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RESEARCH ARTICLE

THERMO GRAVIMETRIC STUDIES OF FERROELECTRIC CERAMIC $PbBaTiO_3$

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ABSTRACT

The nano crystalline ferroelectric perovskite ceramic Lead Barium Titanate ($PbBaTiO_3$) is designed and synthesised by high temperature solid state reaction method (weighing, mixing, milling and calcination of raw materials). This perovskite is made in a specially designed furnace which allows oxygen flow during cooling process after calcination. Final calcination temperature is optimised by trial and error method at 900 degree Celsius to obtain desired crystal structure, crystal system and phase formation. This paper discusses the thermal properties of PbBaTiO3 using TGA, DTG and DSC and IR spectroscopy methods of thermal characterization.

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INTRODUCTION

Lead Barium Titanate or $PbBaTiO_3$ is a newly designed ceramic material, synthesised via assisted solid state thermo chemical reaction method. It is a ferroelectric polycrystalline solid having particle size in nanometer range. It is a perovskite oxide in tetragonal crystal system belonging to the family of barium titanate. Perovskite oxide ceramics are very significant in research field because their high dielectricity enable them to contribute in high storage capacitors and their good optical properties make them suitable candidates in imaging devices working within the infrared region of EM spectrum. Barium titanate ($BaTiO_3$) ceramics have been extensively studied during the last few decades because of its excellent electrical and electro mechanical properties (Othman *et al.,* 2014). $BaTiO_3$ is chemically and mechanically very stable, exhibits ferroelectric properties above room temperature, has Curie temperature at 120^oC (Safitri *et al.,* 2016), high dielectric constant (Gao *et al.,* 2011) at room temperature ≥1500, low dielectric loss (Vijatovic *et al.,* 2008) and enormous band gap energy (Gao *et al.,* 2011). Barium titanate is used in applications such as high-density multilayer ceramic capacitors (Ramakanth and Raju, 2014), Ferroelectric Random Access Memory (FRAM), Dynamic Random Access Memory (DRAM), characteristic of piezoelectric can be used for microactuator and sensor, characteristic of polarizability can be used Nonvolatile Ferroelectric Random Access Memories (NvFeRAMs) (Hadiati *et al.,* 2014). The $BaTiO_3$ ferroelectric material has used as a solar cell material since it generally has a gap energy ± 3 eV and a conductivity of 105 S/cm so that a small band gap can enhance the photovoltaic effect of ferroelectrics (Jiang *et al.,* 2013).

The authors here investigate the thermal properties of $PbBaTiO_3$ whose final calcination temperature is optimised at 900^0C. TGA, DTG, DSC and IR spectroscopy is used to analyse thermal behaviour of nanoparticles at a high temperature (Wendlandt, 1986; Yao *et al.,* 1995; Brown, 1990). The free energy trapped in the grain interfaces and boundaries of nano crystalline materials influence the phase transitions. Usually such materials exist in metastable states of thermal inequilibrium. Hence one can get information regarding the long-term thermal stability of such systems by studying the transition from nanophase-state to thermal equilibrium state. The phase transformations in nano materials due to temperature change is much different from that of bulk crystals and such phase transformations in nano structured materials are reported (Qin *et al.,* 1993). The free energy of nano particles is always higher than that of its conventional counterpart (Potty *et al.,* 2001).

MATERIALS AND METHODS

Preparation of the sample: $PbBaTiO_3$ is prepared by solid state reaction route. We used raw materials in powder form which are of high purity - $BaCO_3$, TiO_2 and PbO_2. They are weighed as per the molecular formula given by

$$PbO_2 + BaCO_3 + TiO_2 = PbBaTiO_3 + CO_2 + O_2$$

Raw materials are then hand mixed in an agate mortar for three days. After mixing, the powders are milled in a ball mill along with zirconium beads. Ball milling is done for three months with daily sieving and mixing so that we obtain a homogeneous mixture. Then the mixture is attrition milled for

three hours. The powder sample mixed and milled, fired at various temperatures - 30˚C, 500˚C, 850˚C and 900˚C in a special furnace followed by oxygen annealing on cooling. Synthesised ceramic after final calcination is then subjected for thermal characterization studies. Thermo Gravimetric Analysis (TGA), Differential scanning calorimetry (DSC), Differential Thermo Gravimetry (DTG) and Infrared spectroscopy are used and information regarding the long-term thermal characteristics are taken out.

