Effects of Mechanical Activation of Precursors in The Synthesis of Ca-Doped BaTiO3 Via Conventional Solid State Reaction Method

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Abstract. The synthesis of pure ceramics with high degree of crystallinity is a major challenge especially in fabricating electronic devices. In this study, Ca-doped BaTiO3 with minimal impurity was successfully synthesized using conventional solid-state reaction method. The effect of mechanical activation of the precursors in the crystallinity and porosity of the material was investigated. For samples sintered at 1000 °C, the crystallite size slightly decreased from 5.410 Å to 5.288 Å which is equivalent to 2.31% reduction upon activation of precursors. At sintering temperature of 850 °C, the porosity increased from 35.985% to 39.217% with mechanical activation of the precursor powders while at 1000 °C, it jumped from 54.803% to 57.084%.

1. Introduction
Due to the current trend in the miniaturization of electronic devices, the synthesis of volume efficient nano- and microcrystals with excellent property, chemical stability and purity is very essential. One ceramic material that stands out is BaTiO3, an ABO3 type perovskite. Its high dielectric permittivity and notable ferroelectric properties make it useful as capacitors, sensors, piezoelectric transducers, thermistors, and memory devices among others [1-3]. Different studies are devoted to doping the said material to modify its properties making it more suitable for certain applications [4-6]. Most papers report the use of A and B site dopants to change the electrical and dielectric properties of BaTiO3.

Belonging to the alkaline earth metals which serves as an A site dopant, special attention is given to calcium (Ca) in altering the properties of BaTiO3. Ca2+ ions are more likely to substitute Ba2+ than Ti ions [7, 8]. The addition of Ca in BaTiO3 reduces the lattice parameters and, hence, cell volume [7] [9]. Ba1-xCaxTiO3 (BCTO), which belongs to the space group P4mm (No. 99) at room temperature, presents wide range of applications. Doping of BaTiO3 with Ca is commonly done to extend the working temperature range of multi-layer ceramic capacitors of up to 150°C [10] for various applications like infrared detectors, piezoelectric transducers, and ferroelectric memories. Dielectric filter, dielectric resonator, as well as stacked piezoelectric actuator utilizing piezoelectricity are also its other uses [11]. Furthermore, it has also promising applications in advanced laser system, optical
interconnects, and photo-refractive applications such as phase conjugation or holographic intra-cavity laser mode selection. BCTO crystals have long been acknowledged for its high potential in environment-friendly, lead-free electro-optic modulators and memory devices [12, 13].

Several ways of synthesizing Ca-doped BaTiO$_3$ are published in papers. Ba$_{1-x}$Ca$_x$TiO$_3$, with $x = 0.12$ and 0.20 were grown by optical floating-zone method by Kim et al [14]. Single crystals of BCTO were synthesized through high temperature solution growth technique using KF flux in a vertical silicon carbide furnace [15]. A-site complex perovskite Ba$_{1-x}$Ca$_x$TiO$_3$ ($x \leq 0.25$) plate-like particles with high aspect ratio and micron sizes were produced via designed topochemical microcrystal conversion reaction between the platelet Bi$_4$Ti$_3$O$_12$ and the powdered BaCO$_3$–CaCO$_3$ mixture [16, 17]. Ba$_{1-x}$Ca$_x$TiO$_3$ crystals of various composition were grown using a solution method developed by Balakumar et al [18]. Single-crystal fibers with various compositions were obtained by laser heated pedestal growth method using SrTiO$_3$ and Ba$_{1-x}$Ca$_x$TiO$_3$ seeds, with $x = 0.1$ and 0.2 [9]. Hydrolysis method was employed by Park et al using barium hydroxide monohydrate, titanium isopropoxide and calcium chloride as precursors [7]. Perhaps, the most preferred way of synthesizing ceramics, which includes doped and undoped BaTiO$_3$, is by solid-state reaction (SSR) due to its scalability, economic practicality in using cheap precursors and ease of preparation. Conventional SSR synthesis of BaTiO$_3$ is described elsewhere [19].

