Effect of Calcination and Sintering Temperatures on Physical Properties of Barium Titanate Ceramic

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ABSTRACT: Barium titanate based perovskite structured ceramics are well known dielectrics in the category of functional materials. This study was conducted to investigate the effect on the perovskite structure purity and density due to change in calcination and sintering temperatures of barium titanate ($BaTiO_3$) ceramics; synthesized by conventional solid-state reaction technique. These characteristics are directly affecting the dielectric property of $BaTiO_3$. Calcination of the powders accomplished at five different temperatures i.e., 930, 960, 1000, 1030 and 1060 °C for 4 h and sintering was done of pellet at four different temperatures i.e., 1250, 1300 and 1350 °C for 4 h. XRD patterns of calcined-samples revealed the presence of $BaTiO_3$ as a single phase with low intensity peaks of intermediate phases i.e. $BaCO_3$ and TiO_2. The patterns also confirm tetragonal phase in all the sintered samples. The highest amount 95.15 % of perovskite phase achieved which was calcined at 960 °C temperature. The best sintering temperature was recorded as 1350 °C in terms of bulk density of about 5.8 g/cm^3 and a true porosity of about 3.6 %.
Key Words: Barium Titanate, Calcination, Sintering, Bulk density, True porosity

1. Introduction

Barium titanate ($BaTiO_3$) is commercially available ferroelectric ceramic with ABO_3 type of perovskite structure having a high dielectric constant [1-3], huge range of piezoelectric values [4] would attract more as electronic devices for a diversity of electro optic devices such as piezo sensors, multilayer capacitor (MLCCs), piezo transducer and printed circuit board [1-6].

The crystal structure of barium titanate ($BaTiO_3$) has a major role that provides a high dielectric constant. The crystallographic dimension of this material varies as temperature varies. It has been known that calcination temperatures have a strong effect on the crystal structure and polarization characteristic of $BaTiO_3$ [1-6]. On the other hand, composition homogeneity, particle shape, particle size distribution density, microstructures and single phase are equally important to get good piezoelectric properties of $BaTiO_3$ [6-8]. It has been addressed that the finer size powder would rapidly sintered more, comparatively at lower temperature than coarser powder. Conventionally, $BaTiO_3$ has been prepared through a solid-state method by utilizing $BaCO_3$ and TiO_2 as starting raw powders [1-6].

The rational of this paper is actually to develop the basic understanding for new researchers to understand the calcination and sintering behavior (how to optimize these temperatures), and how to calculate the perovskite phase from the X-ray diffraction (XRD) data of BT. In addition to this, the effect of these temperatures on physical properties of BT was added. Overall processing and purity of Barium titanate materials was essential.

Nonetheless, bulk density of ABO_3 ceramics is very important for ferroelectric properties; porosities are not needed for miniaturizations of devices in the case of thin multilayers. So, this research explored to optimize the calcination and sintering temperatures where single phase was equally important to get the homogenous behavior throughout the sample. The crystal structure, morphology and density with porosity were characterized by XRD, scanning electron microscope (SEM) and Archimedes method, respectively.

2. Experimental

Solid-state reaction technique was used for the synthesis of barium titanate ceramic powder. For this, barium carbonate ($BaCO_3$) (RDH, 99.99 %) and titanium oxide TiO_2 (BDH, 99.99 %) were used as a starting material. These two ingredients were mixed in polyethylene jar for 1 h in a mixer by using ZrO_2 ball. Both ingredients were chosen with equal molar ratio according to the stoichiometric formula given in Equations 1 and 2.

$$\text{Wt\% BaCO}_3 \quad = \quad \frac{(\text{mol \% of BaCO}_3)\,(\text{MW* of BaCO}_3)}{(\text{mol \% of BaCO}_3)\,(\text{MW BaCO}_3) + (\text{mol \% of TiO}_2)\,(\text{MW TiO}_2)} \quad \text{..... 1}$$

$$\text{Wt\% TiO}_2 \quad = \quad \frac{(\text{mol \% of TiO}_2)\,(\text{MW of TiO}_2)}{(\text{mol \% of BaCO}_3)\,(\text{MW BaCO}_3) + (\text{mol \% of TiO}_2)\,(\text{MW TiO}_2)} \quad \text{..... 2}$$

* Molecular weight.

