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FABRICATION AND CHARACTERIZATION OF PEROVSKITE FERROELECTRIC BATIO3 CERAMICS FROM BACO3 AND TIO2

CHERNET MERKNEH
Department of Mechanical engineering Wolaita Sodo University /
College Engineering, Wolaita Sodo, Ethiopia
chernetmerkneh2@gmail.com

MULUGETA TADESSE
Department of Mechanical engineering Wolaita Sodo University /
College Engineering, Wolaita Sodo, Ethiopia
muleriye@gmail.com

ABSTRACT
In this research project, a comprehensible way of preparing Barium Titanate is conducted through series of steps and then gone through specific sorts of analyzing and characterization of particular material undergone. The $BaTiO_3$ precursor solution was made by using $BaCO_3$ and TiO_2 in deionized water and milled the mixed powders to get fine grain size and uniform mixing throughout the product after that dried the powder. We followed the specific experimental procedures, which is firstly, we weighed the powder by balance and then mix and crush by ball milling (12 hrs.) then drying by 100 ^oC for 12 hrs. After that, we sieved using mesh and calcination took place at 1100 ^oC for 10 hrs. Additionally, the powder samples are re-milled for 12 hrs. then dry and fire at 100 ^oC for 12 hours ;again for fining sieved and green body is formed ultimately so that advanced heat treatments like sintering has been accounted in the process ;chilling and finally characterization took place Using X-ray Diffraction machine and also Differential Thermal analysis which means The thermal Decomposition of $BaTiO_3$ powders were studied using DTG.
More specifically; the phase transformation of the crystals due to milling and firing of the has been investigated as result the elevation in sintering temperature gave rise to the increase in density with grain size and the more crystalline the powder gets ,more high peak diffraction patterns are registered. The crystallite sizes (t) of different samples were estimated from the (110) peaks of XRD patterns,

KEYWORDS: Sintering, Barium Titanate, Lattice parameters, Ball Milling.

INTRODUCTION
Barium Titanate is a ferroelectric ceramics with a feature of certain non-conductive crystals or dielectrics that evinces a spontaneous polarization. It is a white powder and transparent as substantial crystals, and it is utilized in capacitors, electromechanical transducers and nonlinear optics [1]. Ferroelectric ceramics is a dielectric material that has a spontaneous polarization with the absence of applied electric field. Dielectric materials are very poor conductors of electric current and used as capacitor that is electrically insulating that exhibits electric dipole structure because of separation of positive and negative electrical charged entities on a molecular and atomic level [2, 3]. This concept leads us into electrical polarization.
Electrical polarization is the segregation of the middle of the positive and negative charge, which makes one part of the crystal positive while the other side negative that can be altered in direction by the application of electrical field [4].

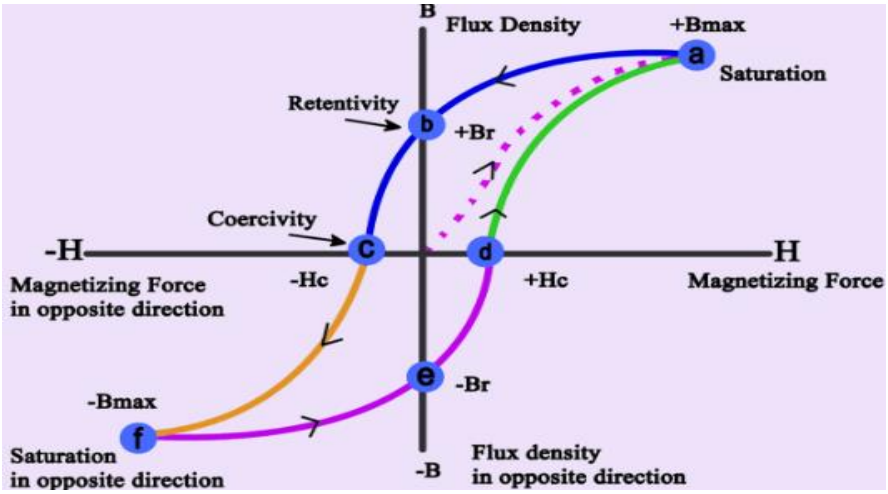


Fig.1: Hysteresis loop of ferroelectric ceramics

The spontaneous polarization is the effect of the positioning of Ba^{2+}, Ti^{4+} and O^{2-} ions with in the unit cell. The reactions to form this powder and create the aforementioned electrical behaviors are shown below as highlight.