In preparing Ca-doped BaTiO$_3$ via conventional SSR, a powder precursor which serves as a source of Ca ions is added prior to calcination [11]. The method has downsides especially when it comes to unreacted precursors and the formation of large crystals, not to mention the high energy consumption due to very high temperature and long duration of heating. From the study of Ashiri et al., highly pure BaTiO$_3$ nanocrystals with improved crystallinity were synthesized even at lower sintering temperature by solid state reaction with mechanical activation of the precursors through ball-milling [20]. This makes the method more appealing, especially in mass production.

The study aims to synthesize Ba$_{0.90}$Ca$_{0.10}$TiO$_3$ using CaCO$_3$ as dopant source and determine whether mechanical activation of precursors through manual grinding would have interesting effects when it comes to doping BaTiO$_3$ with Ca.

2. Experimental Methods

The precursor powders BaCO$_3$ (HiMedia, 98% purity), TiO$_2$ (Aldrich, 99%) and CaCO$_3$ (RTC, 99%) were ground separately in a clockwise manner for about 2h using a ceramic mortar and pestle. Stoichiometric ratios of the precursors were measured to produce Ba$_{0.90}$Ca$_{0.10}$TiO$_3$. The powders were mixed and again manually grinded for 1h to ensure the homogeneity of the solution. Few drops of ethanol were added to make the mixture slurry. At least 1.00 g of the mixed powder were placed in a 15 mm-hole diameter pelletizer and subjected to a pressure of around 15 MPa using a uniaxial hydraulic press for 2 min. Then, the pellets were thermally treated for 3h in furnace (Yamato, FO410C) under air medium at 850 °C and 1000 °C. A ramp up rate of 10 °C/ min was used. The samples were cooled down to 110 °C at a rate of 10 °C/ min before it was taken out from the furnace. To investigate the effect of grinding of the precursors, another set of samples were synthesized without the grinding of initial powders prior to the 1h manual mixing. Table 1 shows the summary of the parameters used in each sample. To determine if the doping is successful, another sample was synthesized without CaCO$_3$.

| Grinding time (h) | Temperature |
|------------------|-------------|
|                  | 850 °C      | 1000 °C |
| 0                | 0h-850      | 0h-1000 |
| 2                | 2h-850      | 2h-1000 |

Table 1. Summary of the parameters used for each sample pellets.
The samples were subjected to x-ray diffraction (SHIMADZU, XRD-7000 Maxima) using Cu Ka radiation with a scan rate of 2.0°/min to investigate the crystallinity and structure of the pellets. The surface texture was investigated through an optical microscope (OLYMPUS, CX31). Finally, the densities under air and ethanol media were measured to assess the porosity of the ceramics.

3. Results and Discussion

The XRD patterns of the samples treated at 1000 °C are shown in figure 1. The two samples have very similar diffraction pattern. The peaks located at approximately 22.21°, 31.54°, 38.91°, 45.31°, 56.25°, and 65.84° matched well with the planes (1 0 0), (1 0 1), (1 1 1), (2 0 0), (2 1 1) and (2 0 2) of a tetragonal structure of pure BaTiO$_3$ ($a = b = 3.9988$ Å and $c = 4.0222$ Å) with a unit cell volume of 64.3166 Å$^3$. [21] No other phases of BaTiO$_3$ was observed. However, there exist a small peak at around 2θ = 28.25° for both samples which may be from an excess unreacted TiO$_2$ (rutile) precursor, though the intensity is negligibly small.

