, is a ternary compound of formula ABO_3 that A and B cations differ in size. It is considered an FCC-derivative structure in which the larger A cation and oxygen together form an FCC lattice while the smaller B cation occupies the octahedral interstitial sites in the FCC array. There is only the oxygen being B cation's nearest neighbor. The structure is a network of corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes and the large cation filling the dodecahedral holes[3].

Structure of BaTiO_3 :-

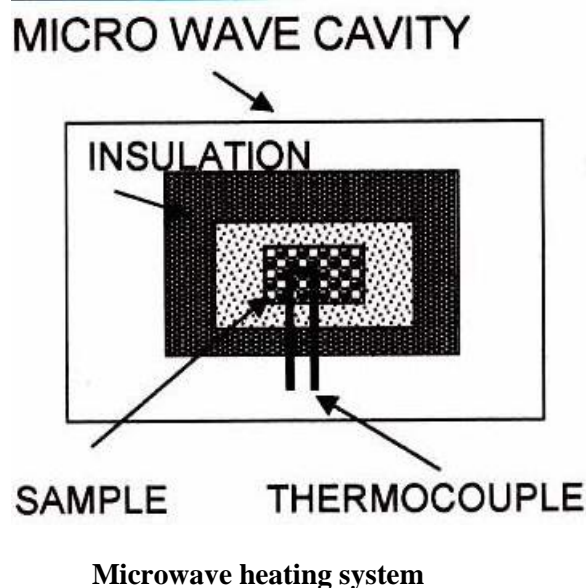


Structure of cubic BaTiO_3 . The red spheres are oxide centres, blue are Ti^{4+} cations, and the green spheres are Ba^{2+} .

Barium Titanate was the first developed piezoelectric ceramic and even now it is still widely used. It is also a well-known material used for capacitors. The crystallographic dimensions of the barium titanate lattice change with temperature. due to distortion of the TiO_6 octahedra as the temperature is lowered from the high temperature cubic form. Because the distorted octahedra are coupled together, there is a very large spontaneous polarization, giving rise to a large dielectric constant and large temperature dependence of the dielectric constant[4].

Microwave Heating system

Microwave technology uses electromagnetic waves that pass through material and cause its molecules to oscillate, generating heat. In conventional heating, the material's surface heats first and then the heat moves inward. Microwave heating generates heat within the material and heats the entire volume at about the same rate. Industrial microwave furnaces have traditionally used fixed-frequency electromagnetic waves that can cause uneven heat distribution. New technology varies the frequencies, eliminating hot and cold spots. Microwave technology can be combined with conventional heating and drying units and is easily automated.



Methodology

1. Synthesis of barium titanyl oxalate (BTO)

BTO used in the present work was synthesized from the aqueous solution of $\text{Ba}(\text{NO}_3)_2$ (BN) and $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ (KTO). Both the chemicals were of AnalaR grade. The method consisted of mixing of equimolar aqueous solutions of BN and KTO with constant stirring. The white BTO precipitate obtained was filtered, washed with distilled water and dried in an oven at 100°C for 12h. From chemical analysis, the product could be assigned the formula $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \times 4\text{H}_2\text{O}$.