TGA analysis: Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere (Mony *et al.,* 2014). It quantifies the mass of the sample against temperature or time due to humidity loss of powders, decomposition of carbonates e.g. $CaCO_3$ --> $CaO + CO_2$, oxidation of metals etc. with high precision and accuracy so that we can document the pathway of thermal degradation and loss in the mass and calculate the thermodynamic parameters of the sample. It can also be used to check the purity of the sample. The thermal analysis instrumentation (Fig.1) involves sample holder, detectors to measure the specific property of the material, an enclosure or chamber for conduction of the experiment and data processing system (Jacob and Isac, 2014). Figure 2 Shows a schematic thermo balance instrumentation. Ceramic undergoes heating and chilling within the furnace. The initial mass of the ceramic is noted and then temperature is raised in uniform steps at a constant rate. Change in mass is documented as a function of temperature (T). Graph with weight on vertical axis (y) plotted against temperature in horizontal axis (x) is called thermogravimetric curve or simply thermo gram.

Some significant factors influencing a thermogram are

- Mass, volume and form of the prepared sample
- Shape and nature of the sample holder
- Nature and pressure of the air in the sample chamber and
- Rate of scanning

Where the rate of reaction is characterized by two temperatures, T_i and T_f, which are called the procedural decomposition temperature and the final temperature (PST 522E). T_i stands for the onset temperature at which the degradation starts while T_f represents the temperature after degradation process and both T_i and T_f are influenced by the experimental conditions (Jacob, 2017).

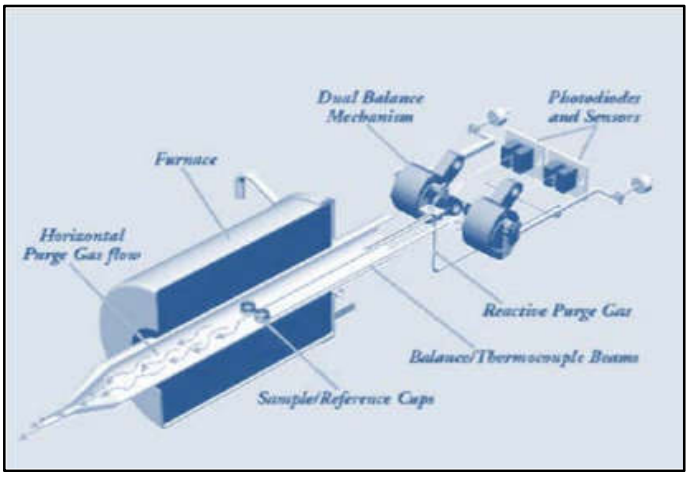

Figure 1. TGA apparatus

DTA analysis: One among the major thermo analytic techniques is Differential Thermal Analysis or DTA. Here, the concerned ceramic and an inert reference material are to come across same thermal cycles and any difference in temperature between the ceramic and the sample are accurately documented. A graph is constructed with differential temperature against time or temperature and it is called DTA curve. Endothermic and exothermic deviations of the sample can be observed in comparison with the reference. So a DTA curve gives information about possible processes that have happened such as phase transitions, dehydrations, melting, crystallization, sublimation etc. The temperature dependence of DTA technique is applied to determine the characteristic temperatures like transition temperature, melting temperature and the crystallization temperature of the material (Pesetskii *et al.,* 2005). A DTA instrumentation system contains a sample holder, thermocouples, sample containers, ceramic or metallic block, furnace, temperature programmer and a recording system (Fig.3).

