The Effect of Mechanochemical on The Formation of Calcium Titanate (CaTiO₃) Prepared by High Energy Milling

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Abstract. Single-phase calcium titanate (CaTiO₃) was successfully synthesized by mechanical milling and the solid-state reaction of CaCO₃ and TiO₂. The speed of high energy ball milling was 700 rpm with the ball and jar were made from stainless steel. The milling time and ball to powder ratio was 10 h and 50 h, respectively. After milling for 10 h, the mixed powder of CaCO₃ and TiO₂ experienced heavy milling, which indicated by the average particle size before and after milling was > 1 µm and 85.56 ± 35.62 nm, respectively. Furthermore, the XRD pattern of milled powder revealed the disappearance of CaCO₃ peaks and a considerable reduction of TiO₂ peaks after milling for 10 h. Moreover, the presence of CaTiO₃ peaks in the milled powder was noticeably detected in the XRD pattern, showing the mechanical alloying of CaCO₃ and TiO₂ was occurred. The milled powder was calcined at 800, 900 and 1000°C for 2 h. The results showed the formation of a single phase of CaTiO₃ after calcination at any temperatures. However, the samples indicated the presence of Fe₂O₃, which from the milling media. The presence of impurities after milling is inevitable due to friction between ball and jar. Further study is needed to obtain the optimum condition of mechanical milling to minimize the contamination.

Keywords: Calcium titanate; mechanical milling; raw materials; calcination; impurities

1. Introduction
Calcium titanate, Ca₃TiO₇, is one of a group of metal compounds with a perovskite structure, has long been known as a dielectric ceramic with a high constant dielectric [1]. Hence, CaTiO₃ has important applications in microwave communication systems owing to ferroelectric properties [2]. Recently,
CaTiO₃ is considered as an orthopedic implant material due to the excellent biocompatibility properties [3–6].

Conventional technique to obtain CaTiO₃ is a solid state reaction between CaCO₃ or CaO and TiO₂ at a high temperature of 1350°C [7]. The heating conditions play an important role in producing crystallized CaTiO₃ powder [8]. However, this process is challenging to produce fine microstructure of CaTiO₃ due to grain growth during heating at high temperature. There are several methods to synthesize CaTiO₃, namely through the wet chemical method, for example, a colloidal sol-gel [9], alkoxide [10], polymeric precursors [11], spray pyrolysis [12], and hydrothermal [1]. A typical characteristic of CaTiO₃ that synthesize by wet chemistry is fine particle size, i.e., nanoscale range, and homogeneous in size. In addition to wet chemistry method, mechanical milling is also used to synthesize CaTiO₃ from CaCO₃/CaO and TiO₂. Mechanical milling of these powder has been effective to induce the reaction faster than a conventional solid-state reaction, called mechanochemical activation.

The mechanochemical process is the combination of the mechanical and chemical processes that used a grinding mill with a high intensity such as planetary mill, high energy milling, and oscillating mills. This process causes defects are being formed. Moreover, the mechanochemical process did not use many organic solvents needed in industrial chemical processes, making them environmental-friendly [13]. High-energy ball mills have been used in producing ultra-fine powder in the sub-micron to the nanometer range. In addition, this process causes severe and intense mechanical action on solid surfaces, which causes the physical and chemical changes in the area near the surface where solids come in contact with mechanical forces, therefore have a great impact on the phase composition, morphology, particle size, and surface area [14]. Currently, this method is used to synthesize inorganic materials because it shows several advantages, such as a reduction in sintering temperature [15–17]. Based on this background, this work aims to synthesize CaTiO₃ through mechanochemical method. The effect of milling parameter and their relationship with the calcination temperature to produce a single-phase CaTiO₃ was investigated thoroughly in this study.

