Studies of dielectric and piezoelectric properties of $\text{PbTi}_{0.8-x}\text{Te}_{0.2}\text{Gd}_x\text{O}_3$ nano ceramics prepared by high energy ball milling

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Incorporation of Te and Gd were done based on the stoichiometric formula $\text{PbTi}_{0.8-x}\text{Te}_{0.2}\text{Gd}_x\text{O}_3$ (PTTeG). TG characterization of green powder revealed the completion of solid state reaction at temperature 450°C . XRD of modified PTTeG powders milled for 10 h was found most suitable as it gives pure single-phase tetragonal structure. Dielectric constant was found as 2543 at curie temperature of 480°C in the case of 5 wt.% of Gd in PTTeG. Piezoelectric Coefficient was found as $241 \times 10^{-12}\text{ C/N}$ at 39 Kv/cm of poling field. The results obtained were comparable and even better than so far reported in similar kind of materials.

Keywords: Lead titanate; high energy ball milling; chalcogenide tellurium; dielectrics.

1. Introduction

Lead Titanate (PbTiO_3 or PT) has a 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 methods of fabrication reported by workers^{5–16} such as sol–gel, Co-precipitation, etc. to obtain nano particle size in fabricated materials. High Energy ball milling (HEBM) method is one of the methods 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.^{7–10} Better densification in finished ceramics is also reported at low sintering temperature in HEBM method in comparison to other existing methods of synthesis, e.g., solid state reaction method, sol–gel method, etc.^{7,8} In the present work, chalcogenide tellurium Te and rare earth Gd ions were selected as modifier. Tellurium dioxide (TeO_2) has high melting point 733°C and is stable oxide of tellurium. Te in lead titanate is expected to contribute in the dielectric and piezoelectric properties interestingly because transitional position of Te is between metal and non metal.¹¹ TeO_2 is reported to have high refractive index (2.6) and as per famous Maxwell's relation on velocity of light $\text{RI} = (\text{dielectric constant})^{1/2}$, thus Te doping has good potential to influence the dielectric property of PT. Gd-ion too has potential to effect the property of PT as it has good ionic conductivity and mobility.^{17–20} 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.% as this range is expected to contribute optimum in PT as far as dielectric property is concerned.¹¹ Gd was incorporated in PT in varying concentration, i.e., 1, 3 and 5 wt.% based on the stoichiometric formula $\text{PbTi}_{0.8-x}\text{Te}_{0.2}\text{Gd}_x\text{O}_3$ (PTTeG). Study of changes in dielectric constant and piezoelectric coefficient in PTTeG due to change in dopant concentration of Gadolinium is reported in this paper.

2. Experimentals

PbO , TiO_2 , TeO_2 and Gd_2O_3 , all having AR grade, were taken as starting materials. Powders were taken based on stoichiometric formula $\text{PbTi}_{0.8-x}\text{Te}_{0.2}\text{Gd}_x\text{O}_3$ (PTTeG), $x = 1, 3$ and 5 wt.% and feed in milling container of HEBM (high energy ball milling) machine for the time period of 1 to 10 h. Detail fabrication method is discussed in other paper of the author.⁷ Additional amount of PbO (2.5% wt.) was added in milling powder to make up the lead deficiency during sintering as reported by others.^{7,8} Differential scanning calorimetric analysis (DSC) and thermogravimetric analysis (TGA) analysis of green powder were carried out to know the completion of solid state reactions and the weight loss that occurred during heating. Pelletization of calcined powder was done by applying a pressure of 15 MPa. Binder used in powder was 5 wt.% polyvinyl acid (PVA). Pellet of diameter 12 mm and thickness 3 mm was then sintered at 650°C , 700°C , 800°C for 2 h at the rate of 5°C per minute heating,

the soaking time was kept for 2 h 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 PTTeG powders milled for 10 h was found most suitable as it gives pure single-phase tetragonal structure having peaks at hkl values [001], [101], [110], [200]. Pellets sintered at 800°C were tested for dielectric constant (at varying frequency as well as varying temperature). Piezoelectric coefficient value of pellet sintered at 800°C were also measured at varying poling fields. 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.% Te and 1 wt.% of gadolinium is shown in Fig. 1. DSC micrograph clearly indicated no exothermic or endothermic peak during change in temperature up to 280°C, but afterward rise in microvolt was observed but no exothermic or endothermic peaks were 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 noticeably indicated formation of required PT phase during milling of powder by HEBM itself.^{30–32} In TGA curve, almost no weight loss was observed between 510°C to 880°C. This helped in selecting the calcinations temperature around 510°C.^{33,34} Sharp decline is seen in TGA curve after 880°C due to fast decomposition of lead present in material at high temperature.^{30–34}

Fig. 1. DSC/TG analysis micrograph of PTTeG (1 wt.% of Gd).