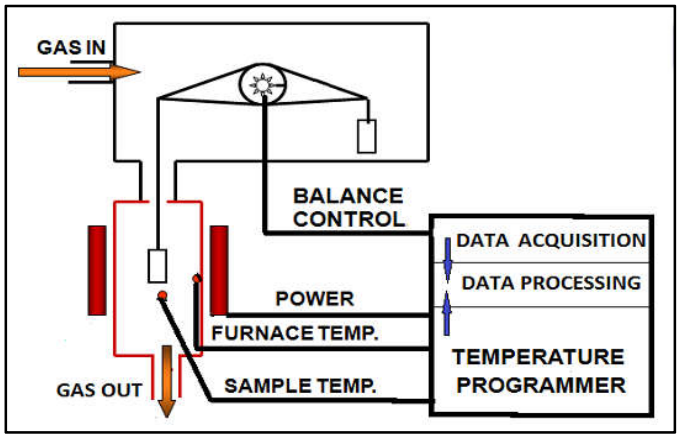

Figure 2. A Schematic thermo balance instrumentation

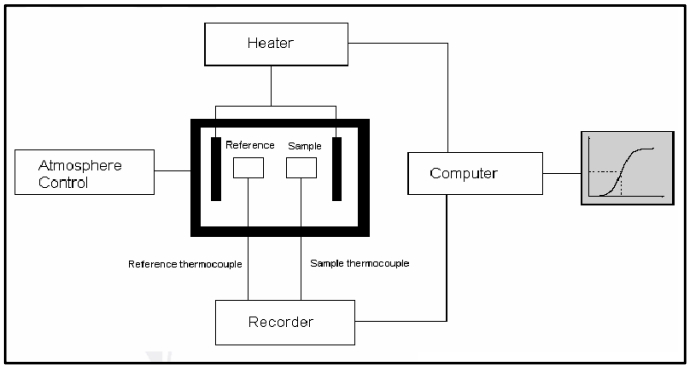

Figure 3. Schematic representation of DTA System

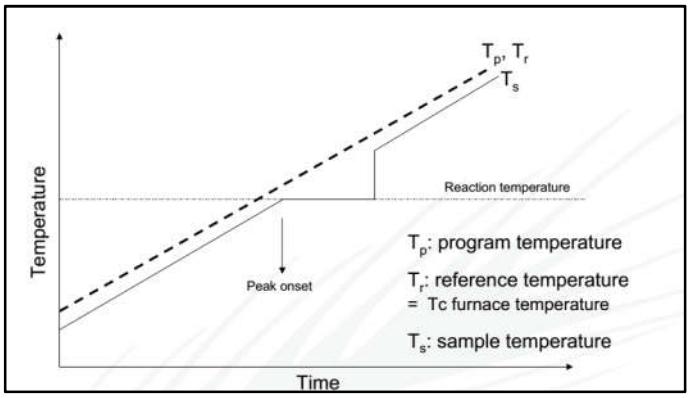

Figure 4. Schematic diagram showing the different temperatures in the DTA system

Thermocouples are placed in the ceramic and the reference material and both are connected to a voltmeter. Changes in the thermal behaviour between the samples cause deflections of the voltmeter. Figure 4 shows schematic diagram showing the different temperatures in the DTA system. DTA curve acts as a finger print for identification purposes and quality control.

DTG analysis: Differential Thermo Gravimetry simply known as DTG is very much alike TGA. We know that in TGA analysis, variation in mass with respect to change in temperature is recorded. In DTG analysis a derivative curve for change in mass is plotted. In a DTG curve what we obtain is – dm/dt. DTG curve helps to find out the temperature at which there is maximum weight loss or maximum weight gain. That temperature is called inflection point.

DSC analysis: Calorimeter is used to quantify the heat flowing into or out of a material. A differential calorimeter is used to quantify the heat flow in or out of a sample with respect to a reference. A differential scanning calorimeter does all of the above. Differential Scanning Calorimeter (DSC), quantifies the heat flows associated with phase transitions in solids as a function of temperature in a controlled atmosphere. It gives quantitative and qualitative data on the physical and chemical changes involving endothermic and exothermic processes. Figure 5 shows a Schematic representation of DSC Curve. Differential Scanning Calorimeter (DSC) is a powerful and feasible tool in thermal studies.

