Comparative Study of effect of Fe doping on properties of $BaTiO_3$

[1]Jyoti Prakash Dwivedi, [2]Ashutosh Mishra,
[1]PhD student, [2]Proffesor,
[1,2]School of physics
[1,2]Devi Ahilya VishwaVidalaya, Indore, India

Abstract: **Batio3 doped with Fe formula $BaTi_{1-x}Fe_xO_3$ (x = 0, 0.03, and 0.05) at different percentage (0% , 3% , 5%) was synthesized by two different method namely solid route method and sol gel method. And then sample obtained in both were compared by different characterization .There XRD and P-E characterization was carried out. It is found that in sample of solid route method the average particle size was 0.72 nm to 0.57 nm . But in sample of sol gel method average particle size obtained was between .40 nm to 37 nm. Also XRD pattern of solid route suggest that cubic phase is present in sample of solid route method. but its P-E characterization suggest that it has gotted ferroelectric properties which is not found in cubic phase. Hence sample of solid route method are in tetragonal phase. In sample prepared by solid route method the obtained values of lattice parameter is a = b = 3.994 nm and c = 4.038 nm. In XRD analysis of sample of sol gel method suggest tetragonal crystal structure with lattice parameter a bit greater than those obtained in solid state sample . also its P-E characterization suggest that the sample prepared by sol gel method have less remnant polarization than the sample prepared by solid route method .sample with 3% Fe have gotted 0.49 µC/cm^2 remnant polarization. But in sample of solid route method remnant polarization is found to be 0.44 µC/cm^2 µC/cm^2. Also on increasing sintering temperature the value of remnant polarization increases.**

IndexTerms **-** X-ray diffraction, , hysteresis, ferroelectric, remnant polarization

I. INTRODUCTION

Ferroelectric bulk ceramic and single crystal are widely used in many electronic devices, acoustio-optics, piezoelectric devices [1,2] . Ferroelectric thin films also finds application in integrated devices [3-6].but it has been found that properties of thin film show a sharp decreases in polarization and other electrical properties. The properties of bulk ceramic and thin film s have been widely investigated [7]. Recently, it has been reported that method of preparation does affect the ferroelectric and structural properties of Batio3 [8]. Vast study has been done on the properties of $batio_3$ prepared by solid route method and how does the different percentage of iron doping affect its properties. Also it was reported by Kniepkamp and Hewing that grain size affects the ferroelectric properties and hence its use as a memory device .within several years of discovery it was observed that polycrystalline Batio3 exhibits an enhanced dielectric response for the grain size nearly 1-5 µm.It has been known that a high dielectric constant and good temperature stability can be achieved through addition of dopants. Pure $BaTiO_3$ has cubic structure .on doping it with some impurity atom its cubic structure gets disturbed and it becomes tetragonal and hence ferroelectric property gets developed in it. Also in the paper M.H Frey and D.A Payne [9] it was reported that for sol-gel processed Batio3 polycrystal, the normal cubic –tetragonal phase transformation does not simply shift down through room temperature , but does depend on crystalline size. In this paper we report that very fine grain size can be obtained by the method of sol gel used here, than the solid route method .and both differs in the ferroelectric behaviour. Also ferroelectricity can be controlled by varying sintering temperature during the process.

II. EXPERIMENTAL TECHNIQUES

The samples were prepared by two methods namely solid route and sol gel method. In solid route method calculated amount of Barium Carbonate (BaCO3) , Titanium dioxide(TiO2) and Ferrous Oxide(Fe2O3) was taken and mixed and grinded mechanically and then it was heated for 12 hr at 900 ^{0}C.after carrying out XRD and PE measurement it was again calcined at 1250 ^{0}C. And same measurements were carried out on that sample. Now for sol gel method, calculated amount of barium hydroxide ($Ba(OH)_2.8H_2O$) was dissolved in mixture of glacial acetic acid and ethanol (both taken in 1.1 volume ratio) by stirring and heating the solution at 70 ^{o}C for 1 hour. After cooling the solution at room temperature; a calculated amount of tetra isopropyl orthotitanate[$Ti(C_3H_7O)_4$] was added in it drop wise, and stirred gently then calculated amount of freshly prepared iron nitrate prepared separately in ethanol was added to the above solution .the clear solution , was obtained after stirring for some time. Then it was allowed to gel at room temperature. Then the gel was dried to powder by heating it at temperature of 90^{0}c. then the powder was calcined at temperature of 750 ^{0}c.then after carrying out XRD and PE measurement again the sample was pressed into palate and it was calcined at temperature 1100^{0}C then same measurement were carried out. the phase analysis of powder samples was carried out using Bruker D8 Advance X-ray diffractometer with $CuK\alpha_1$ radiation.Then powder was pressed into palate by applying 100KN pressure to form the palate of 1.3mm diameter and an average thickness of 1.5 mm . And then its P-E measurements were performed. For both above measurement LOOP TRACER having following specification were used [voltage : 100v to 10kv , frequency range : 0.03hz to 100khz , minimum leakage current : 2pAmp].

