Study of Properties of Fe Doped BaTiO₃ Prepared by Sol Gel Method

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Abstract:
The polycrystalline samples of Fe doped BaTiO₃ (BTO) with compositional formula BaTi₁₋ₓFeₓO₃ (x = 0, 0.01, 0.02, 0.03, 0.04 and 0.05) were prepared by sol-gel method. The influence of the Fe content on the structural, electric properties of BaTiO₃ was investigated using X-ray powder diffraction (XRD), Polarization techniques, and I-V measurement. XRD analysis indicates the formation of double-phase tetragonal structure for some of the prepared samples and single phase for some other. Tetragonal phase is further confirmed by the P-E characterization. Room temperature I-V measurement shows the high resistivity present in it.in P-E measurement the hysteresis loop shows the presence of dipole moment in it, which is also confirmed by PUNDO measurement value of some sample.

Key words: X-ray diffraction, remnant polarization, hysteresis, ferroelectric, pulse up and down (pund)

I. INTRODUCTION

Pure Barium Titanate (BT) and fe doped BT are used for in electromechanical devices such as actuators, thermostors, photonic crystals and non volatile random-access memory devices transducers and capacitors because of their high ferroelectric properties [1–3]. Recently, it has been reported that method of preparation does affect the ferroelectric and structural properties of batio₃. Vast study has been done on the properties of batio₃ 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. Bulk BaTiO₃ has the classical ABO₃ (Ba⁺⁺ as A and Ti⁺⁺ as B) perovskite structure. The ferroelectric properties of BTO can be efficiently controlled by doping with different elements. It has been known that a high dielectric constant and good temperature stability can be achieved through addition of dopants. Pure BaTiO₃ 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 [5] 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 work it has been observed that very fine grain size can be obtained by the method of sol gel reported here, than the solid route method .and both differs in the ferroelectric behaviour also ferroelectricity depends on sintering temperature.

II. EXPERIMENTAL TECHNIQUES

In order to prepare the sample of various percentage of Fe doped, calculated amount of barium hydroxide (Ba(OH)₂, 8H₂O) was dissolved in mixture of ethanol and glacial acetic acid(both taken in 1.1 volume ratio) by stirring and heating the solution at 70 °C for 1 hour. After cooling the solution at room temperature;a calculated amount of tetra isopropyl orthotitanate [Ti(C₂H₅O)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°C. then the powder was calcined at temperature of 750 °C.Then the phase analysis of powder samples was carried out using Bruker D8 Advance X-ray diffactrometer with CuKα 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. Also its J-E measurement was carried out. for both above measurement LOOP TRACER having following specification were used [voltage : 100v to 10kv , frequency range : 0.03hz to 100khz , minimum leakage current : 1pAmp ].

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of BaTi₁₋ₓFeₓO₃ (x = 0.01, 0.02, 0.03, 0.04 and 0.05), which represents all the peaks are present in according to JCPDS Card No. 81-1428 .hence suggesting cubic structure. But one small peak at 23.8 deg in some sample shows the presence of some amount of BaCO₃ . Hence sample prepared is not in single phase.

![Xrd pattern for bati₁₋ₓfeₓo₃ (x = 0.01, 0.02, 0.03, 0.04 and 0.05)]](image-url)
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 decreases on increasing the doping percentage of Fe in BaTiO$_3$ as from same table it is found that FWHM increases on increasing Fe percentage doping. It is observed that on increasing the Fe percentage doping in BTO, the lattice constant is found to decrease from 4.01223 Å to 4.00508 Å. FWHM was calculated for the peak having highest intensity at 31.4 deg and is found to increase with increasing doped Fe percentage.

**Table I. Lattice constant, particle size and X-ray diffraction of BaTi$_x$Fe$_y$O$_3$ (x = 0.01, 0.02, 0.03, 0.04 and 0.05)**

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>FWHM</th>
<th>L (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BITF1</td>
<td>4.01223</td>
<td>4.01803</td>
<td>0.38759</td>
<td>0.57151</td>
</tr>
<tr>
<td>BITF2</td>
<td>4.01223</td>
<td>4.01793</td>
<td>0.37915</td>
<td>0.57978</td>
</tr>
<tr>
<td>BITF3</td>
<td>4.01582</td>
<td>4.01644</td>
<td>0.41918</td>
<td>0.34552</td>
</tr>
<tr>
<td>BITF4</td>
<td>4.01223</td>
<td>4.01803</td>
<td>0.42569</td>
<td>0.35747</td>
</tr>
<tr>
<td>BITF5</td>
<td>4.00508</td>
<td>4.01522</td>
<td>0.43644</td>
<td>0.32906</td>
</tr>
</tbody>
</table>

In figure 2, the observation of peak at 45.15 deg 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 I.

