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Thermal Behaviour of Nano Crystalline Ceramic PbSrBaTiO

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Abstract

Nano crystalline ceramic PbSrBaTiO is prepared from mechanically mixed powders of high purity raw materials. Mechanical mixing is done by high-energy ball milling and attrition milling process. The prepared material is then calcined in ambient air and optimum temperature so that the desired homogeneity and phase formation is acquired. EDX analysis is done to find out the elemental composition. Using TGA, DTA and DSC thermal behaviour of the sample at a high temperature is studied.

Keywords: PbSrBaTiO ,TGA, DTA, DSC.

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1. Introduction

Materials crystallizing in perovskite structures are important for a wide range of applications .The perovskite systems are considered as a potential candidate in ceramic industry. A ceramic material is an inorganic non metallic solid comprising metal, non metal or metalloid atoms primarily held in ionic and covalent bonds. Ceramic materials are brittle, hard, strong in compression, weak in shearing and tension. They withstand chemical erosion that occurs in an acidic or caustic environment. Conventional solid state reaction method is a common and effective way to fabricate modern ceramics [1]. Ceramics generally can withstand very high temperatures such as temperatures that range from 1000˚ C to 1600˚ C (1800˚ F to 3000˚ F). The Lead Strontium Barium Titanate (PbSrBaTiO /PSBTO) is a type of perovskite ceramic superconductor with high dielectric constant. Before final heating at 950 ˚ C, the material PSBTO is treated at different temperatures, 30˚ C, 500˚ C and 800˚ C[2]. It is having a complex structure. High dielectric constant (High-K) ceramic composites have become potential candidate materials for integration into high frequency electronics. Detailed understanding of this class of materials will help electronic industry in planning, design and processing of these materials.

In this work the authors are presenting the thermal behaviour of Lead strontium barium titanate (PSBTO) calcined at 950^0C. TGA, DTA and DSC is used to analyze thermal behaviour of nanoparticles [3-5] at a high temperature. Using EDX elemental composition is obtained. Large amount of energy is stored in the grain boundaries and in other types of defects. Nanophase materials are in metastable state 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[6]. The phase transformations in nano materials due to temperature change is much different from that of bulk crystals. Phase transformations in nano structured materials reported [7]. The free energy of nano particles are always higher than that of its conventional counterpart[8].

2.EXPERIMENTAL.

2.1. Preparation of the Sample

Ceramics with the chemical formula PbSrBaTiO is prepared from high purity raw materials Lead oxide, Strontium Carbonate, Barium carbonate and Titanium dioxide. The raw materials are first weighed according to the stoichiometric formula of the ceramics desired. The powders of the required ceramics then mixed mechanically by hand mixing, then ball milled for a long time followed by attrition milling. Then the material calcined at a temperature 950˚C in a special furnace. During the calcination the solid phase reaction takes place between the constituents. Proper calcination at the right temperature is necessary to obtain the best electrical and mechanical properties. After the furnace is off, on cooling the oxygen is allowed to flow into the furnace at intervals (Oxygen Annealing). A final furnace temperature of 950^0C is maintained. Control of temperature is often necessary to ensure that the desired crystalline phase is formed with optimum particle size [9]. Then X-ray diffraction spectrum

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of these materials was taken and analyzed[2]. For thermal studies TGA, DTA and DSC data were analyzed. From EDX, the composition details of the prepared ceramics were determined.

2.2. 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. TGA measures a sample's weight as it is heated or cooled in a furnace. Factors such as sample mass, volume and physical form, the shape and nature of the sample holder, the nature and pressure of the atmosphere in the sample chamber, and the scanning rate have significant influences on the characteristics of the recorded TG curve. Because most events that occur in a TGA are kinetic in nature, any experimental parameter that can affect the reaction rate. The reaction is characterized by two temperatures, Ti and Tf , which are called the procedural decomposition temperature and the final temperature[10]. Figure 1 shows a modern TGA.

