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Synthesize and Characterization of Crystalline Structure and Phase Transition Temperature of Ce Substituted Ba-TiO_3 Ceramics

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ABSTRACT

Characterization and synthesize of $Ba_{1-x}Ce_xTiO_3$ (x=0.01mol.) annealed at three different temperatures (1100°C, 1200 °C, 1300 °C) have been studied. For preparing powder of $Ba_{1-x}Ce_xTiO_3$(x = 0.01 moles), Sol- Gel synthesis was carried out according to the stoichiometric conditions. The powder obtained palletized at 1.5 ton /mm^2 pressure into a 10 mm dia. Pellet using PVA (polyvinyl alcohol) as binder. The pellets were then annealed at 1100°C for 1 hour. Then silver paste was applied on pellet by fully coating the one side and applying asingle dot on other side, for making the pellet as capacitor. The XRD pattern reveals that the lattice parameter increases with the Ce doping and c/a ratio decreased which shows that tetragonality decreases. In all investigated samples it is assumed that the phase transition analysis, after doping Ce in $BaTiO_3$ the Curie temperature decreases.

Keywords- $BaTiO_3$, ceramics, crystalline structure, cure temperature, dielectric properties.

I. INTRODUCTION

Memory devices with a high-speed data, read write processing, miniaturization and low energy consumption arethe requirements of modern industry and these devices are basically developed on ferroelectric and ferromagnet- ic properties. Ferromagnetic materials possess a permanent magnetic moment in the absence of an external field and exhibit very large permanent magnetization. Ferromagnetism is the basis for electric and electromechanical devices such as magnetic storage (hard disks) etc. Materials exhibiting more than one ferroic orders are known as multiferroics. Among the family of multiferroics, the materials that features both ferromagnetic and ferroelec-tric order are classified as magnetoelectric-multiferroics (ME-MF) exhibiting magnetelectric (ME) coupling.ME coupling have gained much attention in memory applications. ME coupled multiferroic property is com-monly explored in single phase material like $BiFeO_3$[1], $BaTiO_3$ as they readily exhibit strong ferroelectric order- ing at room temperature. The ME coupling was not much explored in conventional ferroelectric material such as $BaTiO_3$ because of the absence of magnetism by $3d^0$ (Ti^{4+}).ME coupling can be achieved by Doping ferroelec- tric perovskite with transition metal/ rare earth metal.

More recently, P. Senthlikumar et.al has reported structural,[2] multiferroics, and magnetoelectric properties of$Ba_{1-x}Ce_xTiO_3$. system, which motivated us to prepare and study Ce doped $BaTiO_3$ ceramic. The present project work reports on synthesis of $Ba_{1-x}Ce_xTiO_3$ (x=0.01mol.) annealed at three different temperatures (1100°C, 1200 °C, 1300 °C) by sol-gel[3,4] methods. The investigation of crystalline structure and phase transition temperature of these samples has been also carried out in this work.

II. THEORECTICAL ASPECTS

$BaTiO_3$

Barium titanate is a ferroelectric material that is used in capacitors,[5] electrochemical transducers and nonlinearoptics .[6] The solid barium titanate exist in one of the four phases (cubic, tetragonal, orthorhombic, and rhombo- hedral) depending on temperature. All these phases exhibit the ferroelectricity effect apart from cubic phase. $BaTiO_3$ has versatile application in the electronic industry. Due to its excellent ferroelectric properties, high dielectric constant and relatively simple structure, $BaTiO_3$ has been well studied and widely used in forms of single crystal and ceramics.

Origin of ferroelectricity in $BaTiO_3$

A lattice of opposite charges is inherently unstable. It is the short-range repulsions between neighboring electronclouds that stabilize ionic materials. In ferroelectric perovskite, besides the short-range repulsions, there is an additional bonding, which might stabilize the distorted phase there exists a delicate balance between the short- range repulsions which prefer the cubic phase, and the long-range electrostatic forces which favor the ferroelec- tric state.

It is found that in perovskites like $BaTiO_3$and $PbTiO_3$, the short-range repulsive forces tend to stabilize crystals without off-center displacements. Using the local density approximation (LDA) method to study the electronic structures, Cohen in 1992 found an overlap of the Ti 3d partial densities of states with the O 2p valance bands. This hybridization between the titanium 3d states and the oxygen 2p states is imperative for ferroelectricity, and the hybridization is further enhanced by the ferroelectric distortion. The interaction between barium and oxygen is largely ionic in nature, and then less affected by the distortion. In addition, according to the characteristic “double-well” potential energy for Ti cation as a function of its position between the oxygen anions this small cation in ferroelectric perovskite oxides should lower its energy by shifting toward one of the negative O^{2-} ions.

