Low temperature formation of barium titanate in solid state reaction by mechanical activation of BaCO₃ and TiO₂

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Abstract
In this study, the effects of mechanical activation on BaTiO₃ formation from BaCO₃ and TiO₂ powders were investigated. Differential thermal analysis (DTA), high-temperature x-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR) studies were performed following the mechanical activation of the powder mixture to reveal the phase formation and structural changes. In addition, the powder mixtures were sintered at 1350 °C for 3 h. Structural differences between the non-activated and activated samples were observed with scanning electron microscopy (SEM), and their electrical properties were measured to study the effects of mechanical activation. It was observed that mechanical activation increased the chemical reactivity of BaCO₃ and TiO₂ powders, causing amorphization and structural disorder in their structures. These were confirmed with XRD and FT-IR analysis. The 120-min activation of a mixture of barium carbonate and titania caused a decrease in the formation temperature of the Ba₂TiO₄ phase from 815 °C to 640 °C, while the formation temperature of the BaTiO₃ phase decreased from 1095 °C to 890 °C. It was observed that the dielectric constants of the samples were increased by increasing the mechanical activation time.

1. Introduction
Materials used in applications where ferroelectric properties are needed have a generalized chemical formula of AIITiIVO₃, where A can be Ca, Pb, Sr, Ba, Zn, Fe, etc. These materials have wide band gaps that are affected by their chemical composition and, consequently, their structure and microstructure [1]. One of these titanium-based oxides is barium titanate (BaTiO₃) with perovskite structure. Barium titanate has unique properties, including a high dielectric constant ranging from 100 Hz to 1 MHz and a high piezoelectric coefficient (d₃₃, 191 pC/n). These properties make it useful for applications such as multilayer ceramic capacitors (MLCCs), dielectric capacitors, dynamic random access memory (DRAM) capacitors, positive temperature coefficient (PTC) resistors, energy storage, and thermistors [2–6]. For MLCC production, BaTiO₃ powders with small grain sizes are essential in order to downsize capacitors formed from thin ceramic layers with high dielectric permittivities [3].

Conventional solid-state BaTiO₃ synthesis has consisted of three main stages since its ferroelectricity was discovered in 1940. In the first stage (equations (1)–(2)), barium carbonate decomposes into BaO (equation (1)). In this stage, TiO₂ particles act as a catalyst and a rapid reaction proceeds between the contact surfaces of the reactants. The diffusion of Ba²⁺ ions into TiO₂ forms a surface layer of BaTiO₃ on the outer surfaces of the TiO₂ particles, separating the reactants (equation (2)). In the second stage, barium oxide reacts with the previously formed BaTiO₃ via further diffusion of Ba²⁺ through BaTiO₃ into the TiO₂ grains to form Ba₂TiO₄ (equation (3)). The third stage is the reaction of the formed Ba₂TiO₄ and residual TiO₂ to form the final phase of BaTiO₃ (equations (4)–(5)) [7–11].

\[
\begin{align*}
\text{BaCO}_3 & \rightarrow \text{BaO} + \text{CO}_2 \\
\text{BaO} + \text{TiO}_2 & \rightarrow \text{BaTiO}_3
\end{align*}
\]
showed three structural phase transitions
attrition-type milling apparatus. They reported that the particle size of the obtained BaTiO3 was about 10 nm
The stoichiometric mixtures 2. Experimental and the milling conditions of BaCO3. They observed that mechanically milling the BaCO3 particles accelerated
formation, the basic formation mechanism of barium titanate remained the same. Kong
powder. In their study, they found that high energy grinding produced high lattice defects in BaTiO3 powder.
The literature shows that the conventional sintering process requires temperatures as high as 1300 °C for complete densification and that sintering aids are necessary for liquid phase formation. This results in grain growth that negatively affects the sintering and densification process by causing deceleration due to the transportation of substances by solid-state diffusion [5]. Although some processes, such as hot-pressed sintering (HP) or spark plasma sintering (SPS), exist for the synthesis of small-grained BaTiO3, economic concerns limit its production, leading researchers to seek more economical and simpler routes. The mechanical activation of the starting materials, BaCO3 and TiO2, and the mechanochemical synthesis of BaTiO3 have been frequently intensively studied in this respect.
Ghosh et al[12] examined the effects of mechanical activation on structural defects in a commercial BaTiO3 powder. In their study, they found that high energy grinding produced high lattice defects in BaTiO3 powder. Ohara et al[13] produced single-phase, fine BaTiO3 nanoparticles using a mixture of BaCO3 (50 nm in size) and TiO2 (7 nm in size) as a constituent powder via rapid mechanochemical synthesis as short as 12 min using an attrition-type milling apparatus. They reported that the particle size of the obtained BaTiO3 was about 10 nm and that residual BaCO3 was observed in the product. Barium titanate powders have also been prepared by a modified Pechini process using polymeric precursors. Attrition milling was used to prevent the agglomeration of the nanopowders and to improve their CT properties. The synthesized (BT) and milled (BTA) powders were sintered at 1300 °C for 8 h and it was observed that the temperature dependence of the relative permittivity showed three structural phase transitions [14]. In another study, a BaCO3 and TiO2 powder mixture was mechanically activated by a planetary ball mill for up to 4 h in an air atmosphere and gradual formation of the BaTiO3 phase arising from mechanochemical reactions was reported by Stojanovic et al[15] Gomez-Yanez et al [16] investigated the effects of prolonged milling (24 h and 72 h) of a mixture of BaCO3 and TiO2 powders in an attritor on the synthesis reaction of BaTiO3. They reported that, despite the acceleration of BaTiO3 and Ba2TiO4 formation, the basic formation mechanism of barium titinate remained the same. Kong et al[17] also studied the formation of barium titinate by the mechanical activation of a BaCO3 and TiO2 mixture, finding that no reaction started during milling but that the formation temperature was decreased. Manzoor and Kim [18] studied the size control of BaTiO3 in a solid-state reaction between TiO2 and BaCO3 by varying the size of TiO2 and the milling conditions of BaCO3. They observed that mechanically milling the BaCO3 particles accelerated the diffusion process and decreased the calcination temperature.

