

Minimizing Fabrication Time Of Calcium Modified $PbTiO_3$ Nanoceramics By HEBM Technique

Sona Kumari, S. K. Sinha, R. K. Choudhary

Abstract: Lead titanate is one of the family member of ABO_3 structure (perovskite) having piezoelectric as well as pyroelectric properties in nature. It shows high ferroelectric property as ceramic materials. Ca modified lead titanate termed as $P_{1-x}C_xT$ synthesized by HEBM at $270^\circ C$ of room temperature. The stoichiometric ratio was taken as $Pb_{1-x}Ca_xTiO_3$ where CaO was taken in various ratio. Structural and electrical properties were studied by taking measurement with standard instruments (LCR metre). Analysis of XRD gives that doping of calcium produce a decrease in tetragonal size and hence the volume. As a result on A-site substitution observed. Graph of electrical parameters shows that impedance decreases exponentially with frequency.

Keyword: HEBM, lead oxide, LCR meter, perovskite, stoichiometry, transition temp, XRD etc.

1. Introduction

Lead titanate is a ceramic material having perovskite structure (ABO_3). It has ferroelectric and piezoelectric properties. As $PbTiO_3$ has high curie temperature ($490^\circ C$) and high internal polarisability, bigger tetragonal size produces a barrier to form highly dense ceramic materials. $PbTiO_3$ has a perovskite structure in which A - site has Pb^{2+} ion and B - site contains Ti^{4+} ions with central site occupied by oxygen atoms. The piezoelectric behaviour depends on structural defects including the random distribution of oxygen defect, which appears in the materials before polling process [1]. The perovskite structure (ABO_3) has an internal ability to absorb different size of ions due to which different properties of the ceramics differ as - 1- solubility and 2 - ionic radius [2]. The simultaneous study of electrical and structural properties of ferroelectric material reveals out physical behaviour of material as piezoelectricity, dielectric constant and pyroelectricity, because these properties varies with the variation in conductive capacity. Perovskite structure (ABO_3) have amazing physical behaviour as magneto resistance and ferroelectric behaviour. They also have electromagnetic and optoelectric influence upto a wide range for applications in important use of electronic field [3],[4]. An expanded range of complex material (compound) can be synthesized by substituting suitable oxides or hydroxides of different element at any one site of lead titanate according to the application of electronic components as actuator, transducer, MEMS, NEMS and memory chips. Doping of different elemental ions cause changes in curie temp (T_c) as well as structure of lattice arrangement and size.

Also electrical properties of materials changes due depending on crystallinity. Doping element chosen on the basis of electron mobility as well as solubility etc. Calcium doping in lead titanate lower the grain sizes as well as the curie temperature. It shows higher anisotropy [5]. In this work we have taken calcium as doping element in Pb site. Using various method structural and electrical properties as well as dielectric constant of $PCaT$ ceramic material examined which synthesized by HEBM method for very low concentration ($x= 0.00, 0.015, 0.025, 0.035$) which work is not done earlier by HEBM method. Nanosize particles prepared till now by various method as mechanical, chemical root solid state methods over which HEBM method produce more advantages with lower complexity in preparation [6],[7]. Dielectric properties also examined by equivalent circuit having parallel RC element [8]. Perovskite structure material used widely in electronic and electrical devices [9]. Different method as solid route method [10] and chemical route method called as MOCVD [11],[12] already used to synthesize these materials. In solid state method there is problem in homogenous distribution of the cations. HEBM technique extends advantages over the all other methods, since wasting of material during synthesis is minimum. Till today few reports have been available for the fabrication of this material by HEBM technique [13] but reduction in tetragonality is found maximum in only few hours (10hrs) milling with small balls. The objective of current research is to study the structural and electrical properties of materials synthesized by HEBM technique.