III. RESULTS AND DISCUSSION

3.1 XRD measurement

Figure 1 shows the XRD pattern of $BaTi_{1-x}Fe_xO_3$ (x = 0.00, 0.03, and 0.05), prepared by two different methods and sintered at different temperatures .which represents all the peaks are present in according to JCPDS Card No. 81-1428 .hence suggesting cubic structure. But in sample prepared at low temperature in both solid state at 900 ^{0}C and sol gel at ^{0}C method one small peak at nearly 23.7 deg shows the presence of some amount of $BaCO_3$. Hence these samples are not in single phase. But when the sintering temperature is increased in both method (in solid route 1250 ^{0}C and in sol gel 1100 ^{0}C) then the sample comes in single phase , as the peak at specified point representing presence of $BaCO_3$ disappears .The samples prepared at low sintering temperature are also noisy reflecting amorphous sample , may be due to coexistence of cubic surface layers and tetragonal grain cores , whose proportion changes with changing their heat treatment. Hence at higher sintered temperature XRD pattern revels only cubic structure, but from later PE discussion it will be confirmed that actually tetragonal phase is present.

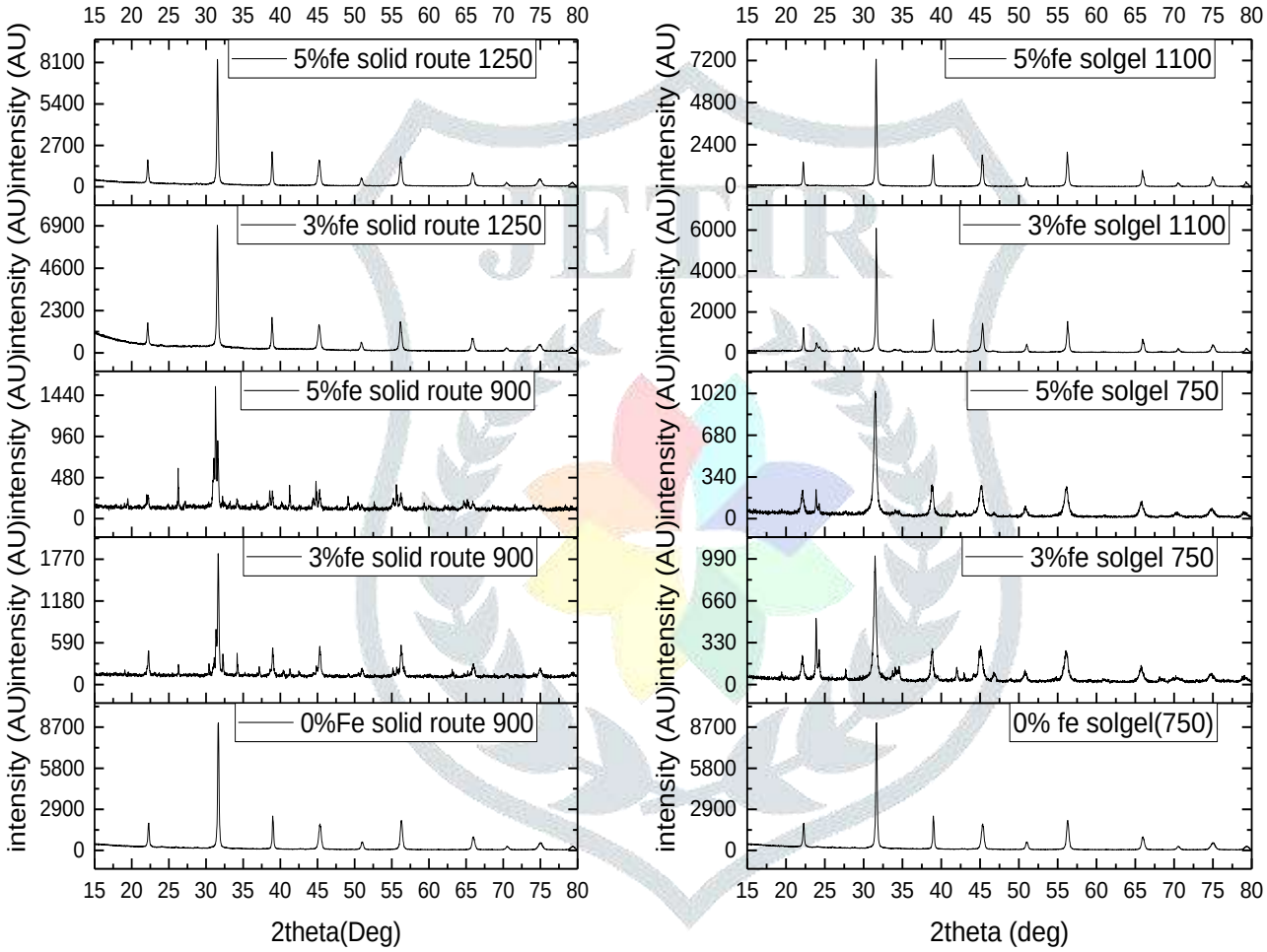

Figure I. XRD pattern for $BaTi_{1-x}Fe_xO_3$ (x = 0.00, 0.03, and 0.05) prepared by different method and sintered at different temperature

The average crystallite size was calculated from Scherer's formula and the obtained values are mentioned in table I.From table I it is found that the average particle size for the samples prepared by solid route method is large in comparison to the samples prepared by sol gel method. Hence sol gel method helps in obtaining very small particle size. The same is suggested by the fwhm calculation of all the sample, which is large (0.41 on an average) for sol gel samples than for those prepared by solid route(0.25 on an average). also it has been found that on increasing the sintering temperature of a particular sample, in both solid route method and sol gel method the lattice parameter (a,b,c)decreases, which may be due to increase in oxygen vacancies. One more thing can be observed from figure that on increasing the sintering temperature , in both solid route and sol gel method , the intensity of main peak at 31.4 deg also increases , which revels the differed