

PREPARATION OF $\text{PbTi}_{0.8-x}\text{Tb}_{0.2}\text{Mg}_x\text{O}_3$ NANO CERAMICS BY HIGH ENERGY BALL MILLING AND ITS CHARACTERIZATION

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Incorporation of Te and Mg were done based on the stoichiometric formula $\text{PbTi}_{0.8-x}\text{Tb}_{0.2}\text{Mg}_x\text{O}_3$ (PTTbM). TG characterization of green powder revealed the completion of solid state reaction at temperature 450^o C. XRD of modified PTTbM powders milled for 10 hours was found most suitable as it gives pure single phase tetragonal structure. Dielectric constant was found as 265 in the case of 5 wt percent of Mg in PTTbM at room temperature. Piezoelectric Coefficient was found as 218×10^{-12} C/N at 39 Kv/cm of poling field. The results obtained were comparable and even better than so far reported in similar kind of materials.

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1. Introduction

Lead Titanate (PbTiO_3 or PT) is having perovskite structure and is a member of ferroelectric materials. It exhibits dielectric and ferroelectric properties comparable to similar materials such as barium titanate, lead zirconate titanate etc. [1-4]. Variation of Properties of ferroelectric materials are dependent on method of fabrication, at the same time, incorporation of foreign element in lattice site of material changes the property radically. There are different method of fabrication reported by workers [5-16] such as sol. gel. Co-precipitation etc to obtained nano particle size in fabricated materials. High speed ball milling (HSBM) method is one of the method in which required phase can be obtained during milling itself without applying any additional heat and this method is reported to produce nano powders of ceramics [6-10]. Better densification in finished ceramics is also reported at low sintering temperature in HEBM method in comparison of other existing method of synthesis e.g. solid state reaction method, sol. gel method etc. [6-8]. In present work chalcogenide tellurium Te and alkali Mg ions were selected as modifier. Tellurium dioxide (TeO_2) have high melting point 733^o C and is stable oxide of tellurium. Te in lead titanate expected to contribute in the dielectric and piezoelectric properties interestingly because transitional position of Te is between metal and non metal [11-13]. TeO_2 is reported to have high refractive index (2.6) and as per famous Maxwell's relation on velocity of light $RI = (\text{dielectric constant})^{1/2}$, thus Te doping has good potential to influenced the dielectric property of PT. Mg ion too have potential to effect the property of PT as it has good ionic conductivity and mobility [14-20]. Double doping in lattice site of a perovskite structure is also reported to better compensatory effect to enhance the dielectric and piezoelectric property. Te was incorporated in 2 wt percent as this range expected to contribute optimum in PT as far as dielectric property is concerned [11-20]. Mg was incorporated in PT in varying concentration i.e. 1, 3 and 5 weight percent based on the stoichiometric formula $\text{PbTi}_{0.8-x}\text{Tb}_{0.2}\text{Mg}_x\text{O}_3$ (PTTeM). Study of changes in dielectric constant and piezoelectric coefficient in PTTeM due to change in dopant concentration of Magnesium is reported in this paper.

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2. Experimentals

PbO, TiO₂, TeO₂ and MgO all having AR grade was taken as starting materials. Powders were taken based on stoichiometric formula PbTi_{0.8-x}Tb_{0.2}Mg_xO₃(PTTeM), x=1,3 and 5 wt % and feed in milling container of HEBM(high energy ball milling) machine for the time period of 1 to 10 hours. Detail fabrication method is discussed in other paper of author[6]. Additional amount of PbO (2.5 % wt) was added in milling powder to make up the lead deficiency during sintering as per reported by others [7-8]. Differential scanning calorimetric Analysis (DSC) and Thermogravimetric analysis(TGA) analysis of green powder was carried out to know the completion of solid state reactions and the weight loss occurred during heating. Pelletization of calcined powder was done by applying a pressure of 15 MPa. Binder used in powder was 5 wt% poly vinylal acid (PVA). Pellet of diameter 12 mm and thickness 3 mm was then sintered at 650⁰ C, 700⁰C, 800⁰c for 2 hrs at the rate of 5⁰C per minute heating, the soaking time was kept for 2 hours for optimum densification as reported by others [6-8]. Phase analysis in calcined powder of PT was carried out with the help of X ray diffraction (XRD) machine. XRD of PTTeM powders milled for 10 hours was found most suitable as it gives pure single phase tetragonal structure having peaks at hkl values [100],[101],[111] and [200]. Pellets sintered at 800⁰ C were tested for dielectric constant (at varying frequency as well as varying temperature). Piezoelectric coefficient value of sintered pellets were also been measured at varying poling field. Surface morphology such as grain shape and size of pellets were determined by help of SEM (Scanning Electron Microscope) and AFM (Atomic force microscope).