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2$$

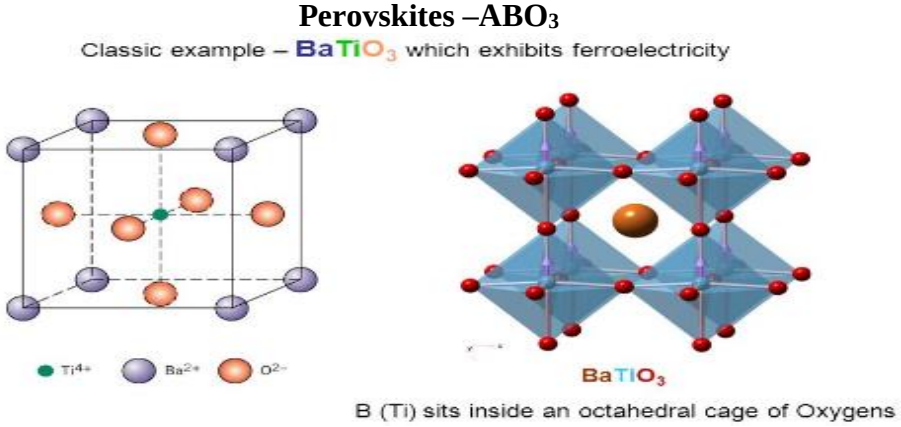


Fig. 2: Transition of Octahedral $BaTiO_3$ to cubic structure [5]

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2 \quad \text{(Reaction-1)}$$
$$BaTiO_3 + BaCO_3 \rightarrow Ba2TiO_4 + CO_2 \quad \text{(Reaction-2)}$$
$$Ba2TiO4 + TiO_2 \rightarrow 2BaTiO3. \quad \text{(Reaction-3)}$$

The reaction: $BaCO_3+TiO2 \rightarrow BaTiO_3+CO_2$ as a major contributor to the formation of $BaTiO_3$ with a trace amount of Ba_2TiO_4.

There is also dissociation occurred by applying the so that Thermal decomposition of reactant occur at the temperature at 120 ^oC

$$BaCO_3 \rightarrow BaO + CO_2$$
$$2BaO + TiO_2 \rightarrow Ba_2TiO_4$$
$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3$$

LITERATURE REVIEW

Various Ceramic Materials with Ferroelectric Properties have been Fabricated and Utilized for a variety of applications. From those, mostly the Perovskites family having a formular structure of ABO_3 is the most popular type [5]. Many Ferroelectric Ceramics Such as Lead Titanate ,Barium Titanate, Lead Lanthanum Zirconate Titanate, Lead Zirconate Titanate, Reaxor ferroelectrics like lead magnesium Niobate have a Perovskites type structure [6].

Significant influence of milling regime on the mean crystallite size and crystal lattice microstarains into obtained $BaTiO_3$ [7, 8]. Gomez-Yanez et al. described that long term milling of $BaCO$-TiO_2 mixture in attriture has gave rise to the remaining of a large Orthotitanate phase amount even after annealing at 1200^0C for one hour Mainly due to preliminary particle agglomeration and production of rather giant and well defined Ba_2TiO_4 crystals During milling. Taking all this into account this paper studies also the particle size of the powders characterizes and in the process additionally milling effects as well in the final ferroelectric $BaTiO_3$ Product [9]

THE RATIONALE OF THE RESEARCH

For decades, a wide variety of synthetic methods have been developed for fabrication of Barium Titanate, but very large scale production is frequently based on Solid state reaction of mixed powders [10]. Despite the Multiple advantages, being a single technique and low cost process, there are some problems with it to be solved. Actually the elevated calcination temperature required by solid state reaction process leads to many disadvantages such as large particle size, high degree of agglomeration which generally limits the ability to fabricate the reliable electronic components out of It. So, it is desirable to lower agglomerations and improper heat treating mistakes while fabricating to obtain fine and homogenous $BaTiO_3$ powder [11]. This is where High energy ball milling which is also called Mechano chemical system is engaged in the researches which results in time consuming and loss of the sample.