Experimental detail:-

The raw powder commercially having formula PbO (lead oxide, yellow colour) and TiO_2 (titanium oxide, 99% pure, white colour). Both powder material have different average size of their particles range as 3.0 to 5.0 μm . $PbTiO_3$ powder is synthesized by HEBM (high energy ball milling) method using PbO and TiO_3 powder in machine. Nano sizing Mill (HEBM machine) is used for preparing stoichiometric powder of $PbTiO_3$ as reported in earlier paper [13]. In order to inverse the reactivity of the constituent materials, milling time was carried out for various times ranges from 1-10 hrs. Excess amount of PbO (2.5 % wt) used to compensate the volatilization of Pb during sintering of the pellet made by mixture. Prepared powders were mixed by manually with motor-paddle for 5min with 5% wt. PVA solution. Then the powder was used to get small

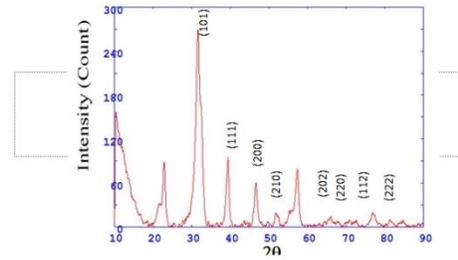
- Sona Kumari is currently pursuing Ph.D. degree program in Applied Physics Deptt. in Birla Institute of Technology, Mesra, University, Patna Campus., India, PH-9334606661. E-mail: sonakumariphy@gmail.com
- S.K. Sinha is currently teaching in Birla Institute of Technology, Mesra, University, Patna Campus., India, E-mail: drsanjay1101@gmail.com
- R. K. Choudhary is currently Ex-Professor and Head of Material Sc. (NIT, Jamshedpur)

pellets of dimension 12 mm diameter and 3mm thickness for measurement in bulk with 150 Pa pressure. Then pellets were sintered at 650 °C, 700°C, 800°C and 1000°C for 2 hrs at the rate of 5°C per minute heating then cooling normally . The dual time is kept constant of 2h. The bulk densities of all the sintered powders as pellet form were calculated using Archimedes method. Prepared pellets are used for XRD(X-Ray Diffraction), SEM (Scanning Electron Microscope), LCR meter reading (for Electrical properties).

Characterization and Analysis:-

Differential Thermal Analysis (DTA/TG):-

DTA/TG curve (fig-1) shows of milled powder PbO and TiO₂ and dopant Ca oxide powder, when calcium oxide powder concentration is 0. 015, 0. 025, 0. 035 mol% respectively. The DTA graph of PC₀₁T, (P_{0.99}C_{0.01}TiO₃) - PC₀₁T composition has exothermic peaks at 285⁰ C, 350⁰ C,585⁰ C, 650⁰ C, and endothermic peaks at 670⁰ C. The corresponding wt. loss in first peak shown at 285⁰ C, which indicate the oxidation decomposition of organic part of material present in it . Second exothermic peak and corresponding peak appear at that temperature indicates the solid state reaction of the composition used . It also indicate the initiation of crystallization process and elimination of some extra oxygen in composition[9],[10]. The XRD graphs also confirm the same reaction which is given latter on the third peak appear at 585⁰C, when no weight loss confirms, which is related to phase formation of modified lead titanate and fourth peak appear again with no wt. loss indicating about the formation of PC₀₁T at 650⁰ C. Fifth peak appears at 670⁰C which gives information about evolution of excess PbO which volatile at higher temperature [11]. Wt. loss in other composition of different concentration of doping element (CaO) is different which gives the result with DTA/TG that wt. loss is directly proportional to the concentration of doping element