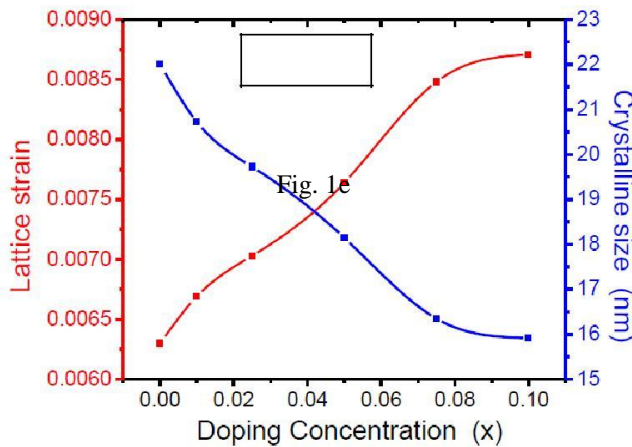
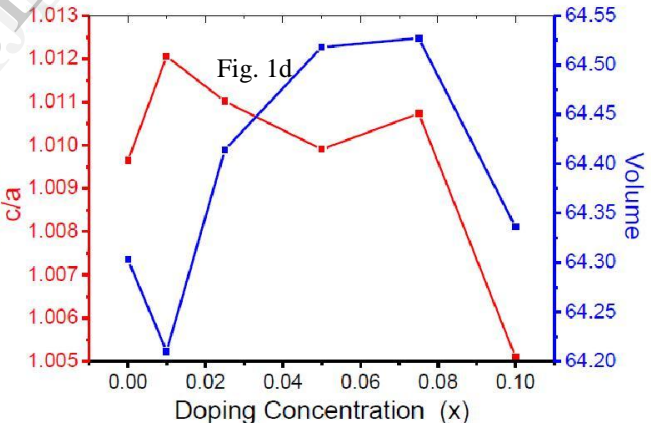
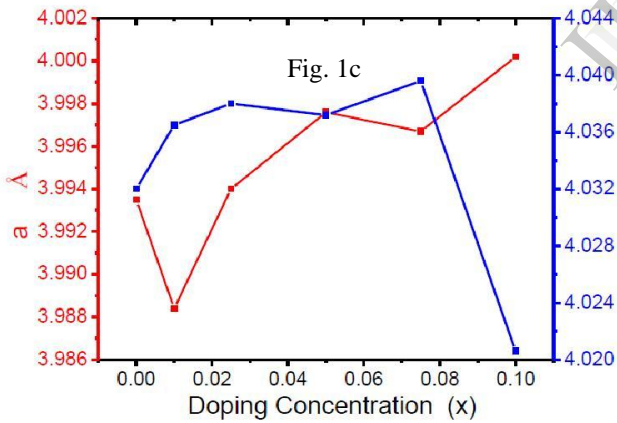
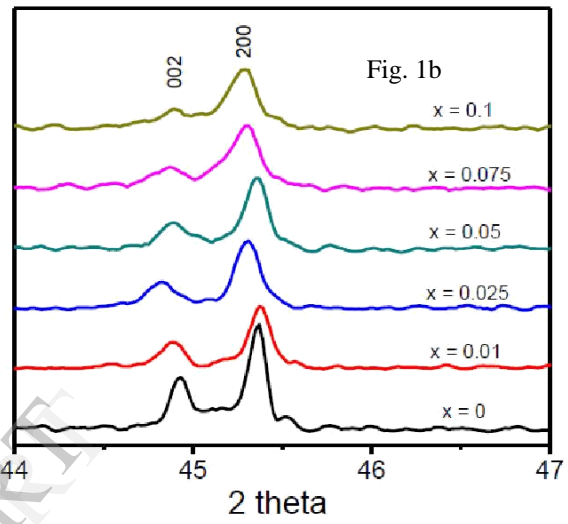
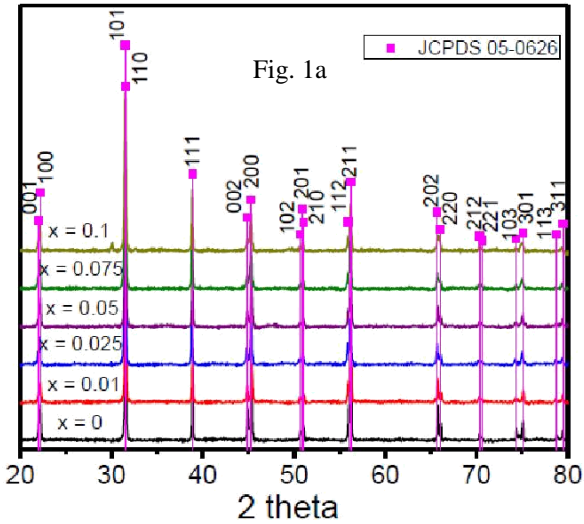
2. Preparation of barium Titanate (BaTiO_3)

