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The Effect of Mechanochemical on The Formation of Calcium Titanate ($CaTiO_3$) Prepared by High Energy Milling

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Abstract. Single-phase calcium titanate ($CaTiO_3$) was successfully synthesized by mechanical milling and the solid-state reaction of $CaCO_3$ and TiO_2. 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 $CaCO_3$ and TiO_2 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 $CaCO_3$ peaks and a considerable reduction of TiO_2 peaks after milling for 10 h. Moreover, the presence of $CaTiO_3$ peaks in the milled powder was noticeably detected in the XRD pattern, showing the mechanical alloying of $CaCO_3$ and TiO_2 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 $CaTiO_3$ after calcination at any temperatures. However, the samples indicated the presence of Fe_2O_3, 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, $CaTiO_3$, 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, $CaTiO_3$ has important applications in microwave communication systems owing to ferroelectric properties [2]. Recently,

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$CaTiO_3$ is considered as an orthopedic implant material due to the excellent biocompatibility properties [3–6].

Conventional technique to obtain $CaTiO_3$ is a solid state reaction between $CaCO_3$ or CaO and TiO_2 at a high temperature of 1350°C [7]. The heating conditions play an important role in producing crystallized $CaTiO_3$ powder [8]. However, this process is challenging to produce fine microstructure of $CaTiO_3$ due to grain growth during heating at high temperature. There are several methods to synthesize $CaTiO_3$, 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 $CaTiO_3$ 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 $CaTiO_3$ from $CaCO_3$/CaO and TiO_2. 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 oscillatig 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 $CaTiO_3$ through mechanochemical method. The effect of milling parameter and their relationship with the calcination temperature to produce a single-phase $CaTiO_3$ was investigated thoroughly in this study.

2. Experimental method

$CaCO_3$ calcite (Kanto Chemical Co. Inc., p.a. 99,5%) and TiO_2 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 $CaTiO_3$. 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 CuK-α radiation (λ=1.5418).

3. Results and discussion

Figure 1 displays SEM images of the microstructure of a mixture of $CaCO_3$ and TiO_2 samples before and after milling. It is obvious that, the mixture of $CaCO_3$ and TiO_2 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 $CaCO_3$ and TiO_2, 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 $CaCO_3$ 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 $CaCO_3$ 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.

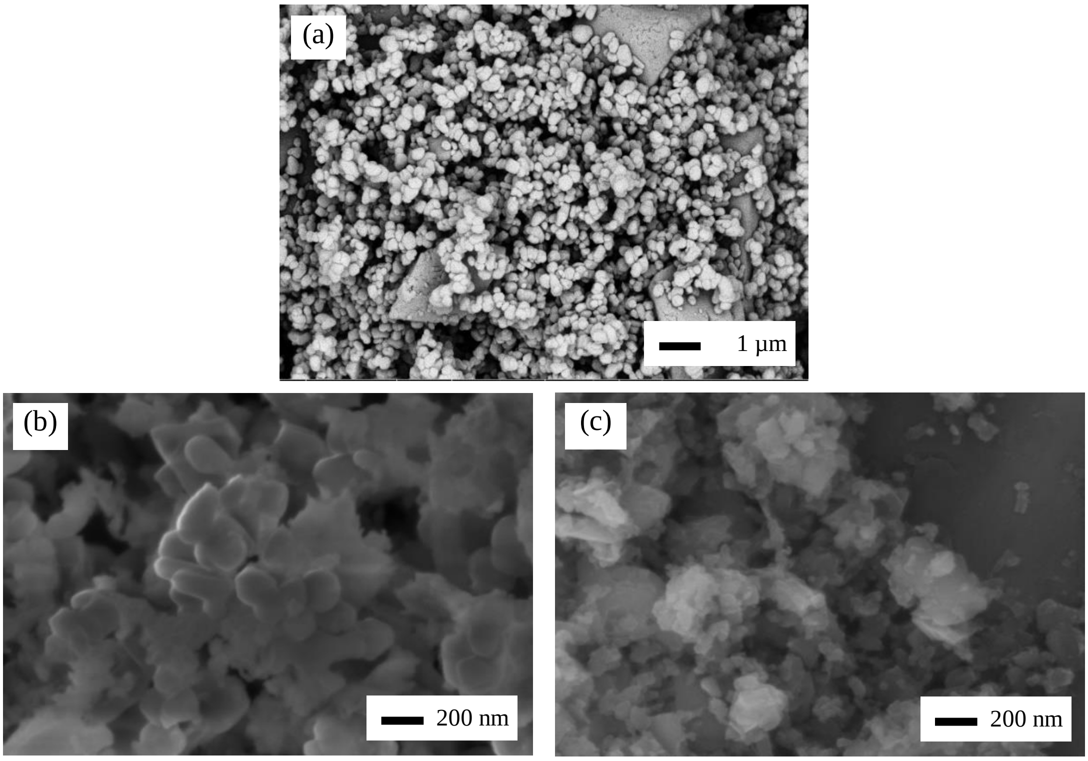

Figure 1. SEM of the $CaCO_3$-TiO_2 powder mixtures (a) before milling and after milling for (b) 1 h and (c) 10 h.

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.