HKL Indexing of PT₁

Fig-2

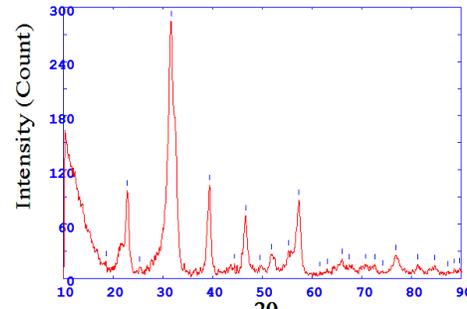


Fig-3

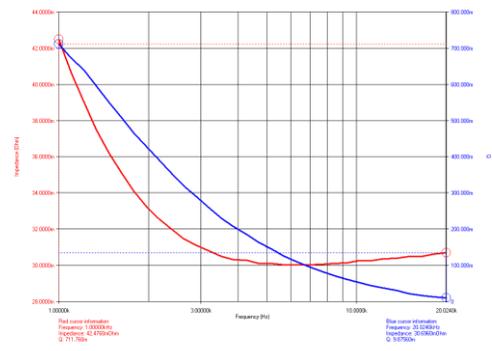


Fig-4

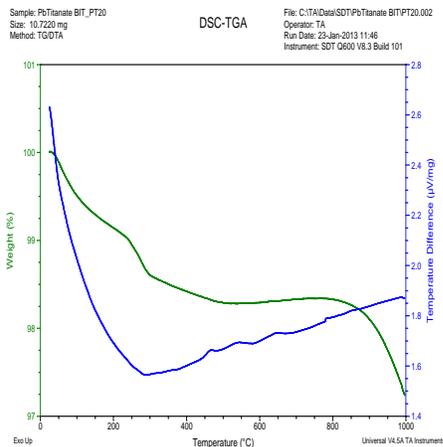


Fig-1

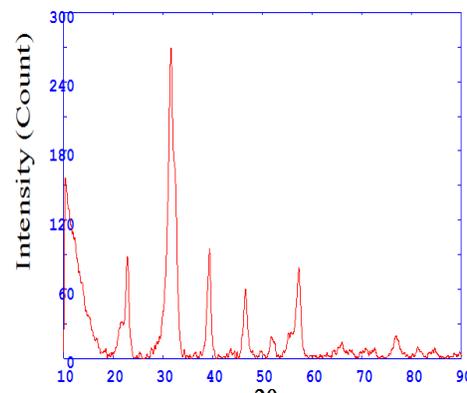
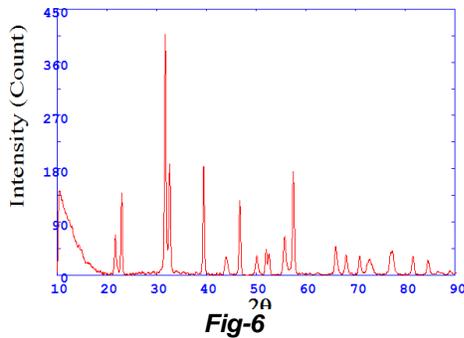


Fig-5



XRD(X- Ray diffraction technique) is used to examine the compositional patterns of molecules and structural states of particles of ceramic powder obtained. X-Ray was taken using Cu radiation having wavelength 1.540598 \AA . From X-ray diffractogram, it has been found that synthesized material is having tetragonal structure by matching the position of most intense peaks which shows agreement with JCPDF file (01-075-1605). Lattice parameters obtained using Powder-X software are $a = 3.900 \text{ \AA}$, $b = 3.900 \text{ \AA}$, $c = 4.1500 \text{ \AA}$. The crystallite size of material calculated by

Paul Scherrer's formula

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where:

- τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;
- K is a dimensionless **shape factor**, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;
- λ is the X-Ray wavelength;
- β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$;
- θ is the Bragg angle

The pattern shows the 002 peak slightly shifting towards lower angle which shows increase in d spacing. The percentage crystallinity calculated from the diffractogram and given in table below:-

Raw Mixture milled

for

Parameters 0 hrs 2 hrs 5 hrs 7hrs 10 hrs

Peak Position 32.841 32.840 32.840 32.840 2.839

d (\AA) 2.84 2.84 2.88 2.89 2.90

Electrical properties:-

It is already concluded that relative dielectric constant increases with increase in concentration of alkaline earth

metal and with the ionic radii of doping element along with relative increase in surface acoustic wave, electro-mechanical coupling factor and constant of frequency [12]. In our work graph of electrical parameters fig-4 obtained smooth which indicates better result over previous results.

SEM graph:-

Scanning Electron Microscopy showed in analysis with the agreement of XRD that particle size of powder obtained is less than 400 nm (fig -7). Since the particle size is fine, high density structure is obtained which is useful in electrical applications.