![Figure 1. XRD patterns of the Ca-doped samples in comparison to the reference BaTiO$_3$ [26].](image1)

![Figure 2. Peak of (1 1 1) plane of the Ca-doped samples in comparison with the reference BaTiO$_3$ [26].](image2)

The peak of (1 1 1) plane for the samples 2h-1000 and 0h-1000 are shown in figure 2 in comparison with the reference BaTiO$_3$. Both the Ca-doped samples’ (1 1 1) peaks are located at 38.913° which are slightly shifted to the right relative to that of pure BaTiO$_3$ by 0.004°. This signifies that the lattice parameters of the doped samples are slightly lower than that of the pure BaTiO$_3$, hence the unit cell volume is also smaller, consistent with the other reports. [7, 9] Though the exact value of the lattice parameters were unable to determine from the diffractogram. The results suggest that conventional solid state reaction method could satisfactorily produce the desired doping without sacrificing the homogeneity of phases of BaTiO$_3$. Assuming a perfect substitutional doping, the theoretical density of the Ba$_{0.90}$Ca$_{0.10}$TiO$_3$ would be equal to 5.769 g/cm$^3$.

Table 2 summarizes the peak profile of the plane (1 1 1) for the two samples and their computed crystallite size. The crystallite size $L$, of the samples were computed using Scherrer’s equation,

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}.$$  \hspace{1cm} (1)

where $B$ is the full width at half maximum (FWHM) of the peak located at 2θ, $\lambda$ is the radiation wavelength (Cu $K_\alpha$, 1.54056 Å) used by the X-ray diffractometer and $K$ is the Scherrer’s constant which varies from 0.6 to 2.08 depending on the crystal morphology. For simplicity, its value is assigned to as 1. The sample synthesized from mechanically activated precursors has a crystallite size
of 5.288 Å. The sample produced from inactivated precursors has a crystallite size of 5.410 Å which is 2.31% larger than the former. The mechanical activation of the precursors could reduce the crystallite size to some extent. The decrease is primarily due to the finer grains of the precursor powders. Since smaller particles are involved in the chemical reaction, tinier crystals are expected to be formed.

| Sample    | 2θ (°)  | Relative intensity | FWHM  | Crystallite size (Å) |
|-----------|---------|--------------------|-------|----------------------|
| 2h-1000   | 38.913  | 25.27              | 0.309 | 5.288                |
| 0h-1000   | 38.913  | 26.93              | 0.302 | 5.410                |
| reference BaTiO₃ [26] | 38.909  | 27.55              | ---   | ---                  |

Table 2. Peak profile of plane (1 1 1) for the Ca-doped and reference BaTiO₃ and corresponding crystallite size.

The images of the samples under optical microscope, taken at same magnifications, are shown in figure 3. Generally, the surface of the pellets contain holes or cavities of various sizes which indicates porous characteristic.

![Optical images](image)

Figure 3. Optical images the Ca-doped samples a) 0h-850, b) 2h-850, c) 0h-1000 and d) 2h-1000.

By examining the ‘average appearance’ of the pellets’ surface, the porosity can be evaluated to good approximation. Comparing the samples synthesized from mechanically activated precursors, 2h-850 and 2h-1000, the sample which was thermally treated at higher temperature, contains more pores. Same thing was observed between the samples produced from inactivated precursors, 0h-850 and 0h-1000.

On the other hand, by comparing the samples treated the same temperature, 0h-850 and 2h-850, it can be noticed that the sample which was synthesized using the mechanically activated precursors, obtained relatively smaller pores. Between 0h-1000 and 2h-1000, the former is characterized by relatively tinier holes or cavities. This is due to the reduction in the grain size of the precursor powder upon grinding. Smaller powder particles decreases the gaps/ voids between grains when pressed upon pelletization. It also reduces the cavities which are formed from the evaporation of CO₂ a chemical byproduct during reaction.

To effectively measure the porosity of the samples, the apparent and actual densities of each pellet were determined. By measuring the dimensions of each pellet and by weighing the pellets in air and in ethanol medium, the apparent and actual volumes were computed, as presented in table 3. The porosity
was evaluated from the difference of the apparent and actual densities of the samples. The results are shown in table 4. Remarkably, the samples which were thermally treated at higher temperature are indeed more porous, consistent with the observations in the microscope. The synthesis at relatively high temperatures results to the formation of larger crystals. For big crystals, the gaps or void in the grain boundaries tend to be large as well.