The BTO precursor was heated in the range $300\text{--}750^\circ\text{C}$ microwave heating system fabricated indigenously. The power to the unit could be maintained to a constant set value to fix the desired temperature needed for the experiments, employing the proportional type (PID) temperature controller coupled to a solid state relay (SSR). A shielded chromel–alumel thermocouple was used as a sensor for controlling the input power to the microwave oven at the set temperature. The thermocouple shield had to be grounded to obtain steady temperature values at the set point. The temperature of the sample could be maintained constant to $\pm 1^\circ\text{C}$ and measured by a separate calibrated chromel–alumel thermocouple. The products obtained after heat treatment of reactants at different temperatures were analysed by X-ray diffraction, SEM, EDX, FTIR, Dielectric constant.

Result Analysis and Conclusion

XRD Analysis

The $Ba_{1-x}Bi_{2x/3}TiO_3$ ceramics were prepared by solid state reaction route. The synthesized powders were characterized by X-ray diffraction using a PANALYTIC diffractometer. XRD patterns were obtained using $Cu K\alpha$ radiation and the Fig.1(a) show the XRD pattern of the Bi doped $BaTiO_3$ range from 20-80° in 2θ scale at the rate of 0.04°/second. According to JCPDS no.05-0626, all the peaks in the patterns are matching and its showing purely tetragonal single phase crystal related to tetragonal $BaTiO_3$.



From Fig.1(b), it is well known that the tetragonal phase was identified by an analysis of the peaks [002] and [200] at the 2θ from 44.5-46. The splitting of [002] and [200] peaks indicates the tetragonal phases. While increasing the concentration of Bi in BaTiO₃, the intensity of its peak [002] at 44.9 is minimizing. This minimization indicates the conversion of tetragonal phase to cubic phase after the certain limit of doping concentration. Fig.1 (c) and (d) shows the lattice parameter as well as the unit cell volume results of Ba_{1-x}Bi_{2x/3}TiO₃ ceramics.

Table 3, shows the parameters about the peak position, FWHM, a, b, c parameters, volume, c/a, crystallite size, lattice strain, D_{hkl} and d_{hkl} for all x values at the major peaks of the XRD patterns at 31.4. In Fig.1(e) variation of crystalline size as a result of Bi substitution is clearly seen. Crystalline size decreases with increasing concentration of the Bi in BaTiO₃ and these effects is clearly seen in the peak broadening of Fig.12.

Sample	Conc. (x)	2θ in degree	FWHM	Θ in rad	a = b	c	volume	c/a	Crystalline (in m)	Lattice strain	d_{hkl}	D_{hkl}
i	0	31.5099	0.00209	0.274836	3.9947	4.0308	64.32201	1.009037	2.20E-08	0.0063	2.838357	689.2854
ii	0.01	31.4899	0.00251	0.274662	3.9924	4.0376	64.35635	1.011322	2.07E-08	0.00669	2.840114	573.9186
iii	0.025	31.4300	0.00251	0.274139	3.994	4.038	64.41432	1.011017	1.97E-08	0.00703	2.84539	573.8342
iv	0.05	31.4899	0.00293	0.274662	3.994	4.038	64.41432	1.011017	1.81E-08	0.00764	2.840114	491.6504
v	0.075	31.4699	0.00377	0.274487	3.9966	4.0395	64.52217	1.010734	1.64E-08	0.00848	2.841873	382.0862
vi	0.1	31.4915	0.00377	0.274676	4.0002	4.0214	64.34883	1.0053	1.59E-08	0.00871	2.839973	382.1065

Peak position, FWHM, a, b, c, volume, c/a, crystalline, lattice strain, d_{hkl} and D_{hkl} parameters for all composition of x.

SEM

Fig.2 shows the surface structures of all sintered pellets at 1300°C for 4 hours. The microstructure of the sintered specimens of the BaTiO₃ with x=0 to 0.1, Bi were shown the grain increment when the doping concentration is increasing and these result also exactly related to the crystalline size of the calcined powders from the XRD pattern. Due to surface volume ratio of the calcined powder reduces the melting temperature and increasing the grain size at the time of sintering. But in the undoped (x=0) BaTiO₃ having high grain and well sintered.