The mixed powder was then grounded in alumina jar with ZrO_2 ball for 2 h using 80 ml ethanol as a liquid medium. It was later dried in an oven at $90^{\circ}C$ for 12 h. Dried powder was calcined at five different temperatures i.e. 930, 960, 1000, 1030 and 1060 °C for 4 h for evaluation the effect of calcinations temperature on the formation of pervoskite phase. The calcined powder was milled again in the presence of 10 wt% polyvinyl alcohol (PVA) binder to strengthen the green pellets. The powders were pressed into green pellets having dimensions 25 mm diameter and 2 mm thick at 25 MPa pressure. The samples were heated in a furnace for 4 h at 600 °C for binder burn off at a heating rate of 10 °C/min. The green pellets were then sintered at four different sintering temperatures increment of 50 °C, start from 1200 °C to 1350 °C for study the effect on morphology and density.

The calcined powder samples were phase characterized by using x-ray diffraction (PANalytical X'PERT PRO, HOLLAND) with Cu (Kα) radiations λ = 1.54060 Å, operating at 30 mA and 40 KV, step size of 0.02°{2θ} and step time 0.3{s} from 10° to 80°. The percent amount or content of the $BaTiO_3$ (Perovskite) phase was examined by utilizing the XRD pattern data. The percentage of perovskite phase was calculated by the given formula [9]. The relative amount of the phases was determined by measuring the high intensities peak of X-ray for all the phases present.

$$\text{Content of Perovskite Phase (\%)} \quad = \quad \frac{\text{I (Perovskite Phase)}}{\text{I (Perovskite Phase)} + \text{I (Impurity Phase)}}$$

The morphology of the sintered ceramic was investigated by SEM on FEI Quanta 200S at an accelerating voltage of 10 KV. The apparent porosity, true porosity and density (bulk density) of the sintered specimens were determined by using Archimedes method as per standard ASTM-C373-88. The following formulas were used for calculations [10].

$$\text{Apparent Porosity, P} \quad = \quad \frac{W_w - W_d}{W_w - W_s} \; \text{x 100} \qquad \text{..... 3}$$

$$\text{Bulk Density, B} \quad = \quad \frac{W_d}{W_w - W_s} \; \text{x 100} \qquad \text{..... 4}$$

$$\text{True Porosity} \quad = \quad \frac{\rho - B}{P} \; \text{x 100} \qquad \text{..... 5}$$

Where, W_d is dry weight (gm), Ws is suspended weight (weight in water) (gm) W_w is weight after soaking 2h in water (gm), ρ is the true density of a $BaTiO_3$ which is 6.02 g/cm^3.

3. Results and discussion

XRD results of all calcined samples shown in **Figure 1 (a-d).** Where 930 °C sample indicates two secondary phase peaks, like no 2, 3 and 5; whereas 2 and 5 matched with ICDD card no 00-005-0378 which was of barium carbonate ($BaCO_3$); it means $BaCO_3$ was not completely reacted at this temperature. In addition to this, peak around 27° (2θ) was of titanium dioxide (TiO_2), as per ICDD card no. 01-087-0710. The remaining peaks are the characteristic peaks of tetragonal structure of $BaTiO_3$ (ICDD card no. 01-089-1428), where the relative amount of BT phase was 84.86 % as per peak intensities calculations. This phase percentage was determined from the raw data of XRD (**Table 1**) according to the formula given in experimental section**.**

$BaCO_3$ reaction was almost complete at 1000, 1030, and 1060 °C, respectively as shown in the **Figure 1(c-e).** The percentages of perovskite and secondary phases of all calcined samples shown in **Figure 1(f)**. At 10030 °C and 1060 °C, the second phase that is unknown at 29° (2θ) (**Figure1 d-e**). The presence of intermediate phases could be the result of various synthesis parameters such as variation in particle size, trace impurities in raw materials, calculation error, not homogenous mixing and or human error.

Based upon the crystallographic information of the samples, the crystal structure of the sample was found to be tetragonal, which is good agreement with Ogihara et al. [11]. It has been studied by Jose that the barium titanate has four different forms of isomorphs, at very low temperature (below zero-°C) it is rhombohedral and orthorhombic, whereas at above T_{room} it would be tetragonal and cubic depending on processing parameters respectively [7]. Among four crystalline phases, two have been considered the most important crystalline phases of $BaTiO_3$ which are technologically useful in microelectronic industries. These two are cubic and tetragonal structures, while cubic is most suitable for commercial capacitors due centro-symmetrical paraelectric and tetragonal is non-centro-symmetrical best for the application of piezoelectricity [5]. Maison et al. [3] reported that the formation of $BaTiO_3$ starting first at the grain boundaries (i.e., $BaTiO_3/TiO_2$), it was further reacted with barium carbonate and converted into complex Ba_2TiO_4.