MATERIALS AND METHODS

The materials used is this experimental analysis are Ball milling machine, Mesh, Polyethylene bottles, spoons, Muffle furnace, drying oven Alumina crucible, X-ray diffractometer, Differential thermal analyzing machine.

4.1 Experimental Procedures

A. Sample Preparation

The amounts of Barium Carbonate and Titanium oxide were Calculated and mixed and Barium in this reaction Titanate powder was formed.

$BaCO_3$ (4.2312g) + TiO_2 (1.1725g) → $BaTiO_3$ (5 g) + CO_2 (gas)

The reactants are mixed with 150 ml Dl water inside polyethylene bottle. Then after, ball milled with 30 pieces with diameter of 10mm and 60 pieces with diameter 5mm Zirconia ball for about 12hrs in ball milling machine. After mixing, powders are dried at 100 ^{o}C for 12hrs and finally, a uniformly mixed mixture was achieved and finely crushed powders were formed.

Green body forming and calcination

Preliminarily to avoid agglomeration, the powders were grinded and sieved (<150 μm) respectively after that they are filled into the mold and pressed with a uniaxial hydraulic press and green bodies were formed.
The green bodies were thoroughly placed in alumina crucible and put into the furnace and heat treatment takes place at 1200 ^{o}C for 10hrs.
Drying and Firing: A ceramic piece that has been formed hydro plastically or by slip casting retains significant porosity and insufficient strength for most practical applications. In addition, it may still contain some liquid (e.g., water), which was added to assist in the forming operation. This liquid is removed in a drying process; density and strength are enhanced as a result of a high temperature heat treatment or firing procedure

Calcinations

Is the heat treating process before involving sintering. The decomposing of solids or chemical reaction between solids in which the sample stays in the oven at about 350◦C to make the sample more compacted together by removing voids and other impurities like water and gasses within the material. Diffusion in Calcination occurs by atomic motion. Inhomogeneous materials can be turned into homogeneous by diffusion. For an active diffusion to happen, the temperature should be elevated enough to surpass energy

barriers to atomic motion. In this particular Research, the phenomenon that occurs during calcination is decomposition of $BaCO_3$ into BaO and CO_2.

$$BaCO_3 \rightarrow BaO + CO_2$$

Sintering is the heat treatment process after calcination when, the green body is heated at a temperature of 1200 ^oC for 10hours (in our case we heated for 5 hours). During this firing stage, diffusion of atoms takes place between powder particles and the powders are consolidated, porosity is minimized, and the specimen shrinks, and therefore results become a dense material.

B. Pellet preparation and sintering

Sintering

Is a manufacturing process in the heat treatment of powder compacting and forming solid mass of material at elevated temperature. During sintering process the diffusion of atoms improved by liquid-phase sintering and pressure sintering.

Liquid-phase sintering involves use additives that form a small amount of liquid-phase between the grains at the sintering temperature cased to sufficient control of the sintering conditions i.e. sintering temperature, time at sintering temperature, rate of heating, and sintering atmosphere, particle size and composition, which are causes to improve diffusion of atoms in sintering.

Pressure sintering involves the application of an external pressure to the green body during heating in either case of solid-state or liquid-phase sintering. The phases present in the four different specimens i.e. in $BaCO_3$, TiO_2 powders, specimen after calcination and after sintering are namely, hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral.

Both sintering and densification rate rise directly with temperature and inversely increase with particle size.

C. XRD measurement and analysis

X-ray diffraction (XRD) is one of the most important nondestructive tools to analyze all kinds of matter ranging from fluids, to powders and crystals [10, 11]. From research to production and engineering, XRD is an indispensable method for materials characterization and quality control. X-ray diffraction techniques are used for the identification of crystalline phases of various materials and the quantitative phase analysis subsequent to the identification. X-ray diffraction techniques are superior in elucidating the three dimensional atomic structure of crystalline solids.