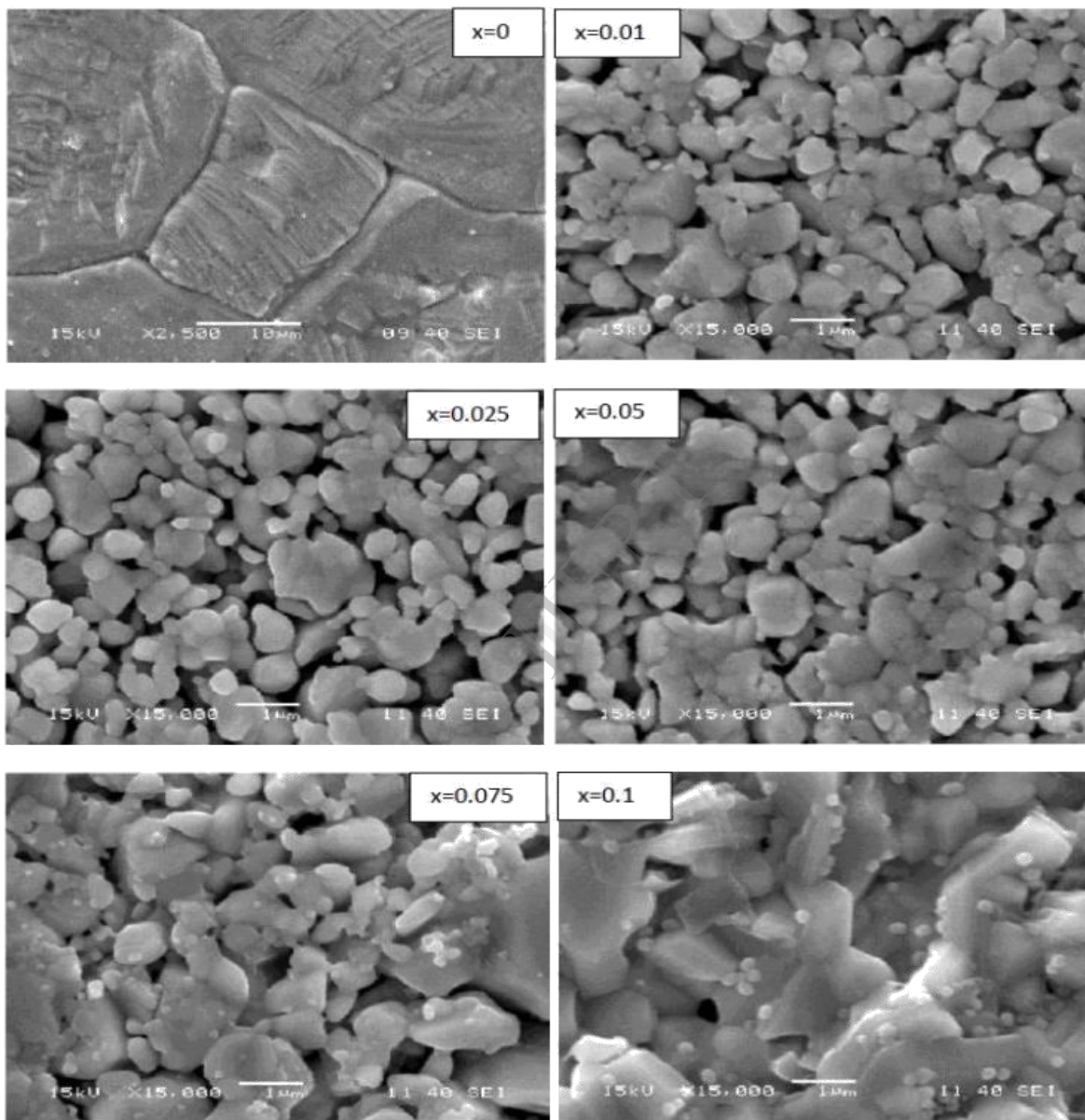


Figure 2 SEM picture of Ba_{1-x}Bi_{2x/3}TiO₃ pellets for all composition of x

EDX

Fig.3 shows the EDX spectra of $Ba_{1-x}Bi_{2x/3}TiO_3$ ceramic, in EDX spectra it is clearly seen that the prepared $Ba_{1-x}Bi_{2x/3}TiO_3$ ceramic compound is only composition of Ba, Bi, Ti, and O. It gives the weight percentage and atomic percentage of the compound. Little amount of Bismuth is modifying the whole part of the crystal symmetry. Table.4 Weight % and Atomic % of all elements present in the $Ba_{1-x}Bi_{2x/3}TiO_3$ pellets.