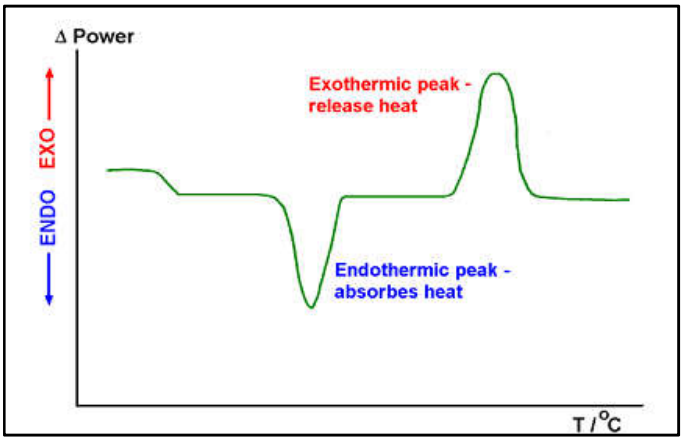

Figure 5. Schematic representation of DSC Curve

IR spectroscopy analysis: IR spectroscopy is a kind of absorption spectroscopy, utilizing infrared radiation belonging to the electromagnetic spectrum of radiations. Molecular vibrations are quantized. Energy levels of molecular vibrations correspond to particular frequencies of IR radiation, especially to the frequencies in the readily accessible mid IR region ranging from 4000cm^{-1} to 200cm^{-1}. Infrared radiation interacts with the molecules for which energy difference between vibrational energy levels and rotational energy levels are small. In such molecules dipole moment can be altered by vibrations. This is the primary condition for a molecule to exhibit IR spectra. When a solid is subjected to IR radiation, certain frequencies corresponding to the vibrations of molecular bonds in the structural constitution of the solid are absorbed by the solid and certain frequencies are transmitted through the solid. Absorbed radiations are used for increasing the vibrational energy levels of molecular bonds. Bonds have two types of vibrations. They are bond stretching vibrations and bond bending vibrations. Absorbed IR may correspond to either bending vibrations or stretching vibrations of molecular bonds. Each compound has a characteristic IR spectra distinguished by a set of characteristic peaks, especially in the region 1500cm^{-1} to 500cm^{-1}. This region is called finger print region of the compound. IR spectroscopy is used to identify solids, their molecular bonds and structural changes in the systems. Figure 6 gives block diagram of an IR spectrometer. Here a Fourier Transform Infrared spectrometer called Perkin - Elmer– Thermo Nicolet, Avatar 370 is used. 400- 4000 cm^{-1} is the range of wave number used for the IR study.

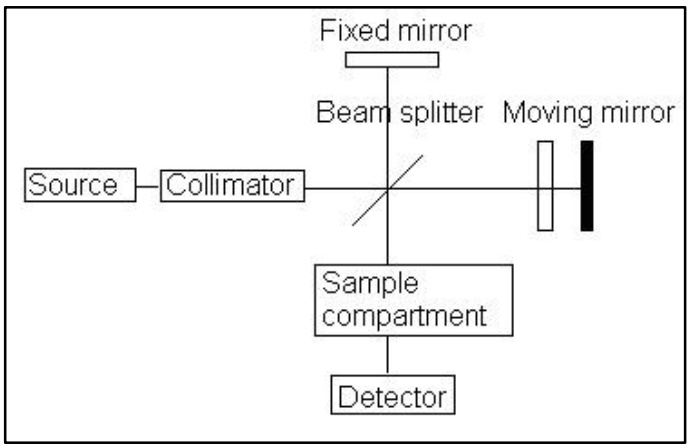

Figure 6. Block diagram of an FTIR spectrometer

RESULTS AND DISCUSSION

TGA analysis: Graphs are plotted constructed with plotted weight on y axis against temperature on x axis (Figure 7) and percentage of weight on y axis against temperature on x axis (Figure 8). Temperature is increased from 40^{0}C to 750^{0}C at a rate of 10 ^{0}C/min. As temperature increases weight of the sample decreases very slowly.