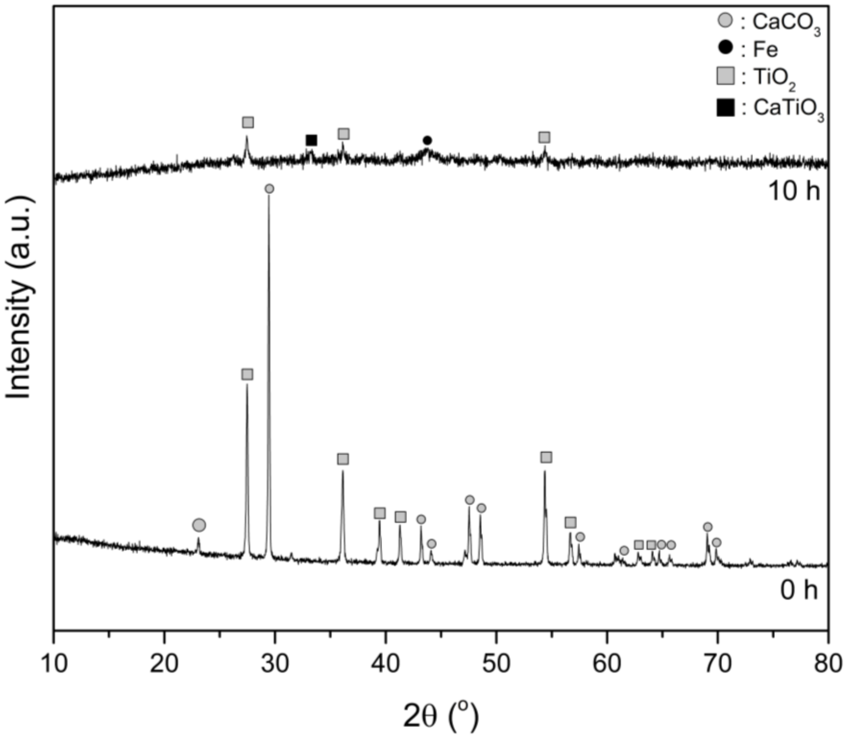

Figure 2. X-ray diffractometer pattern of $CaCO_3$-TiO_2 mixture before milling (0 h) and milling for 10 h (10 h).

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_2O_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 ± 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 $CaTiO_3$.

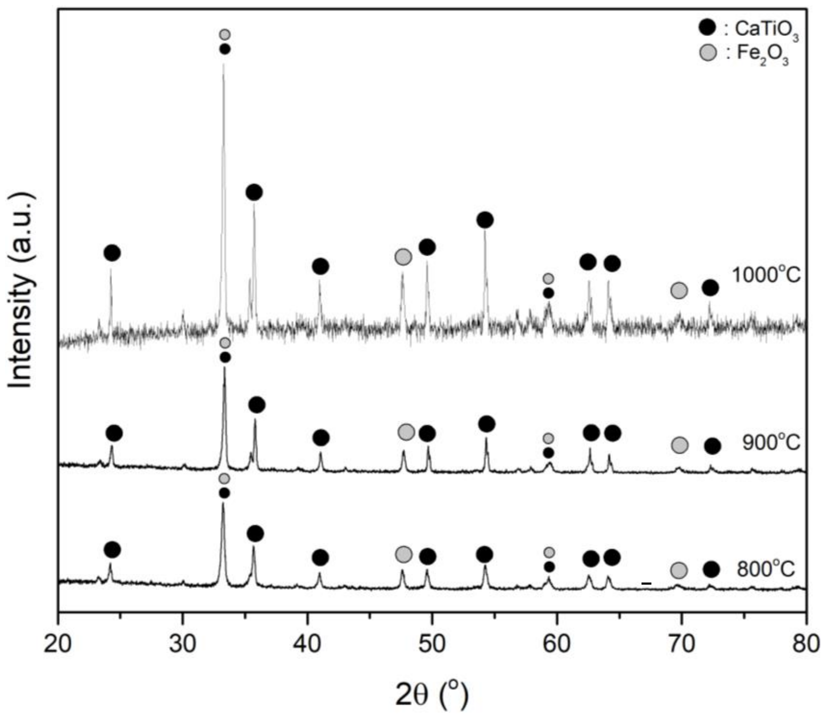

Figure 3. X-ray diffractometer pattern of $CaTiO_3$ with furnace temperature variations: 800°C, 900°C and 1000°C.

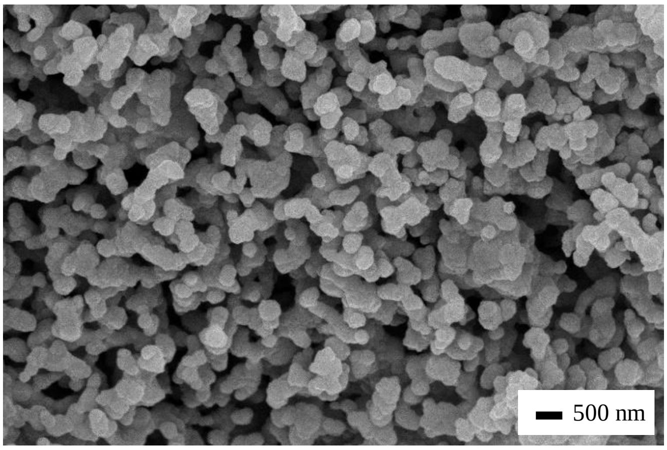

Figure 4. SEM of the $CaCO_3$-TiO_2 powder mixtures mechanically activated 10 h and furnace 1000°C.

4. Conclusion

Single-phase calcium titanate ($CaTiO_3$) 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 $CaCO_3$ peaks and a significant decrease of TiO_2 peaks. The loss of crystallinity of milled powder implied amorphous powder was obtained. Moreover, $CaTiO_3$ peak was observed in the milling time of 10 h, appearing that mechanical alloying between $CaCO_3$ and TiO_2 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 $CaTiO_3$ along with the Fe_2O_3 as impurities regardless of the calcination temperature. Therefore, it can be concluded that single phase $CaTiO_3$ 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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