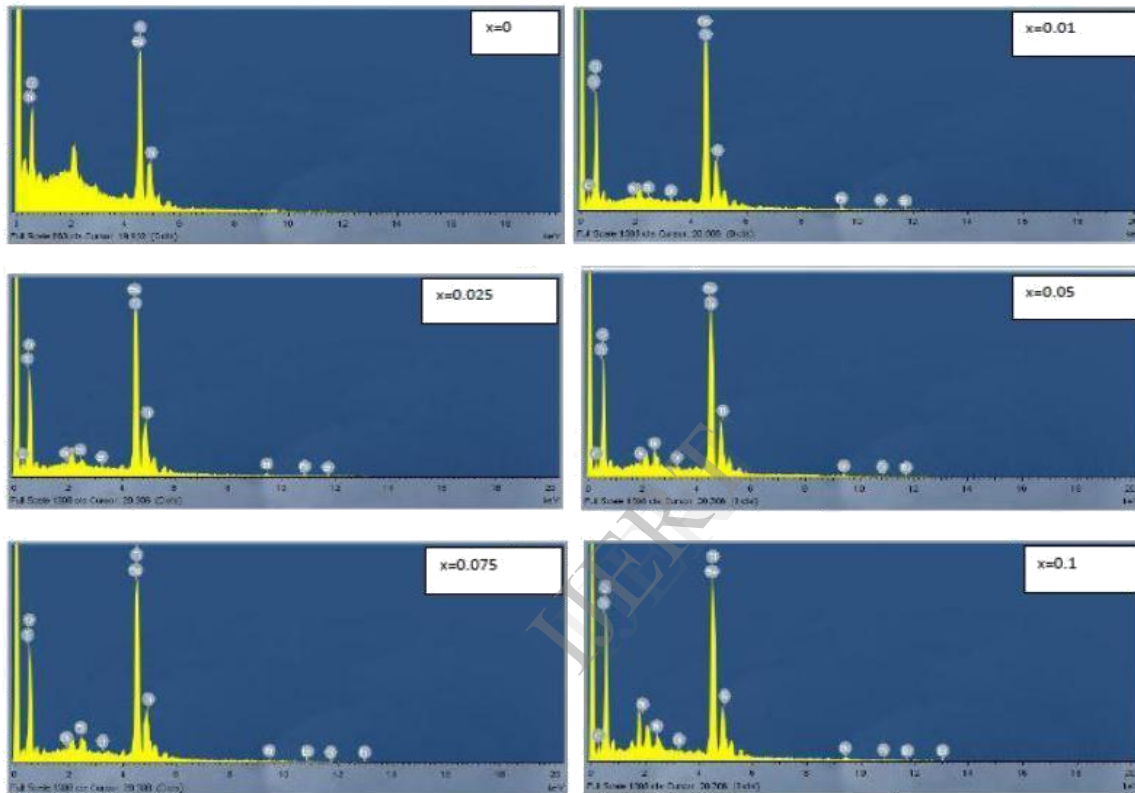


Figure 3 EDX spectrum of $Ba_{1-x}Bi_{2x/3}TiO_3$ pellets

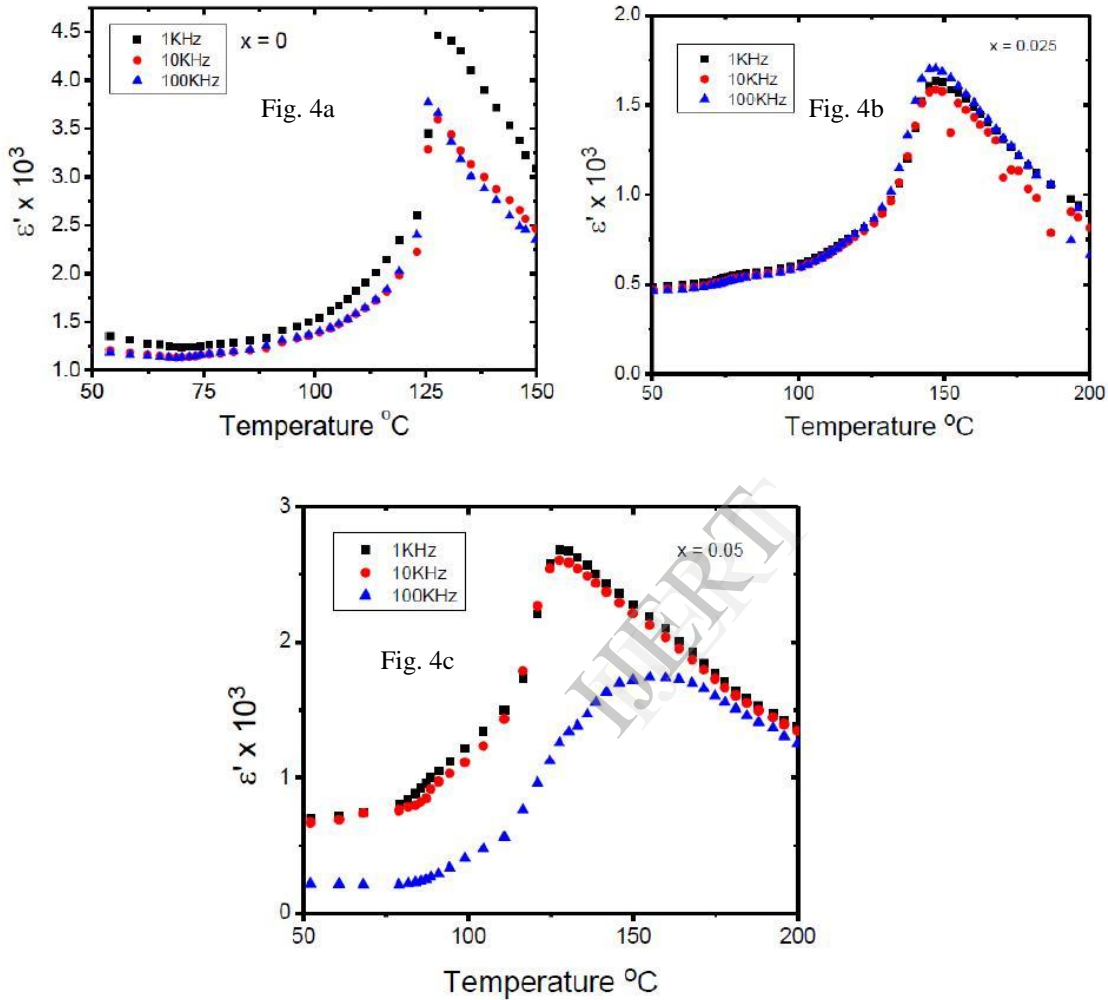
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
	X=0		X=0.01		X=0.025		X=0.05		X=0.075		X=0.1	
O K	17.10	57.43	19.77	55.24	22.36	59.14	19.54	61.21	21.81	57.21	25.34	61.84
Ti K	13.89	15.58	14.26	14.75	15.62	14.79	14.75	15.43	14.75	14.22	14.08	12.49
Ba L	69.01	27.00	64.31	22.90	61.11	20.19	60.76	22.17	59.23	19.92	58.08	17.96
Bi M	---	---	1.66	0.39	0.91	0.20	4.94	1.19	4.19	0.93	2.50	17.96
Total	100		100		100		100		100		100	