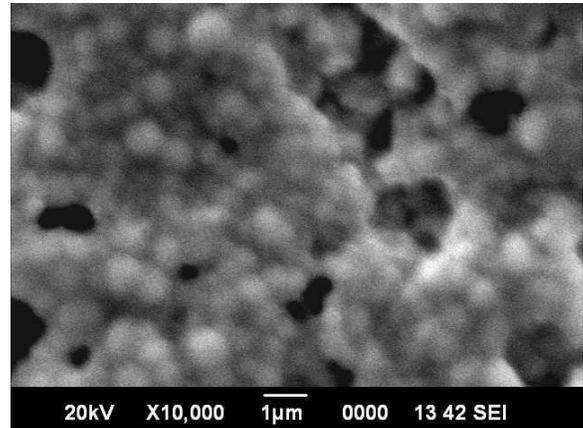


Fig-7

SEM graph of Ca-doped lead titanate annealed at 1000°C

Result and Discussion:-

Ca modified lead titanate ceramic powder with concentration 0.015, 0.025 and 0.035 synthesized by High Energy Ball Milling Method (HEBM) using small size ball which reduces the milling time. Only after nine hours tetragonal structure obtained, which is not reported till now. Dielectric constant and dielectric loss increases with decrease in tetragonal size of lattice structure. Impedance vs frequency graph is parabolic while quality vs frequency graph is exponential. Smoothness of graph shows uniformity of crystal structure which is more helpful in memory chips, transducer and actuators.

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References:-

- [1] D Ramirez-Rosales, Zomaorano-Ulloa, O. Perez-Martinez, sol. stat. Commun. 118 (2001)371.
- [2] C. H. Ahm, J. M. Triscone, J. Mannhart, Nature 424,1015(2003),doi: 10.1038/nature 01878
- [3] S. K. S. Prasar, M. Ghoraneviss and A. Salar Elahi, Advance Material Science and Engineering. volum 2013

- [4] O. Auciello, J. F. Scott, R. Ramesh, *Phys. Today* 51,22(1998) doi: 10,1063/1,882324
- [5] C. Sturm, T. Chavdarov, R. Schmidt-Grund, Rheinländer, C. Bundesmann, H. Hochmuth, M. Lorenz, M. Schubert, M. Grundmann *phys. stat. sol. (c)* 5 (2008) 1350-1353. DOI: [10. 1002/pssc.200777853](https://doi.org/10.1002/pssc.200777853)
- [6] B. S. Murty and S. Ranganathan, Novel Material Synthesis by Mechanical alloying /milling. *International Materials review*, vol-43, no 3, pp. 101-141, 1998.
- [7] C. Suryanarayana, "Mechanical Alloying and Milling". *Progress in Material Science*, vol-46, no 1-2 pp.1-184, 1998.
- [8] S. K. Rout, A. Huyain, J. s. Lee, I. W. Keen and S. I. Woo, Impedance Spectroscopy and morphology of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ceramic prepared by soft chemical method," *Journal of Alloy and Compound*" vol 477, no, 1-2, pp. 706-711, 2009.
- [9] S. R. Gurkovich, J. B. Blum, in: L. L. Hench, D. R. Ulrich (Eds.), *Ultra-structure Processing of Ceramics, Glasses and Composites*, John Wiley and Sons, New York, 1984.
- [10] S. R. Gurkovich, J. B. Blum, *Ferroelectrics* 62 (1985) 189.
- [11] J. B. Blum, S. R. Gurkovich, *J. Mater. Sci.* 20 (1985) 4479.
- [12] Chi-Young Lee a,b,*, Nyan-Hwa Tai b, Hwo-Shueenn Sheu c, Hsin-Ten Chiu d, Shu-Hsu Hsieh b "The formation of perovskite PbTiO_3 powders by sol-gel process" *Materials Chemistry and Physics* 97 (2006) 468-471 .
- [13] Nagarbawadi M. A. a, Jangade P. S. b, Bagwan S. T. c, "The influence of Calcium doping on structural and electrical properties of ferroelectric Lead Titanate ceramic," *IOSR Journal of Applied Physics (IOSR-JAP)* e-ISSN: 2278-4861. Volume 6, Issue 3 Ver. II (May-Jun. 2014), PP 15-19.