Thus, the below picture emerged. At low temperature without strain, the lowest energy off-center displacements of Ti^{4+}in $BaTiO_3$are along the [1 1 1] directions, leading to the rhombohedral ground state. As temperature increases, the off-center displacement disorders over two directions, giving an orthorhombic symmetry. A tetra- gonal symmetry is formed with disordering over four directions, finally leading to cubic phase at higher temper- ature.[7].

Dielectric Constant and phase transition temperature

Dielectric[8] or electrical insulating material ate understood as the material in which electrostatic field can persist for long times. Layers of such substance are commonly inserted into capacitors to improve their performance, and the term dielectric refers specially to this application.

An electric field polarizes the molecules of dielectric producing concentrations of charge on its surface that create an electric field opposed (antiparallel) to that of capacitor. This reduces the electric potential. Considered in reverse, this means that, with a dielectric, a given electric potential causes the capacitor to accumulate a large charge.

The dielectric constant (ϵ) of a dielectric material can be defined as the ratio of the capacitance using that ma- terial to the capacitance using a vacuum as the dielectric.

Dielectric constant (ϵ) is given by

$$\epsilon = \frac{C}{C_0}, \quad C_0 = \frac{\epsilon_0 A}{t}$$

Where

C =capacitance using the material as the dielectric in the capacitor,

C_0 = Capacitance using vacuum as the dielectric

ϵ_0 =A =Permittivity of free space $(8.85 \times 10^{-12} \frac{F}{m})$

Area of the plate/sample cross section area

t =Thickness of the sample

All ferroelectric material has a transition called the Curie point[9] (Tc). At T > Tc, the crystal does not exhibit ferroelectricity ,[10] while for Tc. it is ferroelectric. If there is more than one ferroelectric phase, the temperature atwhich the crystal transforms one phase to another is called transition temperature. Near the Curie temperature point or transition temperatures, the thermodynamic properties including dielectric, elastic, optical and thermal constants show an anomalous behavior.

X-ray Diffraction (XRD)

XRD method is not only used for the determination of the lattice structure and for the modeling of the basic unit cell but is also used for phase identification, particle and unit cell size determination. It is a very powerful and accurate experimental technique for studying the crystal structure of solids and thin films. In XRD analysis, a collimated beam of X-rays with a wavelength typically ranging from 0.7 to 2Å is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law, which is given as

$$2d\sin\theta = n\lambda \qquad (1)$$

Where ‟ d „ is the spacing between atomic planes in the crystalline phase and 'λ' is the X-ray wavelength. The dif- fracted X-rays from the atomic planes will interfere constructively only if the path difference between them sa- tisfies the equation (1). The intensity of the diffracted X-ray is measured as a function of the diffraction angle θ. This diffraction pattern is used to identify the crystalline phases present in the thin films or in powdered sample.

Determination of grain size or crystalline size

Crystallite size is the smallest-most likely single crystal in powdered form. The crystallite size is commonly determined by XRD.

The crystalline size 'D' can be estimated from peak width in XRD pattern using the Scherer‟s formula:

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$$D = \frac{k\lambda}{\beta cos\theta}$$

Where,
D = Crystallite size
K = 0.94 (Sherrer constant)
λ= 0.15406 nm (wavelength of x-ray source)
β = full width half maxima (FWHM), in radians
$\frac{\beta}{2} = \frac{\theta_1 - \theta_2}{2}$ Is the full width
θ = peak position in radians

At half maximum of a diffraction peak, θ is the diffraction angle," „is the X-ray wavelength and 'K' is the Scher-er‟s constant of the order of unity for usual crystal and thin films. $'C$

Determination of lattice constants

In X-ray diffraction, the observed pattern comes in the form of the intensity of the diffracted rays as a functionof 2θ.

For tetragonal crystal „a‟ equal to „b‟ but not equal to „c‟ $(a = b \neq c)$To calculate c/a ratio the formula used is: -

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$

Where,
(h, k, l) = (0 0 2)/ (2 0 0)
d = interplanar distancea, c = lattice parameter

III. SYNTHESIS OF Ce DOPED BARIUM TITANATE (BaTiO3) AND EXPERIMENTALTECHNIQUES

For preparing powder of $_{1-x}Ce_xTiO_3$(x = 0.01 moles), sol gel synthesis was carried out according to thestoichiometric conditions. The required molar ratio is $_{0.99}Ce_{0.01}TiO_3$.