Weight % and Atomic % of all elements present in the $Ba_{1-x}Bi_{2x/3}TiO_3$



DIELECTRIC

In Fig.4 shows the Relative permittivity of sintered pellets of $Ba_{1-x}Bi_{2x}/3TiO_3$ for $x= 0, 0.025$ and 0.05 . The sintered samples were coated with silver paste on both sides and heated at $500^{\circ}C$ for 30 minutes for perfect conductivity of the electrodes. The permittivity at 1 kHz as a function of temperature for $Ba_{1-x}Bi_{2x}/3TiO_3$ ceramics under different concentration of $x= 0, 0.025$ & 0.05 .

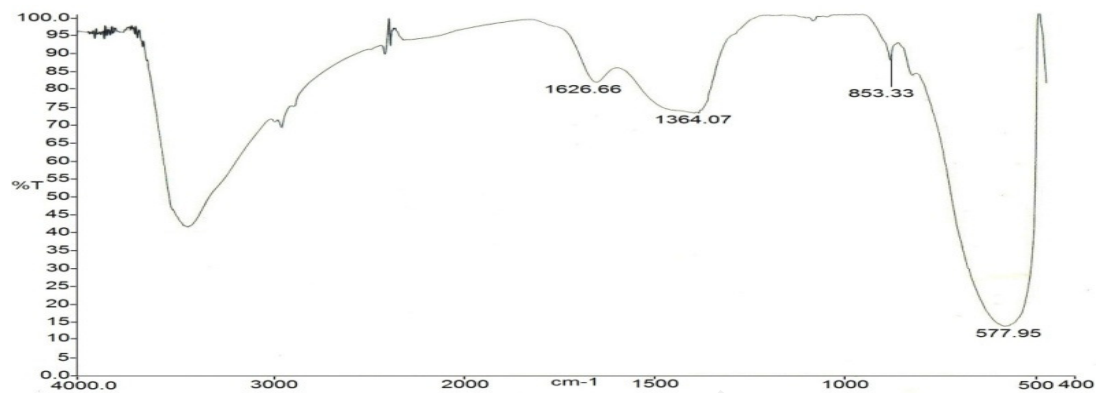


(Relative permittivity Vs Temperature of sintered pellets of $Ba_{1-x}Bi_{2x}/3TiO_3$ for $x= 0, 0.025$ and 0.05)

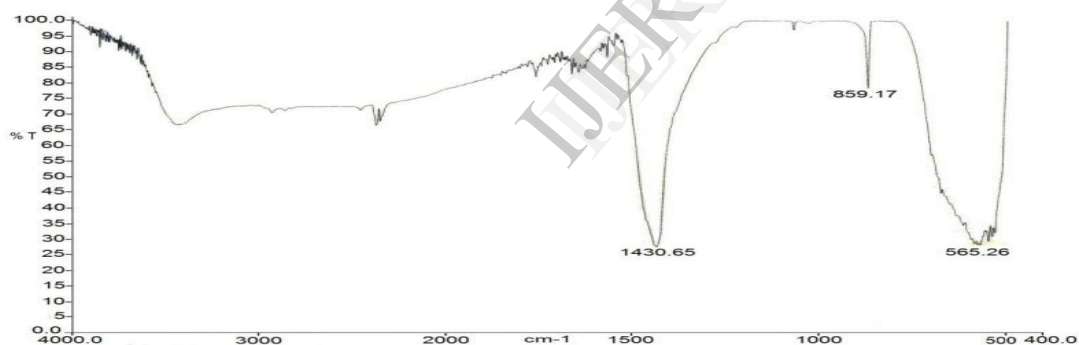
In the relative permittivity versus temperature plots of $x=0, 0.025$ and 0.05 samples displayed sharp peaks at a transition temperature of around $140^{\circ}C$. The $Ba_{1-x}Bi_{2x}/3TiO_3$ ceramics exhibited a decrease in the transition temperature with increased concentration of Bi_2O_3 . The results showed an increase in permittivity up to a maximum for the composition of $x = 0$ is 4455 at transition temperature $128^{\circ}C$, for the composition $x = 0.025$ is 1635 at transition temperature $149^{\circ}C$ and for composition $x = 0.05$ the maximum relative permittivity is 2674 at transition temperature $133^{\circ}C$.