Finally, this complex compound plus TiO_2 appeared into $BaTiO_3$ [3], that could be the reason, getting pure BT is not easier. Maison et al. [3] researched that the cubic phase was dominated at lower calcination temperatures and as temperature raises the phase changes took place from cubic to tetragonal, as well as the morphology of grains converted from spherical to acicular in shape. Jamal et al. [5] reported that, the phase formation at 900 °C was not complete as discussed, the presence of $BaTiO_4$ and $BaCO_3$ constitutes when synthesized by conventional solid-state method. Based upon the highest purity at 960 °C in terms of 2nd phases, this calcination temperature was selected for sintering at different temperatures (**Figure 4**).
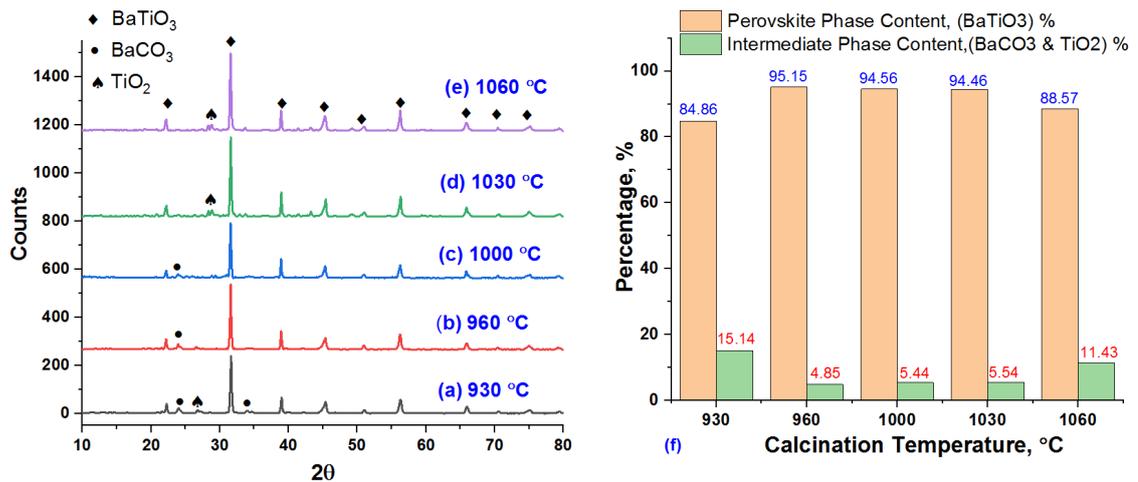

Figure 1: XRD Data of Barium titanate powder calcined at (a) 930 °C, (b) 960 °C, (c) 1000 °C, (d) 1030 °C (e) 1060 °C (f) Percentage of Perovskite phase and secondary phases

Table 1: Peak List of samples calcined at 930 °C

Peak No	Position [°2Th.]	Height [cts]	d-spacing [Å]	Rel. Int. [%]
1	22.131130	22.546060	4.01672	14.00
2	24.094690	23.873790	3.69364	14.82
3	26.852150	13.417960	3.32028	8.33
4	31.654060	161.064900	2.82670	100.00
5	34.256310	4.863602	2.61769	3.02
6	39.002330	40.097650	2.30940	24.90
7	45.355670	58.776370	1.99958	36.49
8	51.042900	14.010190	1.78934	8.70
9	56.315610	60.379030	1.63368	37.49
10	66.058320	29.830100	1.41439	18.52
11	70.562170	6.179924	1.33475	3.84
12	75.160310	17.188770	1.26410	10.67

Figure 2 showing the stereo micrograph of $BaTiO_3$ pellets sintered at 1200, 1250, 1300 and 1350 °C respectively. It was observed that as the sintering temperature increased, the color of sample changed to dark -brown at 1350 °C. This might be the result of cationic or anionic losses in the material, as reported by Li et al. in the case of co-doping of Nb and In in rutile TiO_2 [12].