The main goal of the current study is to investigate the effects of mechanical activation on the structure of BaCO3 and TiO2 powders and on the formation temperature and electrical properties of barium titinate.

2. Experimental
The stoichiometric mixtures (equimolar 1:1, BaCO3:TiO2) of BaCO3 (purity > 99%, Fluka, Germany) and TiO2 (purity > 99%, Riedel de Haen, Germany) were prepared by mixing them in isopropyl alcohol in a ball mill for 10 hours to obtain a homogeneous mixture. They were then dried in a rotary evaporator. The dried mixtures were mechanically activated in a planetary mill (Fritsch Mono Mill Pulversitë 6) according to the conditions set out in table 1.

Table 1. Experimental conditions for mechanical activation.

| Activation time | 30, 120 min |
|----------------|-------------|
| Sample/ball weight ratio | 1/20 |
| Rotation speed | 600 rpm |
| Grinding media | Dry |
| Grinding bowl | 250 ml tungsten carbide (WC) |
| Grinding balls | Ø 10 mm–8.14 g (WC) |

\[
\begin{align*}
\text{BaTiO}_3 + \text{BaO} & \rightarrow \text{Ba}_2\text{TiO}_4 \\
\text{Ba}_2\text{TiO}_4 & \rightarrow \text{BaTiO}_3 + \text{BaO} \\
\text{TiO}_2 + \text{BaO} & \rightarrow \text{BaTiO}_3
\end{align*}
\]

BaTiO3 + BaO → Ba2TiO4
Ba2TiO4 → BaTiO3 + BaO
TiO2 + BaO → BaTiO3

The grain size of the samples was measured by a Malvern Mastersizer 2000 Particle Size Analyzer and their density was measured by a Micrometrics AccuPyc II 1340 helium pycnometer. The degree of amorphization of the mechanically activated samples (0, 30, 120 min) was calculated from x-ray diffraction (XRD) data obtained at room temperature, with the scanning angle in the range of 10°–90° and the scanning speed at 10 deg min⁻¹. The degree of amorphization (A) of the mechanically activated BaCO3 and TiO2 was calculated from equation (6) [19, 20] by using the highest peaks of BaCO3 (2h: 23.88) and TiO2 (2h: 25.28)
where \( I_0 \) is the integral intensity of the diffraction peak for non-activated BaCO\(_3\) and TiO\(_2\), \( B_0 \) is the background of the diffraction peak for non-activated BaCO\(_3\) and TiO\(_2\), and \( I_x \) and \( B_x \) are the equivalent values for the activated BaCO\(_3\) and TiO\(_2\).

Phase analysis of the products was carried out by using a high-temperature x-ray diffractometer (Rigaku Smartlab TM) under a Cu K\(\alpha\) radiation source with a scanning angle of 2\(\theta\) to 10°–90°, a scanning speed of 10 deg min\(^{-1}\), and a temperature range of 25°C–1400°C. The thermal behavior of the samples was studied with a TA Instruments SDTQ 600 at a heating rate of 10°C min\(^{-1}\) under an air atmosphere. The changes in the bond structure of the samples were examined by Fourier transform infrared spectroscopy (FT-IR) using a Shimadzu IRAfinity system.

The cylindrical pellets (11 mm diameter and 2.5 mm height) were pressed in a cold iso-press (CIP) at 100 MPa and were sintered in air at 1300°C for 1 hour at a heating rate of 10°C min\(^{-1}\). The microstructure of the sintered samples was examined by scanning electron microscopy (SEM) using a JEOL 6060 LV in secondary electron (BSI) mode at 2000 times magnification.