3. Results and discussions

3.1. Differential Scanning calorimetric analysis (DSC) and thermogravimetric analysis (TGA)

DSC and TGA result of PT doped with 2 wt percent Nb and 1 wt percent of Magnesium is shown in Fig.1. DSC micrograph was clearly indicated no exothermic or endothermic peak during change in temperature up to 280⁰ C, but afterward rise in microvolt was observed but no exothermic or endothermic peaks observed. This rise may be attributed to completion of solid state reaction in green powder as well as change in lattice site[21-29]. DSC micrograph was noticeably indicated formation of required PT phase during milling of powder by HEBM itself[30-32]. In TG curve, there is almost no weight loss was observed between 480⁰ C to 870⁰ C. This helped in selecting the calcinations temperature around 480⁰ C[33-34]. Sharp decline seen in TG curve after 870⁰ C is due to fast decomposition of lead present in material at high temperature[30-34].

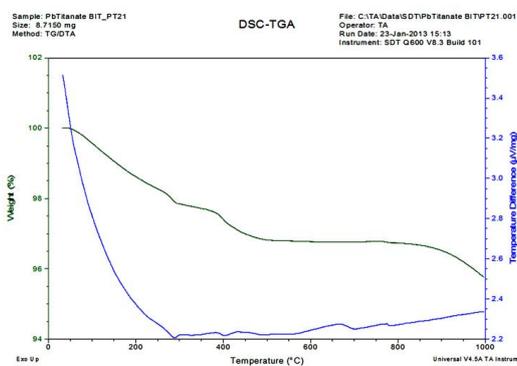


Fig.1.DSC/TG analysis micrograph of PTTeM (1wt% of Mg)

3.2. X-ray diffraction (XRD) studies of PTTeM

XRD micrograph of PTTeM (5wt% of Mg) milled for 10 hours is displayed in Fig.2. XRD was taken using Cu radiation having wavelength 1.540598 Å. From X-ray diffractogram, it had been found that synthesized material was having tetragonal structure, which was also in agreement with JCPDF file (01-075-1605). Pure single phase tetragonal structure having peaks at hkl values [100],[101],[111] and [200] was observed. Lattice parameters obtained using Powder-X ray software were $a=4.9168$ Å, $b=4.9168$ Å, $c=5.4089$ Å. The crystallite size of material was calculated by formula given by Paul Scherrer. Crystallite size was calculated as 433nm.

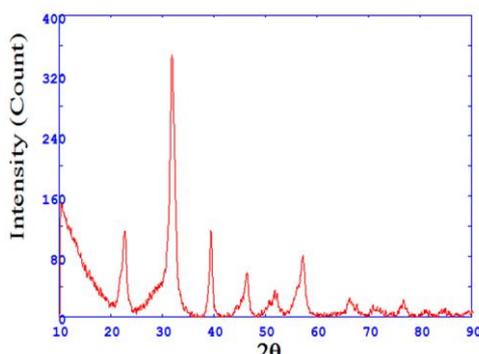


Fig.2. XRD micrograph of PTTeM (5wt% of Mg).

3.3. Microstructure studies of PTTeM

Micro structural study of PTTeM pellet sintered at 800⁰ C was done by Scanning Electron microscope (SEM) and Atomic Force microscope (AFM). SEM photograph of PTTeM (5 wt% of Mg) ceramics is shown in Fig.3. Nano size grains can be seen clearly in the photograph. Average grain size was found as 488.63 nm.

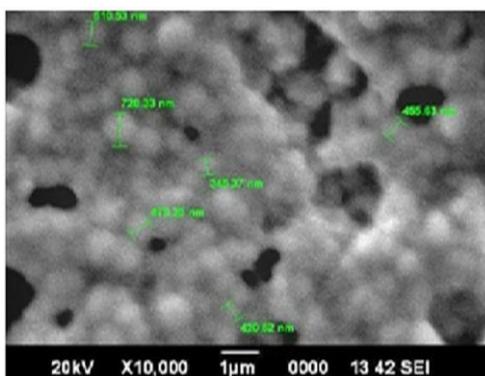


Fig.3. SEM photograph of PTTeM (5 wt % of Mg) sintered pellet.

AFM photograph of PTTeM (5 wt % of Mg) ceramics is shown in Fig.4. Nano size three dimensional grains can be observed clearly in the photograph.

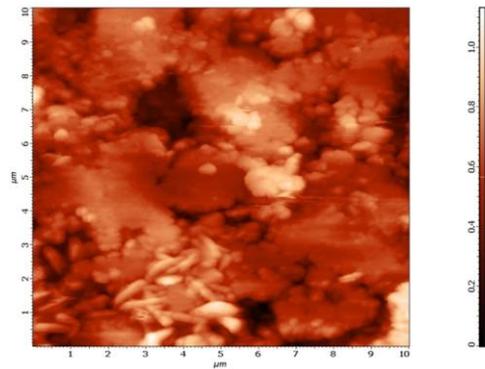


Fig.4 AFM photograph of PTTeM (5 wt % of Mg) sintered pellet.