IV. MATERIALS USED

- Barium acetate
- TNBT (Tetra –n-butylorthotitnate)
- Ce (III) Acetate
- 2-Ethyl Hexonic Acid

V. PROCEDURE

- Add 0.03g of (III) Acetate to the solvent, -Ethyl Hexonic Acid.
- Which is then heated at temperature about and after the Ce has dissolved completely add Bariumacetate. Wait for barium acetate to completely dissolve.
- Add 5 ml. of solvent and 3.4 ml. of TNBT to the beaker.
- Sol formed is left undisturbed and subsequent loss of solvent directs conversion from sol to gel.
- Further drying by heating the sol gel for 5 to 6 hours we, get powder of $_{0.99}Ce_{0.01}.TiO_3$.
- The powder formed is then annealed for at least 5 hours at three different temperatures – 1100ºC, 1200 ºC, 1300 ºC

VI. PELLET FORMATION

The powder obtained above palletized at 1.5 ton /mm^2 pressure into a 10 mm dia. Pellet using PVA (polyvinyl alcohol) as binder. The pellets were than annealed at 1100ºC for 1 hour. Then we applied silver paste on pellet by fully coating the one side and applying a single dot on other side, for making the pellet as capacitor.

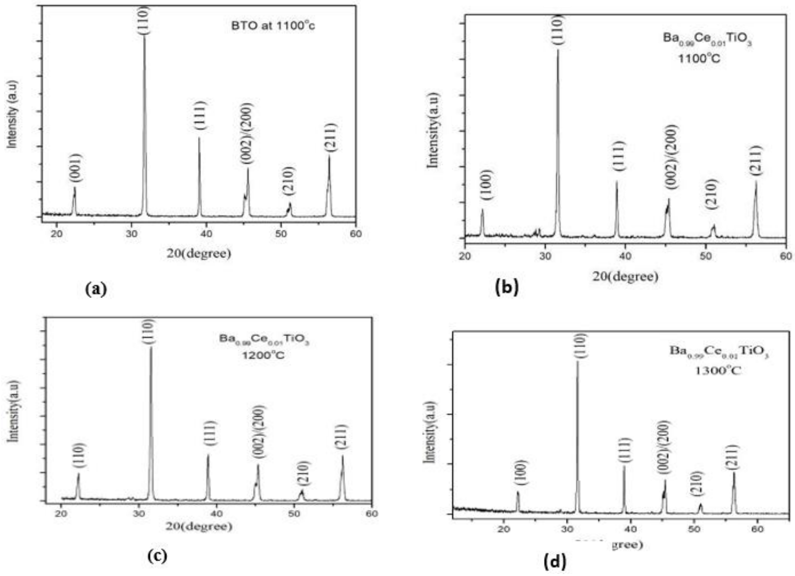


Fig. 3.1 (a) XRD characteristics of pure BTO at 1100^{0}C (b) XRD characteristics of Ce doped BTO at1100^{0}C

VII. RESULTS AND DISCUSSIONS

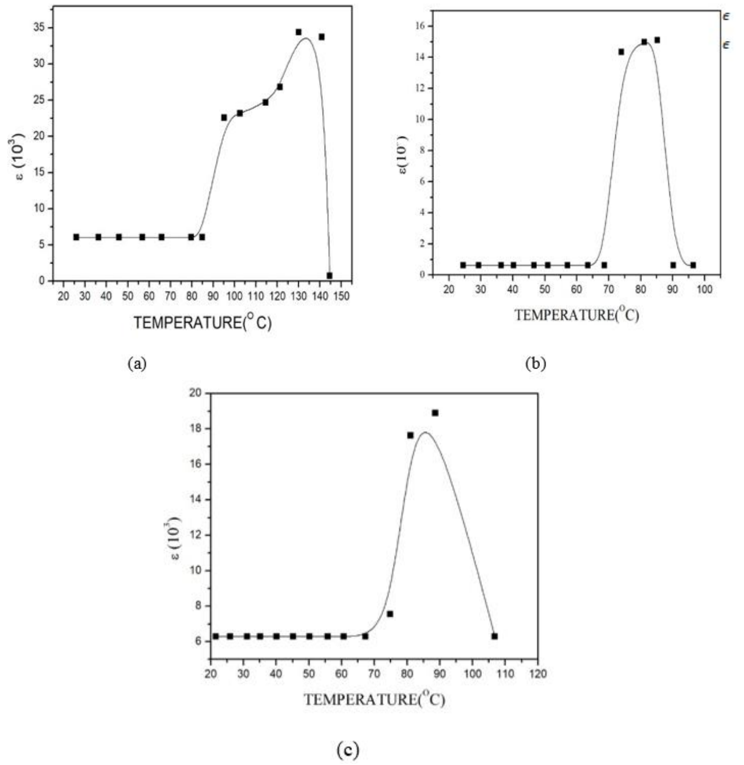
XRD characterization of prepared samples