FTIR analysis

Figure 5 (a-b) shows the FTIR spectra of the Barium Titanate powder and the powder modified with 0.1 wt% of silane. The broad band at 568 to 577 cm^{-1} are due to Ti-O stretching modes of BaTiO_3 while peaks at 1430 and 1625 cm^{-1} are related to the CO_2 absorption. Moreover, peaks at 853 are the characteristic peak of C-C stretching modes. Figure 3 a shows an additional peak at 1364 cm^{-1} corresponding to organic groups of silane [21-22].



IR spectra of 0.1 % silane modified Barium Titanate



IR spectra Barium Titanate

Conclusions

The results obtained in this investigation show that Ba-TiO_3 in the cubic form could be synthesized from BTO at temperature as low as 500°C . Thermal decomposition of BTO presumably yields hypostoichiometric TiO_2 by virtue of the presence of evolved CO in the reaction, which in the presence of the microwave field combines with BaO to yield the cubic phase. The cubic BaTiO_3 transformed completely to the tetragonal form on heating it in the microwave field above 700°C . In the recent studies (Potdar *et al* 1998; Kholam *et al* 2002), it was reported that BTO on heating in the resistance heated furnace above 700°C in air produced cubic form of BT. The production of tetragonal form of BaTiO_3 at low temperatures following the present procedure could provide considerable edge over other existing processes and make it economically much more viable for commercial exploitation.

REFERENCES

- [1] **Y S MALGHE, A V GURJAR† and S R DHARWADKAR***“**Synthesis of BaTiO₃ powder from barium titanyl oxalate (BTO) precursor employing microwave heating technique**”
Bull. Mater. Sci., Vol. 27, No. 3, June 2004, pp. 217–220. © Indian Academy of Sciences. Department of Chemistry, The Institute of Science, Mumbai Condensed Matter Physics and Materials Science Division, Tata Institute of Fundamental Research, Mumbai.
- [2] **HyeongSeok Lee^{1, 2}, Sang Man Koo¹ and Jung Whan Yoo²** “**Characteristics of BaTiO₃ Particles Synthesized by Precipitation from Low-Temperature Aqueous Solutions**”*Journal of Materials Science and Engineering A* 2 (1) (2012) 7-15. *Department of Chemical Engineering, Hanyang University, Haengdang-dong, Seongdong-Gu, Seoul 133-791, Korea.*
- [3] Borkar S A and Dharwadkar S R 2004 *Ceram. Int.* **30** 509 Clabaugh W S, Swigbard E M and Gilchrist R 1956 *J. Res. Nat.*
- [4] **Pusit Pookmanee, Chanitpa Khantha, Sukon Phanichphant** Department of chemistry, Faculty of Science, Maejo University, Chiang Mai, Thailand
- [5] **Guang J. Choi, Sang K. Lee, Kyoung J. Woo, Kee K. Koo and Young S. Cho** “**Characteristics of BaTiO₃ Particles Prepared by Spray-Coprecipitation Method Using Titanium Acylate-Based Precursors**” *Chem. Mater.*, 1998, 10 (12), pp 4104–4113
DOI: 10.1021/cm980520h Publication Date (Web): December 1, 1998 American Chemical Society, Division of Chemical Engineering, Korea Institute of Science & Technology, Cheongryang, Seoul, South Korea, and Department of Chemical Engineering, Sogang University
- [6] **R. Maier and J. L. Cohn** Department of Physics, University of Miami, Coral Gables, Florida “**Ferroelectric and ferrimagnetic iron-doped thin-film BaTiO₃: Influence of iron on physical properties**” R. Maier and J. L. Cohn Department of Physics, University of Miami, Coral Gables, Florida 33124 (Received 14 December 2001; accepted 3 August 2002)