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Synthesis of Barium Titanate Powder Using Nano Sized Titania

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ABSTRACT- Barium titanate is a ceramic widely used in electronic industry because of its high dielectric constant and low tangent losses. The main objective of the research work was to synthesize barium titanate from micron sized barium carbonate and titanium oxide having different particle size (0.7 µm, 50-60 nm and 80-90 nm). The calcination temperature of barium titanate was 1150 ºC when micro sized barium carbonate and titanium oxide were used as starting materials. However, calcination temperature decreased to 900 and 950 ºC when micro sized barium carbonate and nano titanium oxide with particle size 50-60 nm and 80-90 nm were used respectively. Formation of phase pure tetragonal barium titanate powder was confirmed using x – ray diffraction (XRD) in each case. The morphology of the powders was studied using scanning electron microscopy (SEM). The particle size of barium titanate reduced from 0.7 µm to 0.5 µm when nano sized titania was used as starting material.

KEYWORDS: Barium titanate, particle size, titania, XRD.

I. INTRODUCTION

Barium titanate is a ceramic widely used in electronic industry because of its high dielectric constant and low tangent losses. It is often used as basic ferroelectric material in electronic components such as multilayer ceramic capacitors (MLCC), positive temperature coefficient thermistors (PTC), electro-optic devices, memory applications, sensors and actuators etc. [1].

Traditionally, $BaTiO_3$ is prepared using a high-temperature (>1100 ºC) solid-state reaction between $BaCO_3$ and TiO_2 which yields large crystal grains (>3 µm) with a wide range of shape and size. Moreover, these powders result in less chemical homogeneity. Even if the ratio of $BaCO_3/TiO_2$ is one it may result in intermediate phases which are retained in end product. However, wet chemistry methods such as co precipitation, hydrothermal, micro emulsion and sol gel process offer advantages in terms of processibility, phase purity, homogeneity and controlled stoichiometry but still these methods also pose serious problems. For example, first three methods have complicated washing conditions which are difficult to control. Sol-gel process requires precursors that are highly expensive and are not commonly available. Thus, despite several drawbacks of solid state reaction method, it becomes necessary to study some new aspects of this method because of its amenability to large scale production [2-3].

In view of the above discussion, the main objective of this research was to synthesize barium titanate using micron sized barium carbonate and nano sized titania of different particle size by solid state reaction route.

II. EXPERIMENTAL

Barium titanate powders were synthesized using barium carbonate ($BaCO_3$) of fixed particle size and titania (TiO_2) of different particle size. AR grade micro sized $BaCO_3$ (catalogue no: 23710-8) and TiO_2 (catalog no: 232033) were purchased from Aldrich chemical company, USA. Nano sized TiO_2 powders were purchased from TIONA USA

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(catalog no: 10285) and Degussa Germany (catalog no: P25). Fig. 1 (a) and (b) show SEM micrographs of micro sized $BaCO_3$ and TiO_2 while Fig. 1 (c) and (d) show TEM images of nano sized TiO_2 TIONA and Degussa powders respectively. Morphology of micro sized $BaCO_3$ is cylindrical while TiO_2 (micro sized and nano sized as well) particles are nearly spherical. Mean particle size of micro sized $BaCO_3$ is 2 µm and TiO_2 is 0.7 µm. It can be seen that particle size of TIONA TiO_2 is around 50 nm. However, Degussa TiO_2 is slightly coarser than TIONA TiO_2 and is heavily agglomerated. TIONA TiO_2 particles are nearly spherical while Degussa TiO_2 particles have irregular morphology with some bigger particles present along with smaller particles giving rise to bimodal distribution with particle size of around 80 nm. In order to determine decomposition temperature of $BaCO_3$, thermo gravimetric analysis (TGA) was carried out (Universal V4 7A TA Instruments). Onset of decomposition temperature of $BaCO_3$ is 825 ºC and there occurred 22.46% weight loss during heating up to 1300 ºC. Weight loss of TIONA TiO_2 powder was 14.42% up to 800 ºC. There was 1.558 wt% gain in TiO_2.