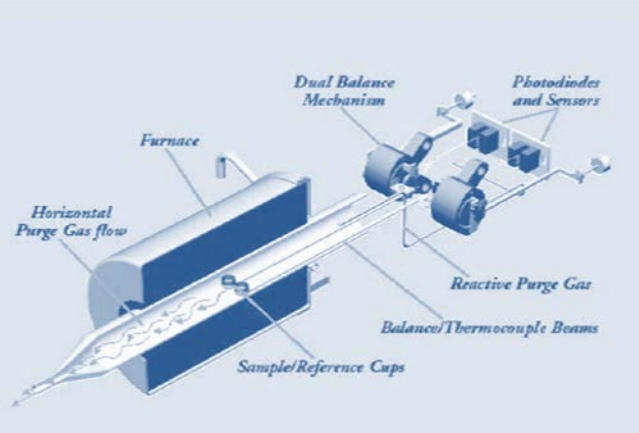

Fig. 1 A modern TGA

Thermogravimetric Analysis (TG) determines the weight changes of a sample, whereas Differential Thermal Analysis (DTA) measures changes in temperature between a sample and a reference, as a function of temperature or time.TG and DTA curves of the sample were recorded using Perkin Elmer, Diamond TG/DTA with Flexible axial and radial view instrument, with high concentration capabilities. TGA is plotted in figure 2 (a) & (b). DTA/DTG is plotted in figure 3.

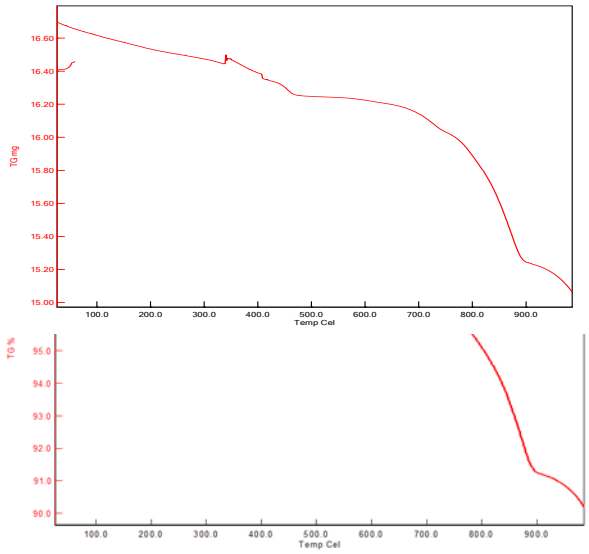

Fig.2 (a) & (b) TGA curve of PSBTO (in weight and in percentage vs. Temp.)

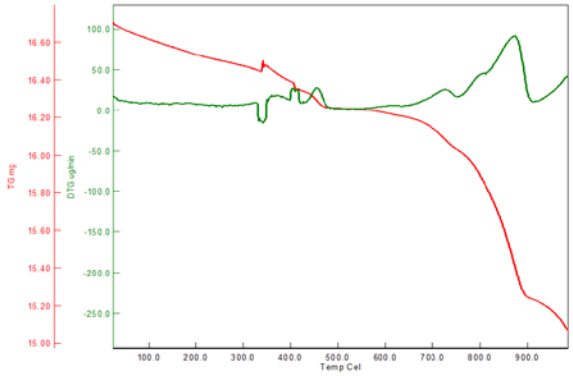

Fig.3. DTA /DTG curve of the sample PSBTO

2.3. DSC Analysis

DSC (Differential Scanning Calorimetry) measures the amount of heat energy absorbed or released by a sample, as it is heated, cooled or held at a constant temperature. The applications of DSC are numerous, either for routine quality control measurements or in research, where high sensitivity and flexibility are important aspects. DSC curve was plotted using Mettler Toledo DSC 822e which is shown in figure 4.

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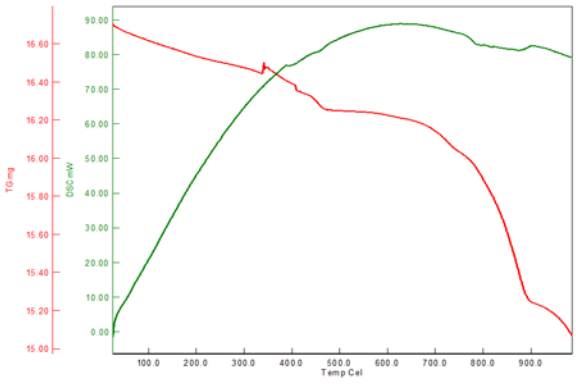

Fig. 4 DSC curve of PSBTO

Differential scanning calorimetry (DSC) monitors heat effects associated with phase
transitions and chemical reactions as a function of temperature. In a DSC the difference in heat
flow to the sample and a reference at the same temperature, is recorded as a function of temperature.. The reference is an inert material such as alumina. The temperature of both the sample and reference are increased at a constant rate. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes. The heat flow difference between sample and reference can be either positive or negative. In an endothermic process, such as most phase transitions, heat is absorbed and, therefore, heat flow to the sample is higher than that to the reference. Hence dH/dt is positive. In an exothermic process, such as crystallization, dH/dt is negative.