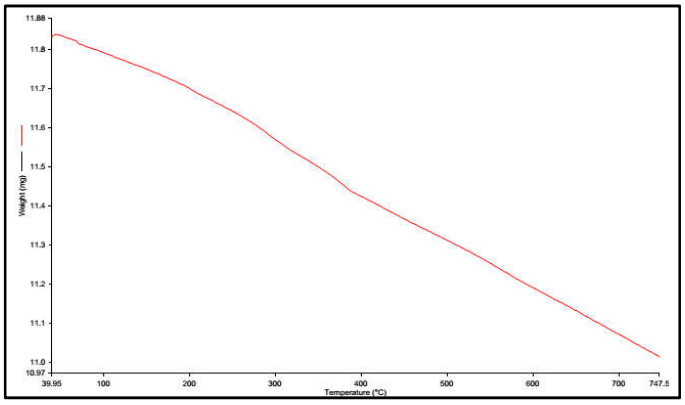

Figure 7. TGA Curve (Weight vs.Temperature)

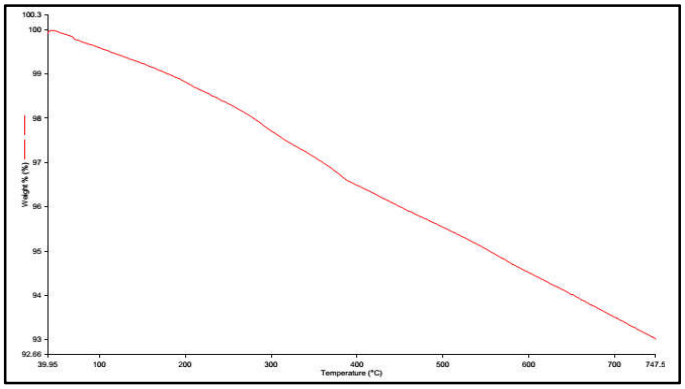

Figure 8. TGA Curve (Weight percentage vs. Temperature)

The material $PbBaTiO_3$ initially has a weight of 11.836 mg at 40 degree Celsius. As temperature increases weight slowly decreases in a linear way and attains a value of 11.02 mg at 750°C. So as temperature increases from 40°C to 750°C the loss in weight is 0.816 mg. From the weight percentage vs. temperature graph, we can see that the loss of weight in percentage is 6.89 %. The endothermic peak visible at 77.2 degree Celsius at a weight corresponding to 11.826 mg or 0.084 % from the initial weight implicates dehydration. Water content is 0.01 mg which is insignificantly small. The endothermic peak visible below 400 degree Celsius corresponding to a weight loss of 3.5 percentage from the initial weight represents escape of freely bound molecules. So weight loss up to 750 °C shows that the sample is a good ceramic which can withstand high temperatures. Very small deviations from the linear curve represent minute lattice distortions. Much weight loss is not expected. Sample is carbon free and has poor water content. This indicates the purity of the sample.

DTG analysis: The DTG curve of $PbBaTiO_3$ is given in Figure 9. Derivative weight of the sample is taken on y axis which is marked against temperature on x axis. All peaks are clearly visible in the DTG profile. Result obtained from TGA study contains information about the thermal stability of the sample. The endothermic peak visible at 77.2 degree Celsius corresponding to dehydration and the endothermic peak visible below 400 degree Celsius corresponding to the escape of freely bound molecules confirm the TGA profile. DTG profile is complimentary to TGA study but it is more adaptable than the TGA graph. Phase transition of $PbBaTiO_3$ is taking place at a high temperature. Energy trapped in the grain defects like grain boundaries and grain interfaces influences these high energy phase transitions. DTG reveals the inflection temperature, i.e., the temperature at which a maximum peak or a maximum depression is obtained. Inflection temperature is defined as that particular temperature for which mass change is maximum. Maximum degradation temperature in this case, otherwise known as inflection point is obtained at 77.2 degree Celsius for $PbBaTiO_3$. At 77.2 degree Celsius weight of the sample is 11.826 mg. 0.01 mg amount of moisture is lost. This amount is negligible. This proves that trapped moisture is very small. Hence there is only 0.084 % weight loss from the initial weight. So TGA and DTG analyses clearly indicate the thermal stability of the sample. It also confirms that the sample is pure.