The SEM images of $BaTiO_3$ ceramic samples fired at 1250 °C and 1350 °C temperatures are shown in **Figure 3(a-b)**. It was noted that the samples sintered at 1250 °C were containing less bulk-density (58.13 %) with definitely higher porosities. Despite to this, the samples sintered at 1350 °C, shown less porosity with density improved to 96.34 %, as in **Figures 4(a-b).** This change could be inferred mainly due to the mobility of grain boundaries; because grain boundaries are influenced by some processing parameters such as sintering temperatures, mixing/milling, diffusion coefficient of compositions [13]. It was also reported that the average grain size would be increased at higher sintering temperatures as was in the case of BZT ceramics [14].

Figures 4(a-b) indicates the variation in bulk density, true porosity and apparent porosity with sintering temperature. The higher sintering temperature than calcination is always set to reduce porosity and enhance density, which consequently enhances the relative permittivity [16]. In addition; doping, microstructure, mainly grain size and density, are also major contributing factors to modify the dielectric constant. Moreover, higher sintering temperature generally lead to higher diffusion rate that in result to affect the grain growth [15].
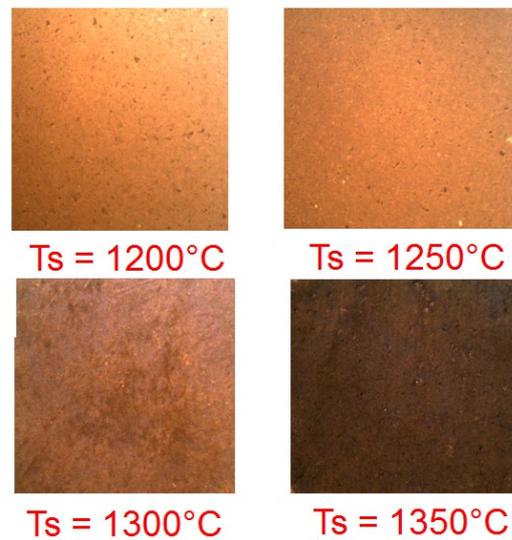

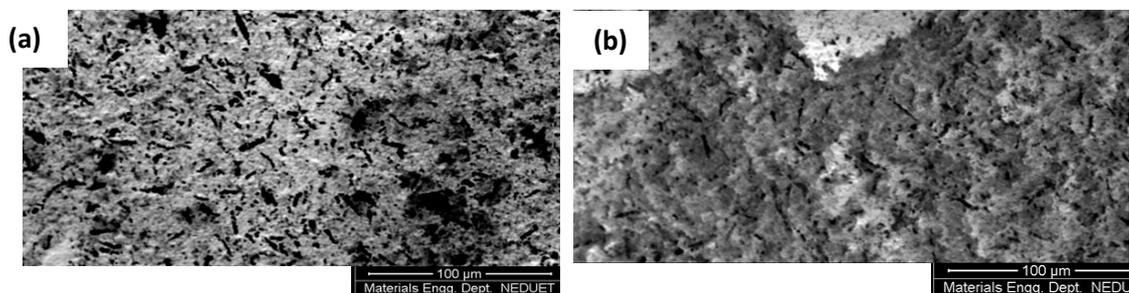**Figure 2:** Stereo Micrograph at 7x, Ts= Sintering Temperature

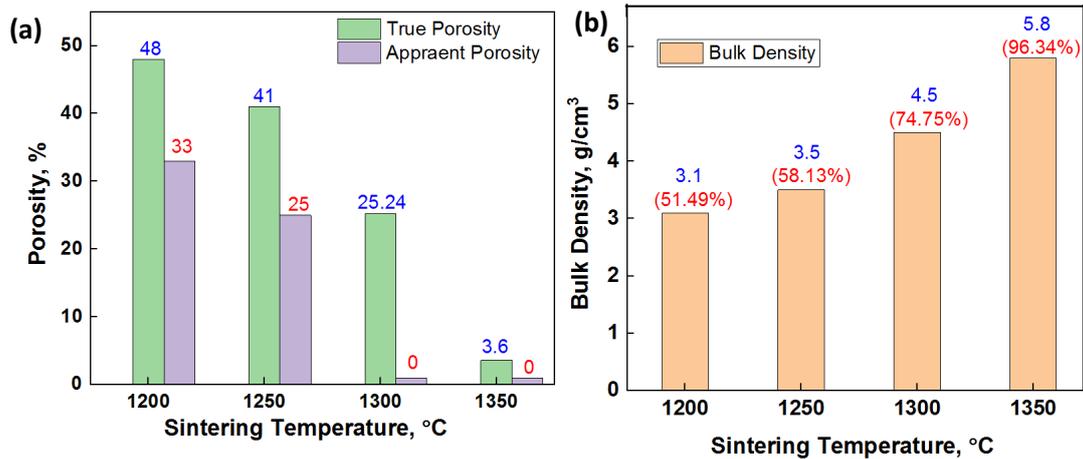**Figure 3:** SEM Micrograph of Sintered $BaTiO_3$ Pellet (a) at 1250 °C and (b) 1350 °C