To measure the electrical properties of the sintered samples, the sample surfaces were coated with silver paste. The capacitance of the pellets was measured at frequencies from 500 Hz to 5 \(\times\) \(10^6\) Hz with a Hioki 3532-50 LCR Hi-tester. The dielectric constant (\(\varepsilon_r\)) was calculated by using equation (7) [21]

\[
\varepsilon_r = \frac{C.l}{\varepsilon_0.A} \tag{7}
\]

where \(C\) is capacitance, \(l\) is the film thickness, \(A\) is the area of the film, and \(\varepsilon_0\) is the permittivity of free space (\(\varepsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}\)).

3. Results and discussion

3.1. Characterization of powders

The effects of mechanical activation on the phases of the powder mixture are given in figure 1. Due to the mechanical activation, the intensity of the peaks decreased. In addition, some peaks detected in the non-activated mixture became impossible to distinguish after mechanical activation. The existing peaks of the activated sample also broadened, in contrast with the non-activated sample. The XRD peak broadening indicates changes in the microstructure, rather than the phase structure [21, 22]. Grinding causes a decrease in the crystallite size and usually in the particle size as well. The decrease in these sizes favors the reaction between the two phases, which is why the formation temperature of BaTiO\(_3\) is lowered. After this point, structural defects occur with milling. Lattice imperfections cause amorphization and can be detected by a decrease in intensity and peak broadening in XRD analyses [19, 25, 24]. The intensity decrease for peaks belonging to BaCO\(_3\) may be
caused by the partial decomposition of the carbonates due to the temperature increase in the milling media. Any new phase formations could not be detected.

The degree of amorphization of BaCO₃ and TiO₂ as a function of mechanical activation time was calculated by equation (6) and is given in figure 2. The degree of amorphization of TiO₂ increased from 81.88% to 95.17% as the mechanical activation time increased from 30 to 120 min. The degree of amorphization of BaCO₃, meanwhile, increased from 52.13% to 72.70% as the mechanical activation time increased from 30 to 120 min.

The grain size and specific surface area as a function of milling time are given in figure 3. The mean grain size of the non-activated sample was measured as 42.23 μm. As the mechanical activation time was increased to 30 min and 120 min, the sample size decreased to 24.44 μm and 8.80 μm, respectively. As a result of the grain size reduction, the specific surface areas of the samples increased with increasing activation time and were 0.97, 1.31, and 3.1 m² g⁻¹ for activation times of 0, 30, and 120 min.

FT-IR analysis of the non-activated and activated mixtures is given in figure 4. For the purposes of having a clear view of the bands present in the 4000 cm⁻¹–1200 cm⁻¹ and 1200 cm⁻¹–500 cm⁻¹ regions, these graphs are given separately. In the literature, asymmetric stretching of the simple carbonate CO₃²⁻, out-of-plane bending of CO₃²⁻ and in-plane bending of CO₃²⁻ are determined to be at 1415 cm⁻¹, 856 cm⁻¹, and 693 cm⁻¹ respectively [24–26]. The non-activated mixture exhibits asymmetric stretching of the simple carbonate at 1413 cm⁻¹, and this band tends to shift to a higher frequency range with mechanical activation. Meanwhile, the transmittance percentage is decreased with prolonged mechanical activation times. The same phenomenon can be seen for the out-of-plane bending mode of CO₃²⁻ located at 856 cm⁻¹. The wavenumber of the in-plane bending mode of CO₃²⁻ did not change, but its percentage of transmittance decreased with mechanical activation as for the other modes. The 1058 cm⁻¹ centered band is attributed to the δ mode of CO₃. The complete disappearance of the
carbonate bands could not be obtained. After 120 min of mechanical activation, a broad band centered at 910 cm\(^{-1}\) was observed but could not be identified. Weak bands present from 600 cm\(^{-1}\)–500 cm\(^{-1}\) may be attributed to Ti-O bending vibrations \[25\]. Mechanical activation decreased the transmittance of the broad peak related to TiO\(_2\). From the results, it can be said that the carbonate structure was partially destroyed, as the related carbonate units still exist but do not have the same strength compared to the baseline. Shifting of a band center to a higher position indicates a decrease in the bond strength \[20\].

3.2. Thermal analysis of powders

Two endothermic peaks for the non-activated sample was detected by differential thermal analysis (DTA). The first endothermic peak at 815 °C corresponds to the decomposition of BaCO\(_3\) and the simultaneous formation of the intermediate phase of Ba\(_2\)TiO\(_4\) between BaO and TiO\(_2\). The second endothermic peak at 1095 °C corresponds to the formation of BaTiO\(_3\) from Ba\(_2\)TiO\(_4\) \[17\]. The temperatures of these peaks lowered to 640 °C and 890 °C, respectively, in the DTA curve of the mechanically activated (120 min) sample, as shown in figure 5.