DSC analysis: The DSC curve (Figure 10) clearly indicates that the phase transition is taking place at a very high temperature. The trapped energy inside the grain interfaces of the crystal influences this high energy phase transition. Other minute lattice imperfections arise due to the miniature size of particles. Different or modified behaviour of nanocrystalline materials from bulk crystalline materials is due to these miniature sized particles. The endothermic peaks with slight mass loss obtained in the DSC profile indicating dehydration and the loss of loosely bound molecules once confirm TGA and DTG results. From the Figure, heat reaction is initiated by an endothermic reaction (dehydration) at 77.2 degree Celsius and then followed by an endothermic reaction (escaping of free molecules) below 400 °C. Purity, quality and thermal stability of the sample are again confirmed.

IR analysis: FTIR spectrum of $PbBaTiO_3$ is shown in Figure 11. Various absorption peaks in the spectrum are attributed to the various vibrating bonds between the molecules of the ceramic.

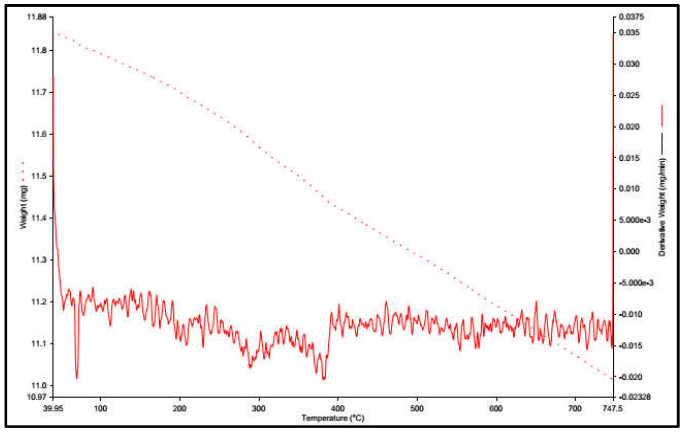

Figure 9. DTG curve of the sample $PbBaTiO_3$

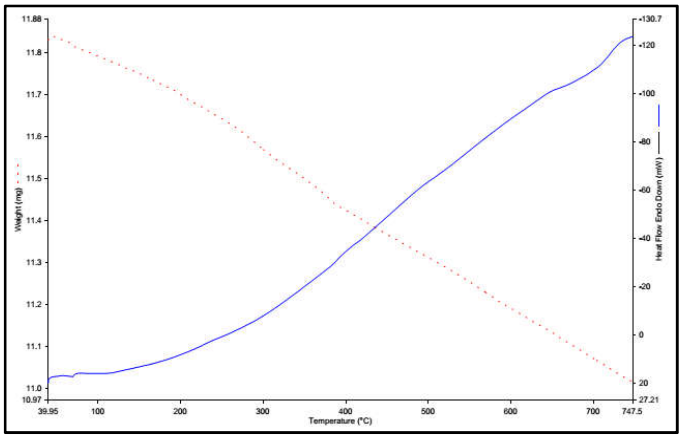

Figure 10. DSC curve of $PbBaTiO_3$

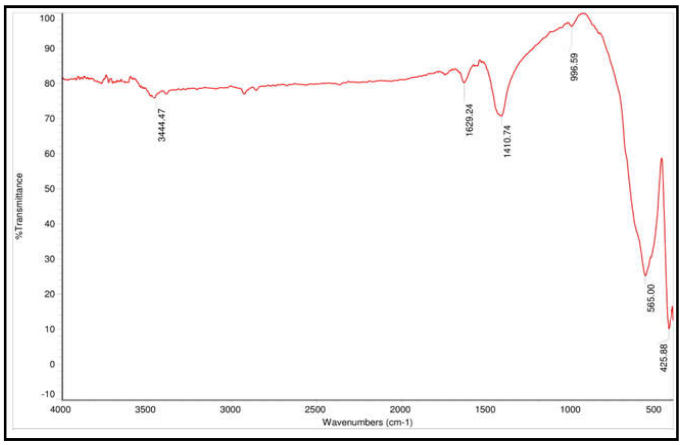

Figure 11. FTIR spectrum of $PbBaTiO_3$

FTIR spectrum contains so many absorption peaks especially in the finger print region, denoting characteristic energy levels and characteristic bond vibrations. The vibrational energy levels of the spectrum are quantised (Nair, 2015). Intense peaks are in the finger print region of the spectrum. There is a strong and intense band visible at 425.88cm^{-1}.This band attributes to the stretching vibrations of Pb-O-O-Ti bond. The band obtained at 565.00cm^{-1} denotes the stretching vibrations of Ti-O bond. This band confirms the formation of $PbBaTiO_3$ (Turky *et al.*). Band at 996.59cm^{-1} indicates the bending vibrations of Ti-O bond and the band at 1410.74cm^{-1} indicates the stretching vibrations of Ba-Ti-O bond. The band visible at 1629.24cm^{-1} indicates the stretching vibrations of Ti-OH bond. The band at 3444.47cm^{-1} is attributed to the O-H stretching vibrations (Liu *et al.,* 2012; Xia *et al.,* 2009). O-H bond is that of absorbed moisture when subjected to surroundings. Absence

of peaks at 1450cm^{-1} of C-O double bond and at 1240 cm^{-1} of C-O single bond suggests that the ceramic is carbon free. So the obtained IR spectrum gives the elemental structure of the ceramic which is in agreement with the molecular formula used while synthesising the ceramic. It also certifies the purity of the sample.

Conclusion