miller indices value(h,k,l) values , at same angular position. The higher value of miller indices takes much time to diffract the X-ray beam. As a result of which, the peak intensity is more, for higher values of miller indices. Hence when sintered at higher temperature would have changed the plane orientation, and hence resulting in more intensity of the peak in the sample prepared by both method. Also some impurities may also have played a role in affecting intensity of peak of the samples sintered at low temperature.

The close observation of peak at 45.15deg does not show any splitting hence suggest cubic structure .but calculation of lattice parameter shows some amount of tetragonality present in it as, a and c are not equal as observed from table 1. Hence c/a ratio being > than 1 , also suggest the absence of cubic phase in sample.

Table I. Lattice constant, particle size and X-ray diffraction of $BaTi_{1-x}Fe_xO_3$ (x = 0.00,, 0.03, and 0.05) prepared at different temperature by solid route method and sol gel method.

method	%Fedoped(temperature)	a=b(Å)	c(Å)	FWHM(deg)	L(nm)
solid route	0%Fe (900^{0}C)	3.982015	3.99882	0.23204	0.701834
solid route	3% Fe (900^{0}C)	3.929807	4.059273	0.28094	0.579537
solid route	5% Fe (900^{0}C)	4.019411	4.058925	0.22840	0.710038
solid route	3% Fe (1250^{0}C)	4.003297	4.011303	0.23814	0.682844
solid route	5% Fe (1250^{0}C)	3.98908	3.996729	0.28094	0.579541
Sol gel	3% Fe (750^{0}C)	4.012233	4.015937	0.41918	0.387703
Sol gel	5% Fe (750^{0}C)	4.005081	4.013736	0.43644	0.372521
Sol gel	3% Fe (1100^{0}C)	3.98908	4.001446	0.39829	0.408704
Sol gel	5% Fe (1100^{0}C)	3.99262	3.99788	0.40915	0.397856

3.2 PE measurement

The results of PE measurement carried out on the prepared samples are mentioned in the Fig II, and Fig III. From fig I it is observed that in the sample prepared by solid route method , the value of remnant polarization for the sample having 3% Fe increases from 0.102 μC/cm^2 to 0.490 μC/cm^2 , when the sintering temperature is increased from 900^{0}C to 1250 ^{0}C. the same behavior is observed in the sample prepared by sol gel method , where the remnant polarization increases from 0.137 μC/cm^2 to 0.449 μC/cm^2 when the temperature is increased from 750^{0}C to 1100 ^{0}C . Hence the sintering temperature helps to increase the value of remnant polarization.