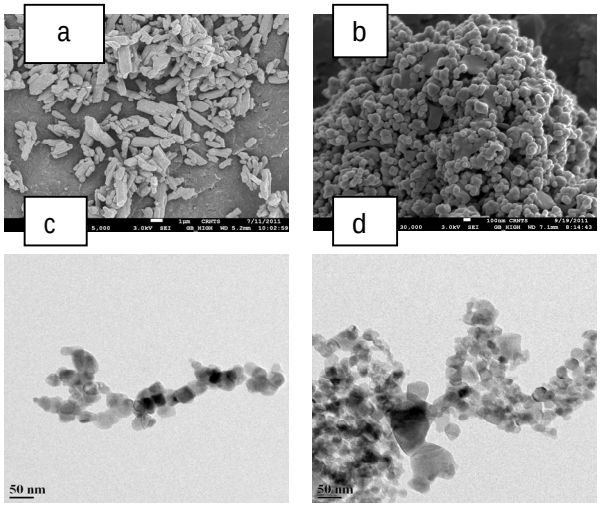
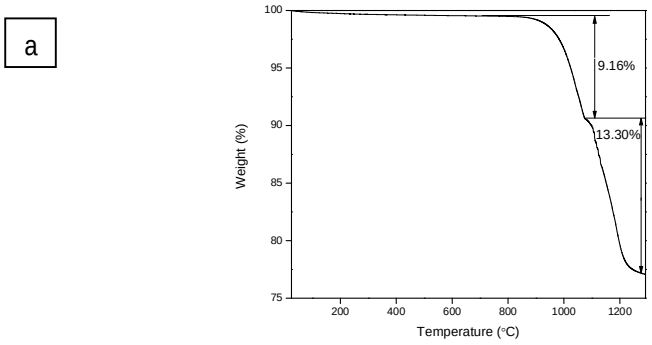


Fig.1 SEM and TEM images of starting materials (a) SEM micrograph of micro $BaCO_3$ (b) SEM micrograph of micro TiO_2 (c) TEM image of TIONA TiO_2 (d) TEM image of Degussa TiO_2



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Vol. 3, Issue 6, June 2014

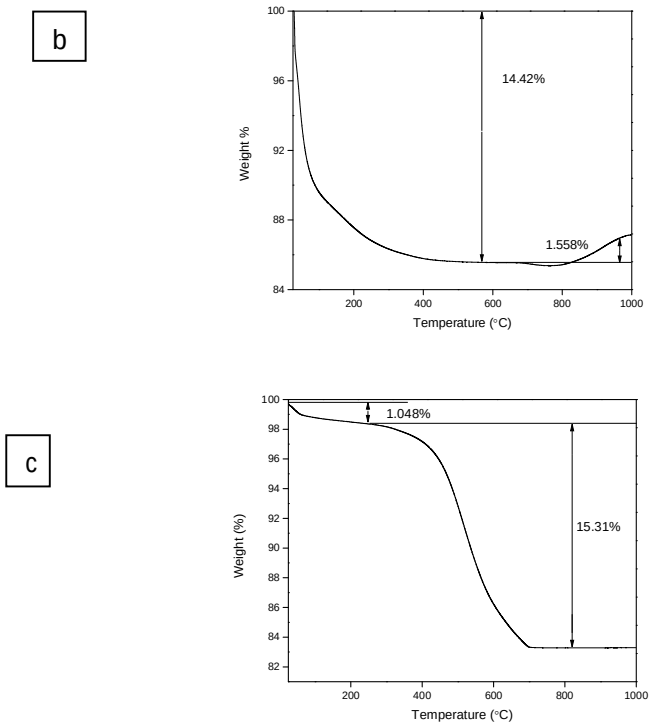

Fig.2 TGA curves for (a) $BaCO_3$ (b) TIONA TiO_2 and (c) Degussa TiO_2

in the temperature range 800 – 1000 ºC. Degussa TiO_2 showed 15.31 wt% loss from 25ºC to 1000 ºC. These weight losses and gains were considered during batch calculation for synthesizing stoichiometric $BaTiO_3$. These TGA curves for these materials are shown in Fig. 2.

In order to synthesize barium titanate, starting materials were first mixed in methanol to make slurry and yttria stabilized zirconia balls were added to mixture. Ball/powder ratio was 5:1 and the mixture was ball milled for 48 hours. After evaporating methanol at 80 °C the dry mass was crushed in agate mortar and pestle to make a fine powder. This powder was calcined at 1150º C for 4 hours. Similar procedure was followed for synthesis of barium titanate using TIONA and Degussa TiO_2 except for the fact that distilled water was used as dispersing medium because nano TiO_2 particles get well dispersed in distilled water with glacial acetic acid as dispersant. The mixed powders were calcined in the temperature range 750-900 ºC and 750-950 ºC for powders containing TIONA and Degussa TiO_2 respectively. The holding time at calcination temperature was four hours. In order to remove traces of $BaCO_3$ recalcination was carried out for these two batches at 900 and 950 ºC for four hours. The codes for different barium titanate powders are shown in Table 1.