The Bragg equation, $n\lambda = 2d\sin\theta$ is one of the keystones in understanding X-ray diffraction. Where, n is an integer;

λ is the characteristic wavelength of the X-rays impinging on the crystallize sample

d is the interlunar spacing between rows of atoms, and

θ is the angle of the X-ray beam with respect to these planes.

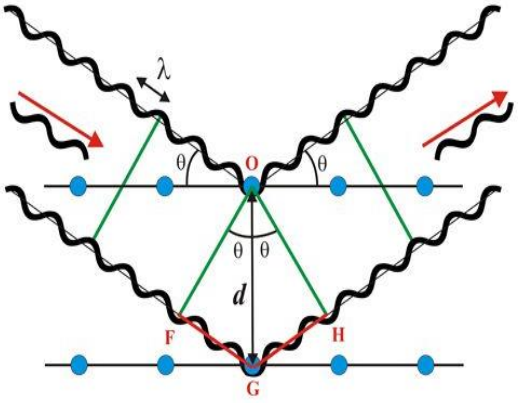
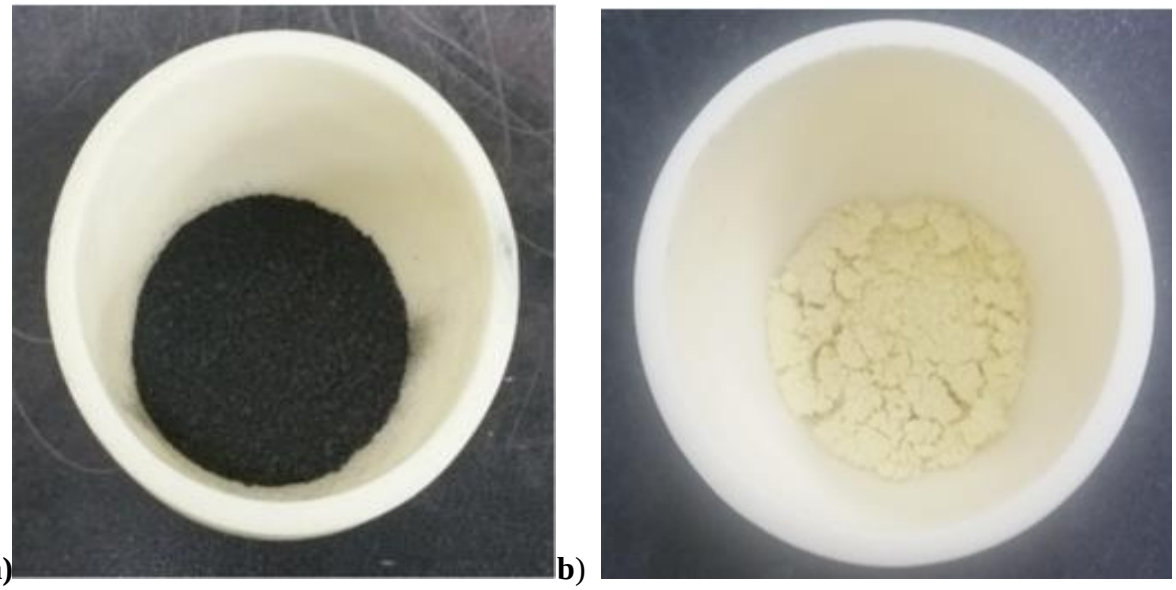


Fig.3: Bragg's angles diffraction in the crystal and measuring derivation

RESULT AND DISCUSSION

A. Phenomenon occurred during Calcination

During calcination of BaCO3 thermal decomposition, phase transition and removal of volatile fractions occurred. The Reaction (Thermal Decomposition) is BaCO3 → BaO + CO2(g)



a) **b)**

Fig. 4: Powders a) Before Calcination b) After Calcination

B. X-ray Diffraction results

X-ray diffraction patterns were recorded for powders after the calcination process. Diffraction patterns were comparing with literature review material at [9]. Figure below shows the XRD pattern for the as milled $BaCO_3$ and TiO2-c powder mixture milled for 12 hrs. It can be seen that, all the diffraction peaks correspond to either $BaCO_3$ or TiO_2 phases. This implies that no reaction took place between the BaCO3 and TiO2-c powder mixtures during the mechanical milling. We used the fine powder sample before sintering because X-ray occurred on the particles those, which are not compact much. We saw peaks of the intensity for crystalline and no peak for amorphous part. Figure below shows the XRD patterns for two equi-molar mixtures of $BaCO_3$ and Titanium dioxide.