2. Experimental method

CaCO₃ calcite (Kanto Chemical Co. Inc., p.a. 99.5%) and TiO₂ rutile (Kanto Chemical Co. Inc., p.a. 99.0%) were used as raw materials in this study. The powder was mixed with a mass weight based on stoichiometric calculations of CaTiO₃. The mixed powder was milled for 10 h in the high energy ball milling (HEM Shaker Mill, Fisika Laboratoria, Indonesia) that has speed of 700 rpm with the ball to powder ratio was 50. Stainless steel mill jar and ball were used in this study. In order to increase the effectiveness of milling and homogeneous mixture of the powders, ethanol was used as an immersion medium during milling. Subsequently, the milled powder was calcined at 800, 900 and 1000°C for 2 h with heating rate 5°C/minute in the air atmosphere.

The morphology of milled and calcined powder was observed using scanning electron microscopy (SEM, FEI Quanta 650, USA). The average particle size was estimated by measuring the diameter of 100 particles from the SEM images and analyzed statistically. The crystalline phase after milling and calcination was examined by X-ray diffraction (XRD, Shimadzu Maxima-X 7000, Japan) with CuKα radiation (λ=1.5418).

3. Results and discussion

Figure 1 displays SEM images of the microstructure of a mixture of CaCO₃ and TiO₂ samples before and after milling. It is obvious that, the mixture of CaCO₃ and TiO₂ before milling distinguish two particles that differ in size, as shown in Figure 1 (a). The big and fine particle in Figure 1 (a) were CaCO₃ and TiO₂, respectively. After being milled for 1 hour (Figure 1 (b)), the particle shape begins to collapse and the size becomes smaller with the same contour. No evidence the presence of big particle, which indicates that CaCO₃ powder is already pulverized after milling for 1 h. Moreover, it is found that the particle shape is irregular, which is more likely from the CaCO₃ powder. Further milling time until 10 h, revealing the existence of slab shaped particle, as shown in Figure 1 (c). This means
that the milling process is related to the agglomerate process to produce a small particle size and a wider surface [18]. Indeed, the particle size of the milled powder decreased with increasing milling time. The average particle size for 1 and 10 h milling was 185 ± 57 and 85 ± 35 nm, respectively. This is confirming the advantage of high energy milling to obtain the nanoparticle powder only in 10 h of milling time.

Figure 1. SEM of the CaCO$_3$-TiO$_2$ powder mixtures (a) before milling and after milling for (b) 1 h and (c) 10 h.

Figure 2 shows the XRD pattern of a mixture of CaCO$_3$ and TiO$_2$ before and after milling for 10 h. The diffraction peaks of the sample before milling had high intensity and highly crystalline phase of CaCO$_3$ and TiO$_2$, which reveals the composition of initial powder that consists of CaCO$_3$ and TiO$_2$ powder. However, a dramatic change occurred after milling for 10 h, where CaCO$_3$ peaks disappear. The disappearance of CaCO$_3$ peaks implied that the crystalline phase of CaCO$_3$ become amorphous, thus could not detected in the XRD. Contrary, although TiO$_2$ powder experienced the same heavy milling with CaCO$_3$, small peaks of TiO$_2$ still exist after 10 h of milling. This difference is more likely due to the difference in hardness of CaCO$_3$ and TiO$_2$, where the hardness of CaCO$_3$ and TiO$_2$ was 3.0 and 6.5-7.0 GPa, respectively [19]. This reduction in peak energy implies the formation of amorphous material from the milling material. This is consistent with research conducted by several researchers when high energy milling was carried out on oxide materials [8]. One notable finding in this study is the formation of CaTiO$_3$ phase after milling for 10 h, as shown in Figure 2. The formation of a new phase during mechanical milling is called mechanical alloying [20]. Milling causes a decrease in particle size, hence the diffusion paths to be shortened. Moreover, the particle that went through heavy milling has a lot of energy in their surface. Therefore, the kinetic energy of the system increases so that it could provides energy for the reappearance of new crystallization [21]. However, the formation of CaTiO$_3$ induced by mechanical milling depends on the milling condition, i.e., time, speed of milling and ball to powder ratio. For instance, a single phase of CaTiO$_3$ formed after mechanical milling for 15 h with the ball to powder ratio was 20 and speed of milling was 300 rpm.
[22]. Furthermore, another study showed the CaTiO$_3$ was obtained after milling for 70 h with the ball to powder ratio was 70 [23]. In this present study, the milling condition is moderately mild, where the milling time only for 10 h and the ball to powder ratio is 50, yet the CaTiO$_3$ was already observed. However, after milling for 10 h, Fe peak identified, which it might be the contamination from the milling media and ball mill that made from stainless steel. Impurities during mechanical milling are inevitable, in particular for the high ball to the powder ratio, which increases the wear between ball and mill jar or ball and ball. Therefore, the optimum condition during mechanical milling needs to improve for minimizing the contamination.