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Vol. 3, Issue 6, June 2014

Table I Codes used for different barium titanate powders

Sample	Description
P1	$BaTiO_3$ powder synthesized from micron Sized $BaCO_3$ and TiO_2
P2	$BaTiO_3$ powder synthesized from micron Sized $BaCO_3$ and TIONA TiO_2
P3	$BaTiO_3$ powder synthesized from micron Sized $BaCO_3$ and Degussa TiO_2

To identify the structure of calcined powder, X- ray diffraction was carried out using X-ray diffractometer (PANalytical X-ray diffractometer PW 3040/60) in the 2θ range of 5-90º. X-ray source was Cu- k_α with the wavelength of 1.54 angstrom. Generator voltage and tube current were 40 kV and 30 mA respectively. Room temperature XRD data was collected with a step size of 0.016 and 24.765 second time per step. Morphology of barium titanate powders was studied using SEM (Model HITACHI S3400N).

III. RESULTS AND DISCUSSION

XRD pattern of $BaTiO_3$ powder (P1) synthesized from $BaCO_3$ and micro TiO_2 is shown in Fig. 3. Formation of barium titanate was confirmed with JCPDS database (reference code: 01-079-2264 and ICSD collection code: 067519). The crystal structure of barium titanate powder is tetragonal.

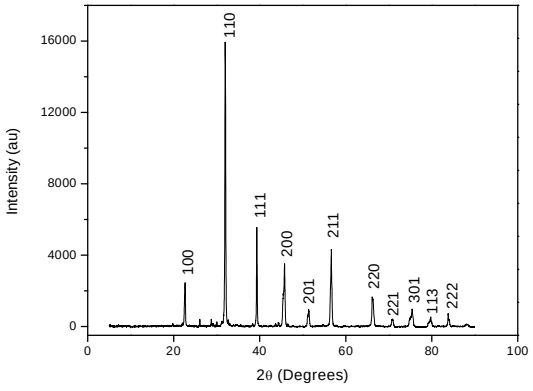

Fig 3. XRD pattern for calcined $BaTiO_3$ powder (P1)

Fig. 4 shows XRD patterns for calcination of $BaCO_3$ and TIONA TiO_2 calcined at temperatures from 750 to 900 ºC, i.e. at 50 ºC intervals and held for 4 hours at each temperature (P2) indicated by curves a-e. Complete phase formation takes place at 900 ºC. Similarly, Fig. 5 shows XRD patterns for calcination of $BaCO_3$ and Degussa TiO_2 at temperatures 750 to 950 ºC, i.e. at 50 ºC intervals and held for 4 hours at each temperature (P3). Phase pure barium titanate gets formed after recalcination at 950 ºC indicated by curves a-f. as shown in Fig. 5. Table 2 shows comparison between the calculated and standard parameters of barium titanate powders P1-P3. It can be seen that actual lattice

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Vol. 3, Issue 6, June 2014

parameters are in excellent agreement with theoretical lattice parameters and hence, it confirms the formation of tetragonal $BaTiO_3$ powder.

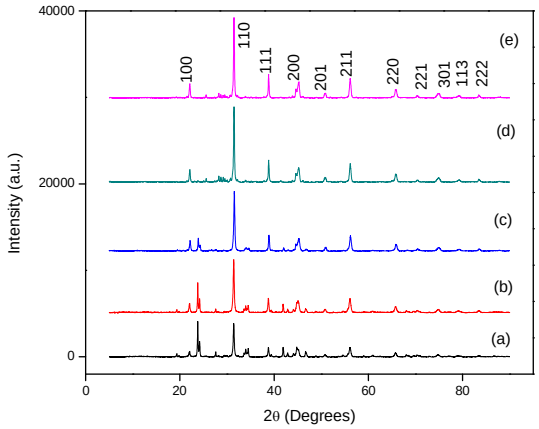

Fig.4 XRD patterns for calcination of $BaCO_3$ and TIONA TiO_2 **(P2)** at (a) 750 ºC for 4 hours (b) 800 ºC for 4 hours (c) 850 ºC for 4 hours (d) 900 ºC for 4 hours (e) recalcination at 900 ºC for 4 hours