Table-1: XRD peak data list of three strongest peaks of all the overall XRD data

Strongest peaks no	Peak no	**2θ**(degree)	d(A)	I/**T_1**	FWHM (deg)	Intensity (counts)	Integrated Int (counts)
1	2	31.5415	2.83418	100	0.21380	2690	33957
2	3	38.8912	2.31383	29	0.18950	793	8691
3	6	56.1844	1.63583	25	0.33030	670	12414

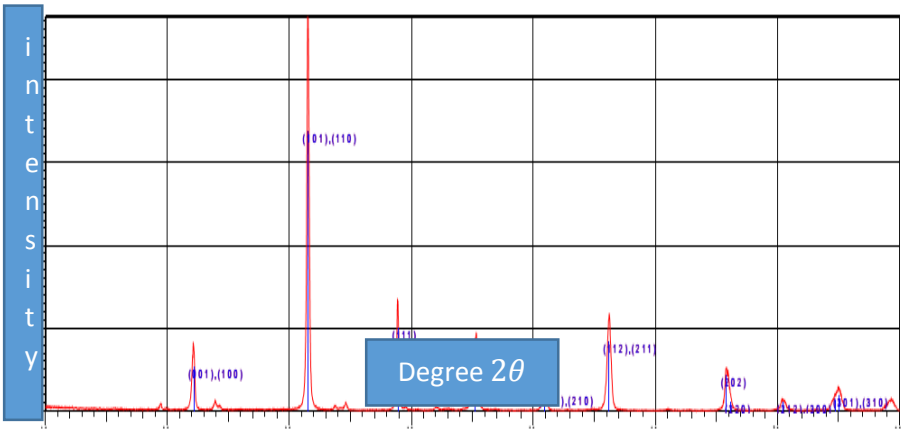


Fig. 5: XRD pattern for milled BaCO3 and TiO2-c powder mixture milled for 12hrs.

For calculating lattice parameters for each of strongest peaks are from the given data and to calculate **t** the particle size we divide 2 theta (2θ) into two finding theta angles, and then evaluate for t. The crystallite sizes (**t**) of different samples were estimated from the (110) peaks of XRD patterns, using Scherrer's

formula: $t = \frac{k\lambda}{B\cos\theta}$ Where, k is the shape coefficient (value between 0.9 and 1.0), λ the wave length, ß is the full-width at half-maximum, and θ the diffraction angle. The full-width at half-maximum (ß) that is used for the calculation of crystallite size must be corrected and using formula of lattice parameter. Where: B is the measured full-width at half-maximum (FWHM) of each phase.

Finding Lattice parameters of the peaks

1. peak 2: $2\theta = 31.54 \rightarrow \theta = 15.77$
   FWHM=0.2138°
   d= 2.834
2. peak 3: $2\theta = 38.89 \rightarrow \theta = 19.445$
   FWHM=0.1895°
   d= 2.313
3. peak 6: $2\theta = 56.18 \rightarrow \theta = 28.09$
   FWHM=0.3303°
   d= 1.635

To find B multiply FWHM by 180 and divide for 3.14 or (π) to convert to rad.

B = $\frac{0.2138\times180}{3.14}$ = 12.256 rad for Peak 2

B = $\frac{0.1895\times180}{3.14}$ = 10.863 rad for Peak 3

B= $\frac{0.3303\times180}{3.14}$ = 18.934 rad for Peak 6

With lattice parameter; $d_{hkl} = \frac{n\lambda}{2\sin\theta} = \frac{a}{\sqrt{h^2+k^2+l^2}}$

$a = \sqrt{h^2 + k^2 + l^2}\, d_{hkl}$ For peak number 2,, $\sqrt{1^2 + 0^2 + 1^2} = \sqrt{2} \times 2.83418 = 4.008$