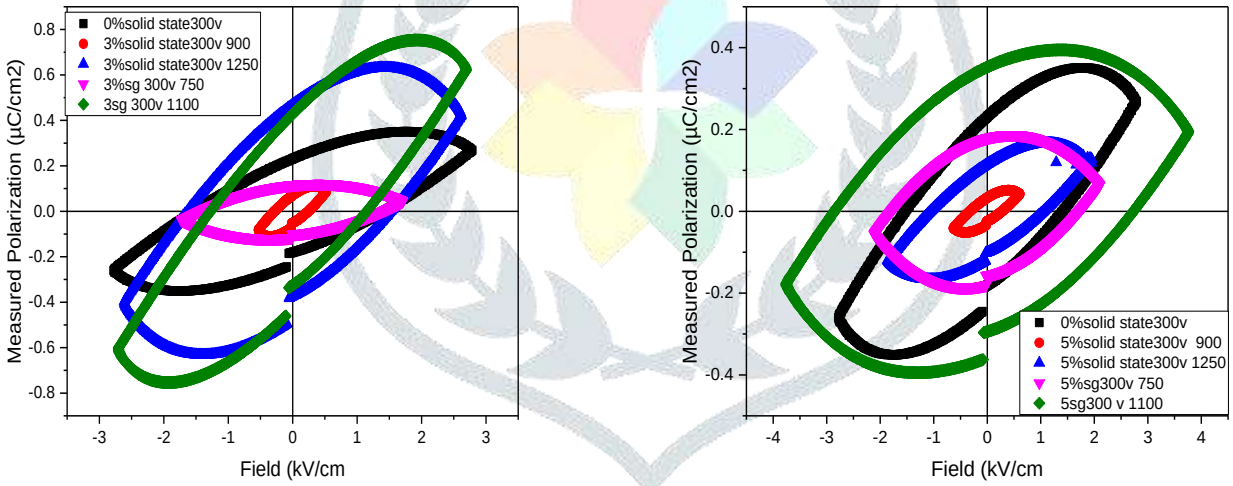

Figure II. PE graph for $BaTi_{1-x}Fe_xO_3$ (x = 0.00, 0.03, and 0.05) prepared by different method and sintered at different temperature.

Also coercive field is found to increase with increasing sintering temperature The above observed behaviour may be due to the existence of the non-ferroelectric layers at the metal-ferroelectric interface and grain boundaries which are also stated by M.N. Kamalsanan and S. Chandra [12].The lower value of the polarization may be due the smaller grain size and lower packing density. Variation of the value of coercive field increases with increase of sintering temperature, which may be due to existence of non-ferroelectric layer at crystal-electrode interface in the sample. Also from the graphs it is obtained that they do not contain the saturation P value which may be present in the general ferroelectric hysteresis loop. It may be because of the sample in prepared pallets may be of loosy nature which may have some free charge particles, which may be responsible for conductance across the two parallel face of pallet .

Table II. remnant polarization of $BaTi_{1-x}Fe_xO_3$ (x = 0.00,, 0.03, and 0.05) prepared at different temperature by solid route method and sol gel method.

Method of preparation	Sintering temperature	Pr for 3% Fe (μC/cm^2)	Pr for 5 % Fe (μC/cm^2)
Sol gel	750 ^{0}C	0.137	0.130