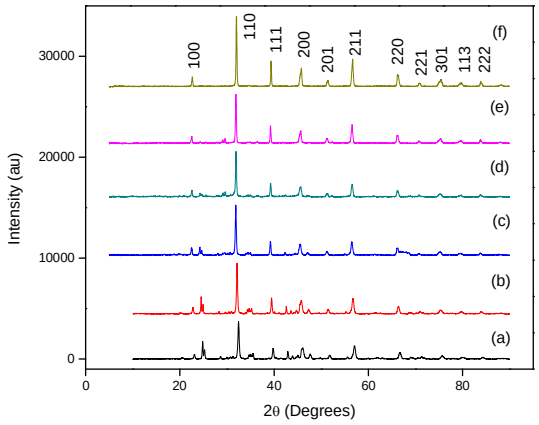

Fig. 5 XRD patterns for calcination of $BaCO_3$ and Degussa TiO_2 **(P3)** at (a) 750 ºC for 4 hours (b) 800 ºC for 4 hours (c) 850 ºC for 4 hours (d) 900 ºC for 4 hours (e) 950 ºC for 4 hours (f) recalcination at 950 ºC for 4 hours

Table II Comparison of Lattice Parameters of Various Calcined $BaTiO_3$ Powders with Standard Lattice Parameters of Barium Titanate

	Samples		
Parameters	P1	P2	P3
Calculated a (Å)	3.983	3.998	3.983
Standard a (Å)	3.9998	3.9998	3.9998
% Change	0.42	0.045	0.42
Calculated b (Å)	3.983	3.998	3.983
Standard b (Å)	3.9998	3.9998	3.9998

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% Change	0.42	0.045	0.42
Calculated c (Å)	4.020	4.04	4.010
Standard c (Å)	4.0180	4.0180	4.0180
% Change	0.0497	0.5445	0.19
Calculated $\alpha = \beta = \gamma$	90º	90º	90º
Standard $\alpha = \beta = \gamma$	90º	90º	90º
% Change	0	0	0
Calculated Volume ($Å^3$)	63.78	64.62	63.61
Standard Volume ($Å^3$)	64.28	64.28	64.28
% Change	0.7778	0.5261	1.04

Fig. 6 (a-c) shows morphology of barium titanate powder synthesized from $BaCO_3$ and micro TiO_2, $BaCO_3$ and TIONA nano TiO_2 and $BaCO_3$ and Degussa nano TiO_2 It can be observed that barium titanate powder particles are nearly spherical similar to titania particles. The particle size of barium titanate reduced from 0.7 µm to 0.5 µm when nano sized titania was used as starting material as confirmed by LASER particle size analysis. It can be inferred that use of nano sized starting materials resulted in reduced particle size of $BaTiO_3$ also. The particle size of each powder is smaller than commercially available $BaTiO_3$ powder [4]. The particle size of powder is also smaller than powder obtained by hydrothermal method [5]. Even though nano sized TiO_2 was used as a starting material, it did not result in formation of nano sized $BaTiO_3$ powder as in case of sol – gel, soft chemistry, solvothermal processes etc. reported earlier [6 - 10].

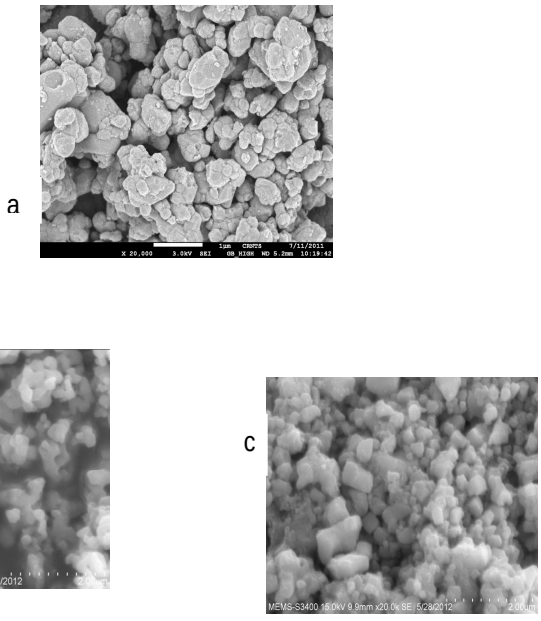

Fig. 6 SEM images of $BaTiO_3$ powders (a) P1 (b) P2 and (c) P3 at magnification of 20,000X

IV. CONCLUSION

Barium titanate was synthesized using micron sized barium carbonate and titanium oxide having different particle size (0.7 µm, 50-60 nm and 80-90 nm). The calcination temperature of barium titanate was 1150 ºC when

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micro sized barium carbonate and titanium oxide were used as starting materials. However, calcination temperature decreased to 900 and 950 ºC when micro sized barium carbonate and nano titanium oxide with particle size 50-60 nm and 80-90 nm were used respectively. Formation of phase pure tetragonal barium titanate powder was confirmed using x – ray diffraction (XRD). The morphology of the powders was studied using scanning electron microscopy (SEM). The particle size of barium titanate reduced from 0.7 µm to 0.5 µm when nano sized titania was used as starting material.

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