The XRD pattern of undoped BTO annealed at temperature 1100^{O}C and Ce doped BTO annealed at temperature 1100^{O}C, 1200^{O}C, 1300^{O}C are depicted in figure 3.1. The sharp diffracted peaks with high intensity confirms the good crystallinity and phase transformation of Barium Titanate. The distinction of tetragonal with cubic system is mainly confirmed by appearance of (0 0 2) plane corresponding to c-axis orientation. The magnified view of diffraction peak at 45^{O} for pure BTO (fig. 3.1) encloses two peaks, one with the lower intensity corresponding tothe (0 0 2) plane and other with higher intensity to the (2 0 0) plane. Thus, pure BTO exist in tetragonal structureagreeing well with the report by P. Senthinl Kumar. Further the data shows that lattice parameter a=b=3.97944, c=4.01988Å giving c/a ratio = 1.0101 and volume $V = 63.66\ \text{Å}^3$ which is less than as estimated in report by P. Senthinl Kumar et.al. The difference can be explained on the basis of crystallite size. The crystallite size of the sample is estimated about 32.99 nm using the Sherrer formula (see table 3.1). For such ultra-fine particles, the surface tension, surface energy is high enough which results in tendency to shrink the lattice which decreases the volume. When Ce is introduced in Barium Titanate lattice, the peak position and doublets are shifted to low-er angle (Fig. 3.1 (b), 3.1(c) and 3.1(d). The elongation of lattice along a-axis increases the unit cell volume V.

Table 3.1. Effect on lattice parameter and crystallite size with Ce doping in BaTiO$_3$

SAMPLE	a (in Å)	c (in Å)	CRYSTALLITE SIZE (in nm)	TETRAGONALITYc/a
BaTiO$_3$ (1100^{O}C)	3.9794	4.0198	32.99	1.0101
BaCeTiO$_3$ (1100^{O}C)	3.9942	4.0205	45.15	1.0065
BaCeTiO$_3$ (1200^{O}C)	3.9975	4.0258	41.18	1.0070
BaCeTiO$_3$ (1300^{O}C)	3.9906	4.0185	43.67	1.0069

Table 3.1 shows that there is a decrease in c/a ratio and increase in crystallite size for doped BTO annealed at temperature 1100^{O}C. Decreased value of c/a ratio depicts decrease in tetragonality. Thus, on introducing Ce the tetragonal structure leaning towards the cubic symmetry which is also confirmed in literature[11].



(a) (b)

(c)

Fig. 3.2: (a) variation of dielectric constant, with temperature for pure BTO. (b) variation of dielectric constant, with temperature for pure Ce doped BTO, annealed at temperature 1100ºC. (c) variation of dielectric constant, with temperature for Ce doped BTO, annealed at temperature 1200ºC.

Study of phase transition temperature of prepared samples

The above figure shows the variation of dielectric constant with temperature. The highest point of the curves shows the phase transition temperature, known as Curie temperature (T_c). fig.3.2 (a) gives the variation curve for undoped BTO which has the Curie temperature at 130^{O} C temperature. It can be seen from fig. 3.2(b) that after doping Ce in BTO (1 mol. %) which is annealed at 1100^{O} C. the Curie temperature shifts to the lower val- ue of 88.6^{O} C from 130^{O} C. and from fig.3.2(c) we can say that Curie temperature again decreased to 85.2^{O} C.

VIII. CONCLUSIONS

Ce doped BT particles have been successfully synthesized by sol gel process. Ce doping is done according to the stoichiometric ratio $Ba_{1-x}Ce_xTiO_3$ (x=0.01mol.). The XRD pattern reveals that the lattice parameter increases with the Ce doping and c/a ratio decreased which shows that tetragonality decreases. From the phase transition analysis, we can conclude that after doping Ce in BTO the Curie temperature decreases.

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