In figure 6, high-temperature XRD analysis of the non-activated and activated powders (barium carbonate and titania) up to 1400 °C are given. As seen in the figure, peaks of barium titanate were seen at 900 °C in the non-activated powders, but these peaks were observed clearly at 700 °C in the activated powders. In addition, the remaining Ba\(_2\)TiO\(_4\) phase was detected in the non-activated powders up to 1400 °C. This result is compatible with the study of Gomez-Yanez et al \[16\]. In contrast, no remaining Ba\(_2\)TiO\(_4\) was detected in the activated powders at high temperatures up to 1400 °C. The only phase observed in this system is barium titanate. This is due to structural disordering in barium carbonate and titania and the increased reactivity of the mentioned materials. The high energy ball milling process has a lowering effect on the formation temperature of BaTiO\(_3\).
Figure 5. DTA graphs of non-activated and activated barium carbonate-titania samples.

Figure 6. High-temperature XRD of (a) non-activated and (b) activated for 120 min powder mixtures [1: BaCO₃ (ICDD 01-071-2394), 2: TiO₂ (ICDD 01-070-7348), 3: BaTiO₃ (ICDD 01-074-1968), and 4: Ba₂TiO₄ (ICDD 01-076-2826)].
Non-activated and activated (120 min) powder mixture samples were sintered at 1300 °C for 1 hour. SEM micrographs of these samples are given in figure 7. It was seen that the non-activated powders of barium carbonate and titania were sintered at this temperature but that they had a body with more porosity than the activated powders. The particles on the sintered body of the activated sample are less than 5 μm, while those in the sintered body of non-activated powders are between 5–10 μm.

The relative and true densities as a function of milling time are given in figure 8. The theoretical density of sintered barium titanate calculated based on the lattice constant is 6.02 g cm$^{-3}$ [27, 28]. As the mechanical activation time increased, the grain size decreased, and denser structures were formed as a result. The relative density of the non-activated sample was measured as 0.95. When the mechanical activation time was increased to 30 min and 120 min, the relative density increased to 0.97 and 0.98, respectively. Similar to the relative density, the true density of the samples increased to 6.14, 6.19, and 6.20 g·cm$^{-3}$ with an increase in activation time from 0, 30, to 120 min.

The dielectric constant versus frequency curves of the mechanically-activated samples at different times are shown in figure 9. While the dielectric constant of the samples remained almost constant between 500 and 10$^5$ Hz, a rapid increase in the dielectric constant was observed beyond 10$^5$ Hz. A significant increase in the dielectric constant was also detected with increasing mechanical activation time. It is known from previous studies that the dielectric constant of materials is particularly dependent on the particle size [29–31]. The maximum dielectric coefficient can be obtained at an optimum grain size. For coarse-grained ceramics, the dielectric constant at room temperature is lower than that of fine-grained ones. However, if the grain sizes are decreased further, then the dielectric constant decreases again to lower values [32]. Miclea et al [33] stated that the maximum dielectric coefficient (5800) of BaTiO$_3$ occurs for a 2 μm grain size. They found that the dielectric coefficient decreases when the grain size is smaller than 2 μm (0.2 μm: 3900) or larger than 2 μm (12 μm: 1000). Marinkovic et al [34] stated that the effect of the particle size of the dielectric coefficient of barium titanate was influenced by the
crystalline c/a ratio. They exposed a mixture of BaCO₃ + TiO₂ that had been mechanically activated for 0, 30, or 180 min to sintering at 1200 °C. They observed that the increase in mechanical activation increased the crystalline c/a ratio, thereby increasing the dielectric coefficient.

4. Conclusion

The structure of a powder mixture consisting of BaCO₃ and TiO₂ was altered with mechanical activation. Lattice imperfections caused amorphization, which was detected from intensity decreases and peak broadening in XRD analyses. This amorphization phenomenon lowered the formation temperature of BaTi₂O₄ from 815 °C to 640 °C and the formation temperature of BaTiO₃ from 1095 °C to 890 °C. In high-temperature XRD analysis, the barium titanate phase was detected at 900 °C in the non-activated powders, but for the activated sample (120 min), it was observed at 700 °C. In addition, XRD analyses showed that the residual Ba₂TiO₄ phase could not be detected for the activated powder mixture. The only phase observed in this system was barium titanate, while the remaining Ba₂TiO₄ phase was detected in the non-activated powders up to 1400 °C. SEM analysis of sintered samples showed that, while the non-activated sample had coarsened particles, the activated sample was composed of fine, regular particles. In addition, the dielectric constants of the activated and sintered samples were higher than for the non-activated sample.

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Figure 9. Dielectric constant of mechanically activated samples at different times (0, 30, and 120 min).
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