	1100 ^{0}C	0.449	0.358
Solid route	900 ^{0}C	0.102	0.014
	1250 ^{0}C	0.490	0.128

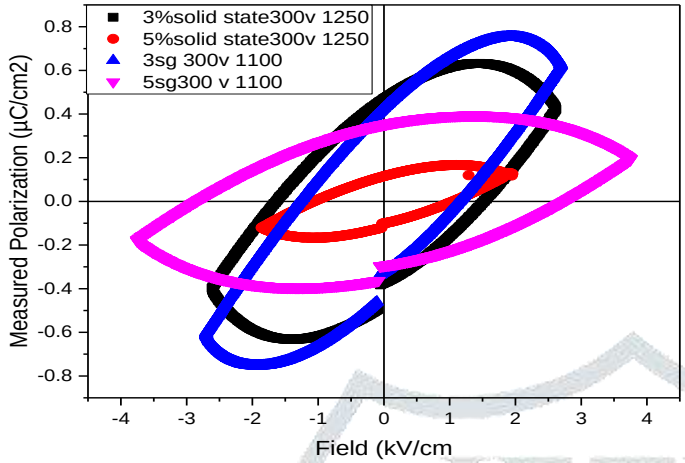

Figure III. PE graph for $BaTi_{1-x}Fe_xO_3$ (x = 0.03, and 0.05) prepared by different method and sintered at same temperature.

In the fig III. the effect of doping has been observed . In the sample of solid route method the remnant polarization decreases from 0.497 μC/cm^2 for 3% Fe to 0.123 μC/cm^2 for 5% Fe sample. For sol gel method sample the same trend is observed .it decreases from 0.4353 μC/cm^2 to 0.3314 μC/cm^2. Hence on increasing the percentage doped Fe the value of remnant polarization decreases. This may be because on increasing percentage doping the oxygen vacancies increases which may resist the motion of ferroelectric domain and hence decrease in polarization is observed.

Hence from above it can be inferred that sol gel method helps in attaining a very small particle size even at low sintering temperature. With desired tetragonal structure. Tetragonality of sample decreases with increase of doped Fe percentage. as value of polarization decreases with increase in Fe doping %. Full width half maxima of the (111) peak, is found to be less than 0.45 deg which is less than the broadened 200 – 002 peak which are separated by 0.55 deg . It has been discussed by Frey and Payne that XRD alone is a not suitable technique to reveal the subtitle unit cell distortions. Same tetragonal structure is also confirmed by obtained polarization, as no polarization would be found if the sample would have been in cubic structure .also P-E values obtained infers that ferroelectric behavior decreases on increasing Fe doped percentage .In general, the polarization and the piezoelectric strength of ferroelectric is known to decrease with the addition of acceptor ions to the host lattice. The oxygen vacancies created as a part of the charge compensation have damping effect on the motion of domain and hence affects spontaneous polarization. Also as the internal electric dipoles of ferroelectric material are coupled to the material lattice so due to doping lattice changes and hence strength of dipole also changes. Therefore it can be inferred that there is coupling between the polarization and lattice strain.

IV. ACKNOWLEDGEMENT

For this work authors would like to express sincere thanks to the management and resource person of UGC-DAE-CSR, Indore as they all helped to carry out all measurement.

V. REFERENCES

[1]. J. C. BURFOOT AND G. W . TAYLOR , ‘polar dielectric and their application ‘(Macmillan London , 1979) p. 76
[2]. M. E. LINES AND M. GLASS , “principles and application of ferroelectric and related materials “(clarendon press , Oxford, 1977) chap . 4
[3]. S . B . KRUPANIDHI, H . HU and C . V . R . V . KUMAR , j.APPL.PHYSICS.71(1992) 376.
[4]. L . H . PARKER and A . F . TASCH , IEE CIRC. Dev. Mag.(1990)17
[5]. A . MANSINGH , Ferroelectric 102 (1990) 69
[6]. P . K . LARSEN, D . J . DORMNS, G . W . TAYLOR and P . J . VEDHOVEN, j.Appl. phys. 76 (1994) , 2405
[7]. B . JAFEE , W . R . COOK and H . JAFEE, “piezoelectric bulk ceramics “ (Academic Press , L ondon , 1971)p. 74
[8]. P . PHAULE and R . H . RISBUD, Mater Res. Soc. Sympo.Proc. 121 (1991) 275
[9]. M.H FREY and D.A PAYNE. American physical society 1996 vol 54 , 5 no
[10]. S. SEN and R.N.P. CHOUDHARY, J. M. Sci. **40** 5457 (2005)
[11]. P. S. DOBAL, A. DIXIT, R. S. KATIYAR, Z. YU, R. GUO, A.S. BHALLA, *J. Appl. Phys*. **89** 8085 (2001).
[12]. M.N. KAMALSANAN and S.CHANDRA,Applied phys.Lett.60(1991)1022