Effect Of Milling Time on Particle Size of Forsterite $(\text{Mg}_2\text{SiO}_4)$ from South Solok District

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Abstract. West Sumatra has considerable serpentine mineral resources, including the Jorong Sungai Padi Nagari Lubuak Gadang Sangir Subdistrict, South Solok District. Exploitation of minerals of serpentine is still processed in raw or semi-finished material so that it has a low selling value. Serpentine minerals contain forsterite minerals that have higher economic value if in the form of nanoparticles. The manufacture of forsterite nanoparticles has been done using synthetic materials, while synthetic materials are expensive and require a long process to make them. The treatment of temperature variations of calcination to serpentine minerals, obtained results found forsterite phase that dominates at a temperature of 800 °C. Serpentine minerals can be used as alternative ingredients for the nanoparticle makers of forsterite that are easy to find in the deep, and do not require expensive to make them. The purpose of this study was to investigate the effect of milling time on the microstructure and grain size of the serpentine forsterite mineral nanoparticles in the form of crystal structure, crystal size, and particle size. The results of the study showed grain size of 5, 10, 20, and 40 hours milling time are 579, 478, 451, and 385 nm respectively. Based on the research that has been done can be drawn conclusion Time milling effect on the grain size of forsterite mineral serpentine from South Solok District, the longer milling time the size of forsterite grains smaller. Optimum milling time to produce nano forsterite is 40 hours with a grain size of 385 nm.

1. Introduction
Serpentine has an important role in the steel industry as a material supporting the establishment of the steel industry. West Sumatra has considerable serpentine mineral resources, one of which is Jorong Sungai Padi Nagari Lubuak Gadang, Sangir Subdistrict, South Solok District. The exploitation of serpentine minerals is still processed in raw material or semi-finished material so it has a low selling value.

Serpentine is a metamorphic rock formed from serpentine minerals due to basalt changes in the high pressure seabed at low temperatures. Serpentine minerals belong to the silicate minerals class Phyllosilicates.

Serpentine has the appearance of various physical properties. The physical properties of serpentine minerals are green to dark green, exhibiting fractures and commonly encountered with silica minerals, calcites that fill rock cavities [1].

Serpentine contains an economically valuable oxide compound with varying levels in each region. Serpentine is an oxide compound, in which there forsterite mineral types $(\text{Mg}_2\text{SiO}_4)$, hematite
(Fe₂O₃), clinoenstatite (MgSiO₃), and Quartz (SiO₂) [2]. Serpentine can be used as a raw material for making Forsterite which has high economic value if it is made into nanoparticles.

Forsterite is a member of the olivine mineral group and is the richest of magnesium minerals. Geologically, the forsterite is present in and forsterite frost rocks also present in dolomite marble which is the result of a limestone metamorphosis with high magnesium content.

Nanoparticles can occur naturally or through the process of making by humans. Preparation of nanoparticles is significant for the manufacture of particles of a size less than 100 nm and as well as changing their properties or functions [3]. People generally want to understand more deeply why nanoparticles can have different properties or functions than similar materials in bulk.

The properties that change in nanoparticles are usually related to the following phenomena. First, quantum phenomena as a result of the limitations of electrons and other charge carriers in particles. This phenomenon impacts on some material properties such as transmitted color change, transparency, mechanical strength, electrical conductivity, and magnetization. Second, the change in the ratio of the number of atoms that occupy the surface against the total number of atoms. This phenomenon impacts on changes in boiling point, freezing point, and chemical reactivity. These changes are expected to be superior to nanoparticles compared to similar particles in bulk state. The researchers also believe that we can control those changes in the desired direction.

The making of nanoparticles can be carried out in solid, liquid, or gas phases. The manufacturing process can take place physically or chemically. The physics-making process does not involve chemical reactions. What happens is only the breaking of large materials into nanometer-sized materials, or the incorporation of very small materials, such as clusters, into nanometer-sized particles without changing the properties of materials. The process of making chemically involves the chemical reaction of a number of precursors so that another nanometer material is produced. An example is the formation of salt nanoparticles by reacting corresponding acids and bases [3].