Figure 2. X-ray diffractometer pattern of CaCO$_3$-TiO$_2$ mixture before milling (0 h) and milling for 10 h (10 h).

Figure 3 shows XRD patterns of the milled powder after calcination at 800, 900, and 1000°C, for 2 hours in an air atmosphere. Despite the presence of Fe$_2$O$_3$ as impurities from the milling media, CaTiO$_3$ phase was formed at all calcination temperatures. Moreover, at the lowest calcination temperature, i.e., 800°C, no excess of CaCO$_3$ or TiO$_2$ were found, indicating that all of those phases react completely and formed CaTiO$_3$ phase, as shown in Figure 3. This is due to heavy milling that decreases the particle size of those powder, as shown in Figure 1 (c). Moreover, smaller particle size has a large surface area, thus the reaction between two particles take places without a significant effort. It should be noted that the complete reaction between CaCO$_3$ and TiO$_2$ to form CaTiO$_3$ occurred at 1350°C [7], while in this study at 800°C. This formation temperature of CaTiO$_3$ in this study is relatively low compared to other studies. For instance, Vukotic et al. [17] reported the formation of CaTiO$_3$ at 850°C, while Evans et al. [23] reported single phase CaTiO$_3$ were obtained at 920°C. Moreover, Berbenni and Marini [16] reported the synthesis of CaTiO$_3$ from the mechanically milled powder of CaCO$_3$ and TiO$_2$ at 750 – 850°C indicates the formation of CaTiO$_3$ along with CaO and TiO$_2$ at any temperature. Furthermore, as shown in Figure 3, the crystallinity of CaTiO$_3$ peaks increased with increasing temperature.

Figure 4 shows the SEM image of milled powder after calcination at 1000°C for 2 h. Although a high temperature was used, i.e., 1000°C, the particle size of CaTiO$_3$ showed $288 \pm 128$ nm,
which is fine particle size. This results was consistent with previous report by Cavalcante et al [11] whereby they explained that the increase in temperature promotes an increase in the average crystallite size or particle size. This relates to aggregate production and nuclei formation. Sreckovic [24] reported mechanical activation of powders during grinding improves their reactivity and further, the calcination process accelerates the formation of a new phase by a solid-state reaction. Moreover, almost homogenous particle size was obtained in this study with the unperfect spherical shape of CaTiO$_3$.

**Figure 3.** X-ray diffractometer pattern of CaTiO$_3$ with furnace temperature variations: 800°C, 900°C and 1000°C.

**Figure 4.** SEM of the CaCO$_3$-TiO$_2$ powder mixtures mechanically activated 10 h and furnace 1000°C.
4. Conclusion
Single-phase calcium titanate (CaTiO₃) was successfully obtained by high energy milling of raw powder followed by calcination. XRD pattern of milled powder revealed the powder experience heavy milling, which indicated by the disappearance of CaCO₃ peaks and a significant decrease of TiO₂ peaks. The loss of crystallinity of milled powder implied amorphous powder was obtained. Moreover, CaTiO₃ peak was observed in the milling time of 10 h, appearing that mechanical alloying between CaCO₃ and TiO₂ occurred during milling. However, Fe peak was also found in the milled powder, which the contamination from the milling media that is inevitable. Calcination of the milled powder led to the formation of CaTiO₃ along with the Fe₂O₃ as impurities regardless of the calcination temperature. Therefore, it can be concluded that single phase CaTiO₃ can be obtained at a relatively low temperature induced by mechanical milling. However, further study needed to minimize the contamination by optimizing the milling parameters.

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