2.4. EDX Analysis

The composition details (EDX) of the prepared nanocrystalline ceramic powder PSBTO at 950°C [2] is plotted in figure 5 using ISIS Link Oxford Instrument UK. In this technique an electron beam of 10-20 KeV strikes the surface of a sample which causes X-ray to be emitted from point of incidence. When an X-ray strikes the detector, it will generate a photoelectron which in turn generates electron-hole pairs. The energy of the X-ray emitted depends on material under examination. The energy of the characteristic X-ray emitted from the different elements is different and thus it gives the unavoidable signature of the particular element. A strong electric field attracts the electrons and holes towards the opposite ends of the detector. The size of the pulse thus generated depends on the number electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. Table 1 indicates the contents of the material.

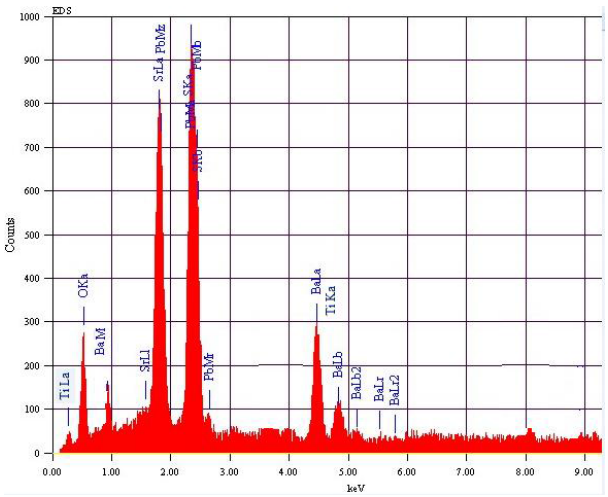

Fig.5 EDAX spectrum of PSBTO

Table 1 shows the contents of the elements in the sample (PSBTO).

Element	(keV)	Mass%
Pb M	2.342	22.43
SrLα	1.806	40.33
BaLα	4.465	
BaM	0.972	18.24
TiLα	0.452	
TiKα	4.508	13.65
OKα	0.525	5.35
Total		100

3. Results and Discussion:

From the XRD profile of the sample (YSBTO) it is understood that the intensities of the peaks decreases on increase of temperature[2]. This intensity anomaly can be explained as the rigorous thermal agitations of the lattice planes resulting in the formation of new phase at the high temperature. When a material heated from room temperature to high temperature, the amplitude of the thermal vibrations increases. That means, as the atomic vibration amplitude increases, the intensity of the diffracted beam also decreases because it has the effect of smearing out lattice planes. the intensity of a diffracted beam decreases as the temperature is raised. [11]. XRD spectrum for the different temperatures gave a clear idea about the maximum intensity peak shifting corresponds to the different treating temperatures. And also get the maximum intensity peak difference [2]. The peak broadening in the XRD patterns clearly indicated the nature of the very small nanocrystals [2].
Heat treatment causes the particles to anneal and form larger grains, which of course indicates that the particles become larger. Hence, the large particle size of sample at 950oC is expected / confirmed. This also agrees with the higher crystallinity, as

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having larger grains means more long-range order, and hence more crystallinity[12, 13].

Thermal Characterization and Testing are Employed to Evaluate and Optimize the Chemical and Physical Properties of Ceramic Materials. From the TGA/DTA curves it is considered to be having mainly four stages. The material PbSrBaTiO which initially has a weight of 16.704mg attains 16.459 mg on heating to a temperature 320.0673 °C began to lose weight and reduces to 16.444 mg at 336.3683°C .The weight percentage gradually reduces and the loss percentage is 2.5.Then there is a small rise in weight and weight becomes 16.445 mg at 337.278°C which is not considerable. This may be due to distortion in lattice. Weight gain is .5 %.Again weight loses down to 16.253 at 474.818°C with a % of loss 1.7.Then there is a parabolic reduction in weight and it becomes 15.272 at 890.9689°C.Weight loss is 6%. From there onwards curve shows another slight parabolic path indicating reduction in weight. Weight reduces to 15.172 mg at 986.114°C with a loss % of 0.9.These can be seen from the TG curve given above. Moisture content is not appreciably observed. Loss on ignition is in total 10% upto 10000C. In these temperatures since the sample is a good ceramic material much loss is not expected.
The DTA curves are in confirmity with these observations. The study of the sample clearly shows that the phase transition is taking at a very high temperature. The free energy inside the interface regions of the nano materials affects the phase transitions. Changes in lattice imperfections also arise due to the miniature size of the particles.Hence nano materials have a different or modified behaviour than that of the bulk materials. Polymorphism in crystalline structure also can be observed.Thus the thermal stability of the sample can be confirmed from the TGA,DTA & DSC analysis. From the DSC curve of the sample it is evident that the process is endothermic.