**Figure 2.**

Plots for 200 peak bati$_x$fe$_y$o$_3$ (x = 0.01, 0.02, 0.03, 0.04 and 0.05)
The room temperature I – V measurement for all different five samples is shown in figure 3. From fig it is clear that on increasing the percentage Fe doping in sample results in decrease of curve slope and hence increase in resistance of a sample which may be due to increase of band gap energy. at 5% Fe doping band gap energy is found to be maximum hence J(current density) to be minimum.

**Figure 3.** J – e graph for bati$_x$fe$_y$o$_3$ (x = 0.01, 0.02, 0.03, 0.04 and 0.05).

**Figure 4.** Represents the variation of polarization present in the sample, w.r.t the applied electric field measured at different voltage, at room temperature. Graph clearly indicates presence of ferroelectricity. from the figure 4(a1,a2,a3,a4,a5) it is found that value of remnant polarization Pr decreases with increase of doping percentage. the value of remnant polarization decreases from 0.0754 μC/cm$^2$ for 1% Fe doped sample to 0.0143 μC/cm$^2$ for 5% Fe doped sample at 200 v and coercive field(Vc) also decreases (from 1.53 KV/cm for 1% Fe to 1.41 KV/cm for 5% Fe sample) with increase of doping. Similar ferroelectric behaviour is observed by other researchers [7-10].
Fig 6. Represents the ferroelectric curve of all 5 samples which were sintered at 800 °C. Sample having 5% Fe is found to have minimum remnant polarization. Only 4%Fe doped sample shows a significant rise in remnant polarization. Also these graphs do not contain the saturation P value which may be present in the general ferroelectric hysteresis loop, the reason for this is that the sample in prepared pallets may be of looysy nature having some free charge particles which may be responsible for conductance across the two parallel face of pallet. In order to observe the amount of polarization present in the sample, PUND(pulse up and down) measurement was carried out at room temperature for two sample having 3%Fe and 5% Fe which is presented in table II. it also infers the same behavior as obtained from above P-E measurement.

Table.2. Variation in polarization due to doping

<table>
<thead>
<tr>
<th>polarization (µC/cm²)</th>
<th>5% at 1000v</th>
<th>5% at 1500v</th>
<th>3% at 1000v</th>
<th>3% at 1500v</th>
<th>-P 1500v</th>
<th>-Pr 1500v</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.81581</td>
<td>1.51361</td>
<td>1.04037</td>
<td>2.09726</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pr</td>
<td>0.96428</td>
<td>1.71150</td>
<td>1.23359</td>
<td>2.31336</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-P</td>
<td>0.85891</td>
<td>-1.5761</td>
<td>-1.1171</td>
<td>-2.2475</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-Pr</td>
<td>1.02809</td>
<td>-1.7949</td>
<td>-1.3291</td>
<td>-2.4815</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Hence from all above discussion it is concluded that sol gel method described above is effective in doping Fe at various desired percentage, with desired tetragonal structure. Also the above method of preparation gives rise to very small particle size in comparison to that obtained in solid route method of Fe doping. But tetragonality of sample decreases with increase of doped Fe percentage. as value of polarization decreases with increase. Also XRD not shows the splitting of 200 or 002 peak which indicates cubic structure, but this does not mean that BTOFe has cubic structure.

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. All of the produced samples though the sample here contains tetragonal structure as obtained from the calculation of table I. The same has been discussed by Frey and Payne that XRD alone is a not Suitable technique to reveal the subtile 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 a sample. J-E curve suggest the decrease in band gap energy with increase of doped Fe percentage. the increased leakage current due to the formation of oxygen vacancies during growth and existence of multiple Fe valences (Fe 3+ and Fe 4+) may have played a vital role in the decrease of polarization. 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 dipole of ferroelectric material are coupled to the material lattice so due to doping lattice changes and hence strength of dipole also changes. Hence it can be concluded that there is coupling between the polarization and lattice strain.
IV. ACKNOWLEDGMENTS

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V. REFERENCES


[7]. J.Rodriguez- Carvajal: FULL PROF version 3.0.0 (Laboratoire Leon Brillion,CEA-CNRS, 1995).