Thermal properties of the nanocrystalline ceramic $PbBaTiO_3$ are studied based on different thermal analysis techniques. Here TGA, DTG, DSC and FTIR analyses are used. In thermo gravimetric analysis when temperature is increased weight of the ceramic suffers minute loss. In a temperature range from 40°C to 750°C there is a minute mass loss of 0.816 mg. As mass loss is insignificantly small we consider that the ceramic has good thermal stability. The ceramic is able to resist high temperatures. Two peaks are obtained in the TGA spectrum-first one at 77.2 °C is the inflection point and the second one below 400 °C. Minute mass loss at inflection point attributes to the loss of absorbed moisture via evaporation. Endothermic peak below 400°C suggests the escape of freely bound atoms in the crystal lattice. Water absorbed by the sample is negligibly small (0.01 mg). Some small variations from linear curve are observable which signify minute lattice distortions. DTG profile is complimentary to TGA study. Phase transition of $PbBaTiO_3$ is taking place at a high temperature. Energy trapped in the grain defects like grain boundaries and grain interfaces influences these high energy phase transitions. DTG reveals that the inflection temperature or maximum degradation temperature in this case is 77.2 degree Celsius for $PbBaTiO_3$. At 77.2 degree Celsius a very negligible amount of moisture is lost. This proves that trapped moisture is very small. So TGA and DTG analyses clearly indicate the thermal stability of the sample. It also confirms that the sample is pure. The DSC curve clearly indicates that the phase transition is taking place at a very high temperature. The endothermic peaks with slight mass loss obtained in the DSC profile indicating dehydration and the loss of freely bound molecules once confirm TGA and DTG results. The analysis of DTG curve of the prepared polycrystalline ceramic sample clearly indicates the presence of high temperature phase transition in the ceramic. High thermal stability of the ceramic sample is confirmed by DTG analysis. The DSC curve confirms the exothermic processes taking place within the sample. Purity and thermal stability of the samples are again confirmed. FTIR spectrum with various bands indicating Pb-O-O-Ti, Ti-O, Ba-Ti-O, Ti-OH and O-H bonds reveals the elemental composition of $PbBaTiO_3$. Very little absorbed water and absence of organic groups testify that the ceramic is pure. On the basis of results from TGA, DTG, DSC and IR thermal methods we conclude that $PbBaTiO_3$ is formed, has very good thermal resistance, quality and purity.

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