Figure 4: Variation in (a) True and Apprent porosity (b) Bulk density

4. Conclusions

The effect of calcinations temperature on the crystallographic properties and sintering temperature effect on the physical properties has been investigated in this work. The $BaTiO_3$ (perovskite phase) was successfully obtained by a well-known conventional method of solid-state reaction. The X-ray diffraction pattern showed the $BaTiO_3$ phase was obtained at all studied calcinations temperature with intermediate phases. The amount of perovskite phase approximately similar when calcined at 960, 1000 and 1030 °C whereas, it was less observed when calcined at 930 and 1060 °C due to the presence of secondary phases. The best reaction temperature was observed 960 °C which has 95.15 % relative amount of $BaTiO_3$ phase. Based upon the crystallographic data, the crystal structure was recorded as a tetragonal at T_{room}. The effect on the bulk density and on porosity was determined by ASTM-C373-88 and it has been observed that, due to increase in sintering temperature the bulk density also increased whereas the apparent and true porosity have been decreased. The colour changes to black which indicate the oxygen vacancies increases as increase sintering temperature. The 1350 °C temperature was observed as optimized sintering temperature which has a bulk density of about 5.8 g/cm^3 and 3.6 % true porosity. The higher sintering temperature led to grain coarsening and reduced porosity had probably accounted for the density enhancement noted in the samples.

Acknowledgement

References

1. L. Simon-Seveyrat, A. Hajjaji, Y. Emziane, B. Guiffard, D. Guyomar, Ceram. Int. 33 (2007) 35-40.
2. S.B. Majumder, V.N. Kulkarni, Y.N. Mohapatraand D.C. Agrawal, Bul. Mat. Sc. 17 (1994) 19-23.
3. W. Maison, R. Kleeberg, R.B. Heimann, S. Phanichphant, J. Euro. Ceram. Soc. 23 (2003) 127-132.
4. A. Sreenivasulu, T.N.V.K.V. Prasad, S. Buddhudu, In. J. Pure & Appl. Phys. 45 (2007) 741-744
5. Asad Jamal, Muhammad Naeem, Yaseen Iqbal, J. Pak. Mater. Soc. 2(2008) 91-95.
6. M. Gromada, M. Biglar, T. Trzepiecinski, F. Stachowicz, Bull. Mater. Sci., 40 (2017) 759-771.
7. H.-L. Wang, Structure and Dielectric Properties of Perovskite-Barium Titanate ($BaTiO_3$), MatE 115, Fall 2002.
8. D.W. Richerson, Modern Ceramics Engineering: Properties, Processing and Use in Design, CRC Press, New York (2005), pp 330-334.
9. G. Feng, D. Zhenqi, Y. Le, C. Lihong, T. Changsheng, Ceram. Int. 35 (2009) 2885-2890.
10. H. Ohuchi, S. Tsukamoto, M. Ishii, H. Hayakawa, J Euro. Ceram. Soc. 19 (1999) 1191-1195.
11. H. Ogihara, C.A. Randall, S.T. McKinstry, J Am. Ceram. Soc. 92 (2009), 110-118.
12. J. Li, F. Li, Y. Zhuang, L. Jin, L. Wang, X. Wei, Z. Xu, S. Zhang, J. Appl. Phys. 116 (2014) 074105-1 074105-9.
13. W. Chaisan, R. Yimnirun, S. Ananta, Ferroelec. 346 (2007) 84-92.
14. W. Cai, F. Chunlin, J. Gao, H. Chen, J. Alloy. Compd. 480 (2009) 870-873.

15. O. Jongprateep, N. Sato, in: Proceedings of Materials Today Conference on the 10th Thailand International Metallurgy (The 10th TIMETC), 30-31 March, 2017, Thailand, 9298-9305.
16. Y.C. Liou, S.L. Yang, Materials Science and Engineering B 142 (2007) 116-120.