**Table 3.** Dimensions, mass and computed densities of the samples.

| Sample | average thickness (mm) | average diameter (mm) | $m_{air}$ (g) | $m_{ethanol}$ (g) | $V$ (cm$^3$) | $V_{actual}$ (cm$^3$) |
|--------|------------------------|-----------------------|---------------|------------------|-------------|-------------------|
| 2h-850 | 3.435                  | 14.645                | 1.132         | 0.855            | 0.579       | 0.352             |
| 0h-850 | 3.115                  | 14.685                | 1.050         | 0.784            | 0.528       | 0.338             |
| 2h-1000| 3.445                  | 15.720                | 1.001         | 0.775            | 0.669       | 0.287             |
| 0h-1000| 3.785                  | 15.735                | 1.088         | 0.826            | 0.736       | 0.333             |

**Table 4.** Computed and actual density and percentage porosity of the sample pellets.

| Sample | $\rho$ (g/cm$^3$) | $\rho_{actual}$ (g/cm$^3$) | % P |
|--------|------------------|----------------------------|-----|
| 2h-850 | 1.956            | 3.219                      | 39.217 |
| 0h-850 | 1.990            | 3.109                      | 35.985 |
| 2h-1000| 1.497            | 3.488                      | 57.084 |
| 0h-1000| 1.478            | 3.271                      | 54.803 |

The mechanical activation of the precursors barely increases the porosity of the pellets. Porosity is an important property since it is correlated to the occurrence of chemical reactions. Generally, greater amount of the desired product can be achieved at higher porosity because of the assurance of higher probability of occurrence of a chemical reaction.

Mechanical activation of the precursors results to a slight reduction in the crystallite size and a small increase in the porosity. Grinding of the precursor powders lead to smaller particles which exposes more areas to come into contact with other particles. This results to better diffusion of ions, improving the reaction between particles. Mechanical activation also induces the formation of lattice defects, specifically dislocations, which accelerates chemical reaction [20]. As a consequence, the formation of BCTO could occur at lower temperature. The growth of smaller crystals is favored at lower temperature, hence the reduction in the crystallite size. Although there are no XRD data for the samples sintered at 850 °C, it is expected that there will be lesser amount of unreacted precursors for the sample that uses mechanically activated precursors.

The computed actual densities of the samples deviate considerably from the theoretical density calculated from the presumed lattice parameters of Ba$\text{0.90}$(Ca$\text{0.10}$)TiO$_3$ ($a = b = 3.9988$ Å and $c = 4.0222$ Å). The presence of unreacted precursor as seen on XRD and the imperfections of the shape of the pellets, which were not accounted for, contributed to the said deviation.

**4. Conclusions**

The synthesis of Ba$\text{0.90}$(Ca$\text{0.10}$)TiO$_3$ with minimal impurity is possible with the conventional solid state reaction method. Mechanical activation of the precursors does not have significant effect in the elimination of unreacted precursors but it favors the reduction of the crystallite size. It also improves the porosity of the ceramic to some extent. Further, mechanical activation in the conventional solid state reaction could only contribute little improvement in the synthesis of Ba$\text{0.90}$(Ca$\text{0.10}$)TiO$_3$ as far as XRD patterns of the samples treated at 1000 °C is concerned.

The effect of mechanical activation of precursors was not properly emphasized. Chemical reaction leading to the formation of BCTO might have been completed at earlier time for all the samples given
the high temperature of thermal treatment. Perhaps, the samples that uses mechanically activated precursors completely transformed to BCTO at lower temperature at an earlier time. But due to the extended thermal treatment and because of the relatively high temperature, even the sample that uses inactivated precursor might have also completely transformed into BCTO. Thus, to properly investigate the effect of mechanical activation, it is highly recommended to characterize samples that are treated at much lower temperatures or sintered at lesser duration time.

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