3.2. XRD studies of PTTeM

XRD micrograph of PTTeG (5 wt.% of Gd) milled for 10 h 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 in agreement with JCPDF file (01-075-1605). Pure single-phase tetragonal structure having peaks at hkl values [001], [101], [110], [200], etc. were 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 435 nm.

3.3. Microstructure studies of PTTeGd

Optimum density in the PTTeG was observed as 7.12 g/cm³ at 800°C. Variation in density in sample at different sintering temperature was observed as 5.96 g/cm³ at 700°C and 6.82 g/cm³ at 750°C. Micro structural study of PTTeGd pellet sintered at 800°C was done by SEM and AFM. SEM photograph of PTTeG (5 wt.% of Gd) ceramics is shown in Fig. 3. Nano size grains can be seen clearly in the photograph. Average grain size was found to be 470.24 nm.

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

3.4. Studies of dielectric constant

Measurement of Dielectric constant of pure PT and modified with Te and Gd at varying concentration are displayed in Fig. 5. Dielectric constant had shown maximum value in the case of 5 wt.% incorporation of Gd and it had shown increase with the increase of dopant concentration and increase of temperature. Dielectric constant in the case of PTTeG (5 wt.% Gd) was found maximum in comparison to others and it was 280 at room temperature and 2543 at cure temperature, i.e., 480°C. This result is comparable and even better in some of the reported values on fabrication of PZT or PT by different chemical method.^{30–36} The distortion may get pronounced if

Fig. 2. XRD micrograph of PTTeGd (5 wt.% of Gd).

Fig. 3. SEM photograph of PTTeG (5 wt.% of Gd) sintered pellet.

Fig. 4. AFM photograph of PTTeG (5 wt.% of Gd) sintered pellet.

the dopant ion is off valent or aliovalent. Te has an ionic radius greater than that of Ti. Gd has an ionic radius much smaller than that of Ti. So that way Gd doping will distort the crystal lattice of lead titanate but Gd ion being isovalent with

Fig. 5. Dielectric constant of PTTeG (Gd = 0%, 1%, 3% and 5%) ceramics at varying temperature.

Fig. 6. Variation of piezoelectric strain coefficient (d_{33}) in PTTeG (Gd = 0%, 1%, 3% & 5%).

lead, the distortion produced may not get pronounced in comparison to Te doping. This may be the reason behind shifting of T_c towards higher temperature side.^{8,9} Double peaks and shifting of peaks toward higher temperature range was an indication of presence of Relaxer behavior^{16,27,29} in PTTeG.

3.5. Piezoelectric coefficient (d_{33}) studies

Piezoelectric coefficient (d_{33}) studies of pure PT as well as PTTeGd (Gd = 1%, 3% and 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 39 Kv/cm. Maximum d_{33} value was observed in the case of PTTeG (Gd = 5%), it was 240×10^{-12} C/N. This value was found greater by 28% as reported by Kour *et al.*¹⁹ in similar material. This high value of d_{33} is comparable to the result reported by other workers adapting different chemical methods of fabrication. Increase in d_{33} value with the increase of poling field can be attributed to the change in polarity and corresponding, increase in polarization.^{36–43}

4. Conclusions

Nano particle size and nano grain size Lead Titanate (PT) doped with tellurium and gadolinium 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 PTTeG powders milled for 10h 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 5 wt.% Gd-doped PTTeG was found as $a = 4.9168 \text{ \AA}$, $b = 4.9168 \text{ \AA}$, $c = 5.4089 \text{ \AA}$. Crystallite size was found as 435 nm. AFM analysis showed clearly the presence of three-dimensional nano particles in the material. As per SEM study, average grain size was observed as 470.24 nm. Dielectric constant had shown maximum value in the case of 5 wt.% incorporation of Gd and it had shown increase with the increase of dopant concentration and increase of temperature. Dielectric constant in the case of PTTeG (5 wt.% Gd) was found maximum in comparison to others and it was 280 at room temperature and 2543 at Curie 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 methods. Double peaks and shifting of peaks toward higher temperature range were an indication of presence of Relaxer behavior in PTTeG. It had been observed that d_{33} value increases with increase of poling field and dopant concentration of Gd. 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 PTTeG (Gd = 5%), it was $240 \times 10^{-12} \text{ C/N}$. This value was found greater by 28% as reported by Kour *et al.* in similar material. This high value of d_{33} is comparable to the result reported by other workers adapting different chemical methods of fabrication. Increase in d_{33} value with the increase of poling field can be attributed to the change in polarity and corresponding increase in polarization.

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