3.4. Studies of dielectric constant

Measurement of Dielectric constant of pure PT and modified with Te and Mg at varying concentration are displayed in Fig. 5. Dielectric constant had shown maximum value in the case of 5 wt percent incorporation of Mg and it had shown increase with the increase of dopant concentration and increase of temperature. Dielectric constant in the case of PTTeM (5 wt % Mg) was found maximum in comparison of others and it was 265 at room temperature and 2460 at cure temperature i.e. 480^o C. This result is comparable and even better in some of the reported value on fabrication of PZT or PT by different chemical method [30-36]. Mg Double peaks and shifting of peaks toward higher temperature range was an indication of presence of Relaxer behavior [16,27,29] in PTTeM

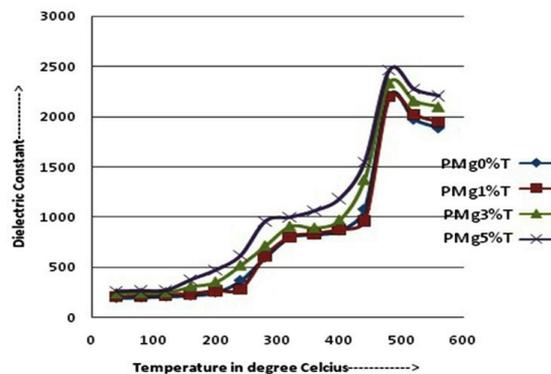


Fig.5. Dielectric constant of PTTeM (Mg= 0%,1%,3% &5%) ceramics at varying temperature.

3.5. Piezoelectric coefficient (d_{33}) studies

Piezoelectric coefficient (d_{33}) studies of pure PT as well as PTTeM (Mg= 1%,3% & 5%) at varying dc poling field were done. Graph of d_{33} vs poling field is placed as Fig.6. It had been observed that d_{33} value increases with increase of poling field and dopant concentration of Mg. d_{33} value reaches its saturation points at a poling field of 39Kv/cm. Maximum d_{33} value was observed in the case of PTTeM (Mg= 5%), it was 218×10^{-12} C/N. This value was found greater by 24 % as reported by P.Kour et. al [16] in similar material. This high value of d_{33} is comparable to the result reported by other workers adapting to different chemical method of fabrication. Increase in d_{33} value with the increase of poling field attributed to the change in polarity and corresponding increase in polarization[36-40].

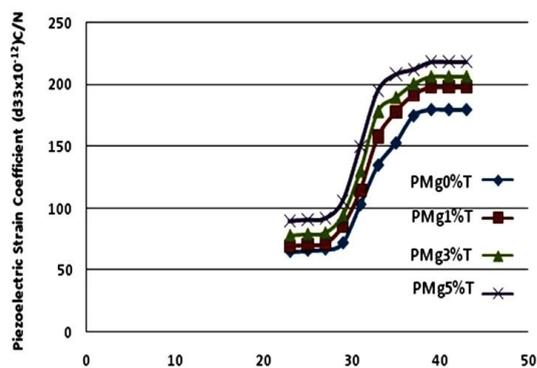


Fig.6. Variation of piezoelectric strain coefficient (d_{33}) with DC field (kv/cm) in PTTeM (Mg= 0%,1%,3% & 5%).

4. Conclusions

Nano particle size and nanograin size Lead Titanate (PT) doped with tellurium and magnesium was prepared successfully by High energy ball milling (HEBM) method. Absence of exothermic or endothermic peaks in DSC examination had indicated fabrication of lead titanate phase at room temperature itself just after treatment of HEBM. XRD of PTTeM powders milled for 10 hours was found most suitable as it gives pure single phase tetragonal structure having peaks at hkl values [100],[101],[111] and [200]. Lattice parameters of 5wt% Mg doped PTTeM was found as $a= 4.9168 \text{ \AA}$ $b= 4.9168 \text{ \AA}$ $c= 5.4089 \text{ \AA}$. Crystallite size was found as 433 nm. AFM analysis was shown clearly the presence of three dimensional nano particles in the material. As per SEM study average grain size was observed as 488.63 nm. Dielectric constant had shown maximum value in the case of 5 wt percent incorporation of Mg and it had shown increase with the increase of dopant concentration and increase of temperature.

Dielectric constant in the case of PTTeM (5 wt % Mg) was found maximum in comparison of others and it was 265 at room temperature and 2460 at cure temperature i.e. 480°C . This result is comparable and even better in some of the reported value on fabrication of PZT or PT by different chemical method. Double peaks and shifting of peaks toward higher temperature range was an indication of presence of Relaxer behavior in PTTeM. It had been observed that d_{33} value increases with increase of poling field and dopant concentration of Mg. d_{33} value reaches its saturation points at a poling field of 39 Kv/cm. Maximum d_{33} value was observed in the case of PTTeM (Mg= 5%), it was $218 \times 10^{-12} \text{ C/N}$. This value was found greater by 24 % as reported by P.Kouret. al in similar material. This high value of d_{33} is comparable to the result reported by other workers adapting to different chemical method of fabrication. Increase in d_{33} value with the increase of poling field attributed to the change in polarity and corresponding increase in polarization.

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