EDX spectrum of PSBTO(Fig. 5) gave the information on the elemental composition of the material. The elemental compositions agree with the stoichiometric relations of the prepared compound. From the EDX spectrum, the five dominant peak positions at, 2.342, 10.550 keV (Pb M, Kα),1.806 keV (Sr Lα), 0.972, 4.465, 4.75, 5.47 keV (Ba M, Lα, Lβ, Lγ), 0.452, 4.508 keV (TiO2 Lα, Kα), 0.525keV (O Kα), correspond quite well to the energy pattern of the corresponding materials reported in the EDAX international chart, giving the evidence that Pb, Sr, Ba, Ti, O are present dominant in the sample PSBTO.Table.1, shows the percentage of the elements in the prepared PSBTO sample.

4. Conclusion

PSBTO ceramics were prepared successfully and characterized by XRD, SEM, and particle size measurement. XRD data confirmed the formation of the perovskite phase structure [2]. In this work TGA,DTA and DSC analysis was carried out and confirmed that much loss on ignition is not observed, characterisitic of a good ceramic material. The EDX analysis indicates the presence and percentage of the elements existing in the sample and it agree with the stoichiometric relations of the prepared compound. Each of these thermal techniques provides unique information that can be used to optimize the thermal and mechanical properties of the end product.

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References

[1]. Leow Chun Yan, Jumian Hassan, Mansor Hashim, Wong Swee Yin, Tan Foo Khoon and Wong Yick Jeng. Effect of Sintering Temperatures on the Microstructure and Dielectric Properties of SrTiO3 World Applied Sciences Journal 14 (7): 1091-1094, 2011 ISSN 1818-4952 © IDOSI Publications, 2011

[2]. Anusha Mony, V. S Vinila., Reenu Jacob, Sheelakumari Issac, Sam Rajan, Anitha S. Nair, D.J Satheesh, Jayakumari Isac. STRUCTURAL AND MORPHOLOGICAL STUDIES OF NANO CRYSTALLINE CERAMIC PbSrBaTiO6 AT DIFFERENT TREATING TEMPERATURES. Journal: Journal of Advances in Chemistry Vol. 10, No. 10,2014

[3]. W. W. Wendlandt, Thennal Analysis, 3'* Edition, John Wiley & Sons, New York (1986)

[4]. Y. D. Yao, Y. Y. Chen, (2. M. Hsu, H. M. Lin, C. Y. Tung, M. F. Tai, D. H. Wang, K. T. Wu, C. T. Suo, Nanostructured Materials 6 (1995) 933

[5].M. E. Brown, Themla1 Analysis, Techniques and Applications, Academic Press, New York (1990).

[6].EXPERIMENTAL TECHNIQUES - shodhganga.inflibnet.ac.in/bitstream/10603/468/8/08_chapter 2.pd a

[7]. X Y Qin,X J Wu,and L F Cheng:Nanostructured materials2,99(1993)

[8]. Sankaranarayanan Potty.S,2001.Synthesis of nanoparticles of certain materials and their Characterisation.

[9]. V.S Vinila,.,Reenu Jacob, Anusha Mony, Harikrishnan g Nair, sheelakumari Issac, Sam Rajan, Anitha S Nair, and Jayakumari Isac, 2014. XRD Studies on Nano Crystalline Ceramic Superconductor PbSrCaCuO at Different Treating Temperatures. Crystal Structure Theory andApplications,3,1-9.http://dx.doi.org/10.4236/csta.2014.

[10]. PST 522E – Synthesis and Characterization of Macromolecules –Ch12 Thermogravimetric Analysis.

ISSN 2348 – 7968

[11]. B.D Cullity,. (1978) Elements of X-Ray Diffraction. 2nd Edition, Addison-Wesley Publishing Company.Inc., Phillippines.

[12]. So, W.W., Jang, J. S,.. Rhee, Y. W, Kim, K. J., Moon, S.J.,. 2001. “Preparation of Nanosized Crystalline CdS Particles by the Hydrothermal Treatment”, Journal of Colloid and Interface Science, Vol. 237, No. 1, , pp. 136-141.

[13]. S. C., Ghosh, and C.Thanachayanont, , J. Dutta, , 2004, “Studies on Zinc sulphide nanoparticles for Field Emission Devices”. The 1st ECTI Annual Conference (ECTI-CON2004), Pattaya, Thailand, 13-14 May 2004, pp.145-148.