B= $\frac{k\lambda}{t\cos\theta} \rightarrow t = \frac{k\lambda}{B\cos\theta} = \frac{0.94\times1.54A^0}{12.256\cos 15.77} = 1.227 \times 10^{-11}$

$a = \sqrt{h^2 + k^2 + l^2}\, d_{hkl}$ For peak number 3,, $\sqrt{1^2 + 1^2 + 1^2} = \sqrt{3} \times 2.31383 = 4.006$

B= $\frac{k\lambda}{t\cos\theta} \rightarrow t = \frac{k\lambda}{B\cos\theta} = \frac{0.94\times1.54A^O}{10.863\cos 19.445} = 1.413 \times 10^{-11}$

$a = \sqrt{h^2 + k^2 + l^2}\, d_{hkl}$ For peak number 6,, $\sqrt{1^2 + 1^2 + 2^2} = \sqrt{6} \times 1.63583 = 4.005$

B= $\frac{k\lambda}{t\cos\theta} \rightarrow t = \frac{k\lambda}{B\cos\theta} = \frac{0.94\times1.54A^0}{18.934\cos 28.09} = 8.667\times 10^{-12}$

C. Differential thermal Gravimetry (DGA)

The thermo-gravimetric (TG) curve shows a weight loss of 18.5% upon heating up to the same temperature. In order to obtain detailed results from the TG curve shown in Figure below, a differential curve DTG was reproduced, and it is shown in Figure together with the TG curve. A DTG peak at 40°C corresponds to a weight loss of 2.47 % on the TG curve from the room temperature to 220°C. A second DTG peak at 293°C corresponds to a weight loss of 2% taking place between 220 and 430°C. Then in the temperature range from 430 to 1000°C, the TG curve shows 15.8 % weight loss taking place in three consecutive stages; characterized by three DTG peaks at 612, 729, and 915°C.

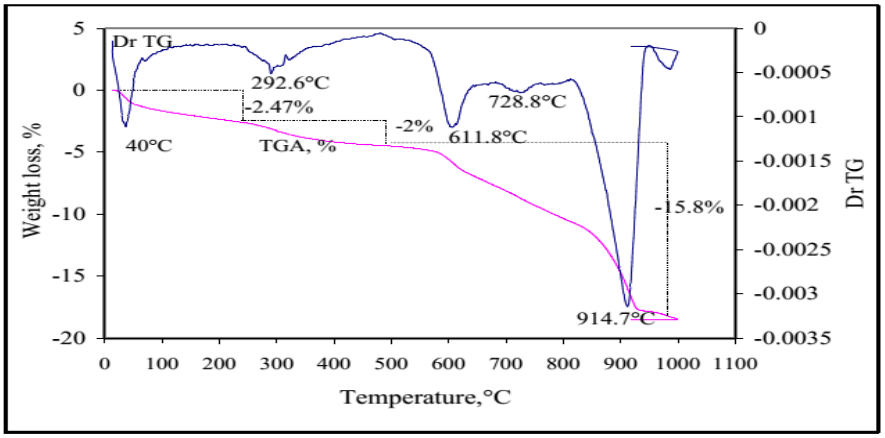


Fig. 6: DTG curves for the BaCO3-TiO2 milled powder mixtures.

CONCLUSION AND RECOMMENDATIONS

The results indicate that the values of sintered density, shrinkage and grain size are all in agreement. With the increase in sintering temperature, the density and the grain size increase. The activation energy for grain growth is determined increases with the increase of sintering temperature. The Curie temperature is progressively higher with increasing grain size. The low sintering temperature of ceramics seems to be attractive.

Before sintering because X-ray occurred on the particles those which do not compact much to found morphology of the pattern and for chemical analysis, we saw peaks of the intensity for crystalline and no peak for amorphous part.

Significant amount of amorphous is also seen which is regarded as defect in the experiment so we need more crystallinity and the both hydrothermal and Mechano chemical systems should be done with much care.

Generally, in this experiment we have seen that how a Barium Titanate (BaTiO3) from Barium Carbonate and Titanium oxide through a solid stat reaction. The hydrothermal route has an interesting advantage for the synthesis of powders consisting in low Sintering temperature. The effects of sintering at different temperatures on density, grain size and dielectric properties, for all solid solutions are studied.

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