In general, the manufacture of nanoparticles will fall into two major groups. The first way is to break up large particles into nanometer-sized particles.

This approach is called a top-down approach. The second approach is to start from the atoms or molecules or clusters that are formulated to form the desired nanometer-sized particle. Top down is the manufacture of nanostructures by minimizing large materials, while the bottom up is a way of assembling atoms or molecules and combining them through chemical reactions to form nanostructures. An example of a top down method is grinding with a milling device, while bottom-up technology is using sol gel technique, and chemical precipitation [4].

The preparation of forsterite nanoparticles with variation of milling time on the mixing of talc and MgO influenced the formation of forsterite nanoparticles formed by mechanical activation method for 20 hours, 40 hours and 60 hours using ball milling with annealing temperature of 1200 °C obtained by nanocrystalline crystal size of 40 nm. While 5 hours of milling using ball milling with annealing temperature 1200 °C obtained crystal size forsterite 60 nm [1]. One of the milling tools is High Energy Milling (HEM) which is a ball roller tool used to perform small-scale mechanical integration process in the laboratory.

Milling is mechanically a simple and effective method for growing solid crystals (the size of the crystalline grains to be smaller) without going through the vapor phase or chemical reactions, as is usually required in other nanoparticle-making processes [6]. This smoothing machine is able to turn a hard and breakable sample into a powdered analytical sample. The manufacture of forsterite nanoparticles has been using talc and magnesium oxide material with ball mill method. The milling time variations used were 5, 10, 20, 40, and 60 hours, to obtain forsterite nanoparticles with grain size.

The manufacture of forsterite nanoparticles has been done by several researchers, but the material used is a synthetic material. Synthetic materials are expensive and require a long process to make them. Treatment of temperature variations of calcination to serpentine minerals, obtained results found forsterite phase that dominates at a temperature of 800 °C [2].

Serpentine minerals can be used as alternative materials for nanoparticle forsterite makers that are easily available in nature, and do not cost a fortune to make them. This research is conducted by
milling time variation on serpentine mineral using High Energy Milling (HEM) method. High energy milling is a unique technique by using the collision energy between the crushing balls and the chamber wall that is rotated and driven in a certain way. The advantage of high energy milling is that it can make relatively large amounts of nanoparticles in a relatively short time [4]. In addition, the milling technique is one of the techniques for growing solid crystals without going through an evaporate phase or chemical reaction treatment as commonly required in the synthesis process in general [2]. This article discusses the process of Mechanical Milling, powder mixed particles will undergo a process of cold welding and repeated destruction, when the ball collide with a number of powders will be trapped between the two balls.

The impact load given by the ball will make the powder deformed and eventually destroyed. The surface of the newly formed mixed powder particles allows the process of cold welding back between the fellow particles to form a new particle size larger than its original size. The particles will then again experience a collision and eventually re-destructed, and so on until it reaches the nano's size. Mechanical Milling process of material properties also affect the final result. Here are some structures that affect the variation of milling time.

Phases are materials that have structures and compositions different from others. The phase difference that occurs can not be separated from the energy effects of the atoms for the diffusion process. Figure 3 can be seen the mechanism of phase formation. The XRD peak width is a function of particle size, then the size of the crystal (D) is expressed in the following Scherrer equation [3]:

\[ D = \frac{\lambda}{B \cos(\theta_B)} \]  

\( D \) is the size (diameter) of crystalline, \( \lambda \) is the wavelength at 1.54 Å, \( \theta_B \) is the Bragg angle, \( B \) is FWHM of the selected peak, and \( K \) is the material constant whose value is less than one. Commonly used values for \( K \approx 0.9 \). Scanning Electron Microscope (SEM) was conducted to determine the sample morphology in various fields. The principle is the wave nature of electron diffraction at very small angles. The electrons can be dispersed by the charged samples, for the non-conducting samples coated with carbon, gold or gold alloys, which serve to drain excessive electrons in the sample to ground. The pattern formed illustrates the structure of the sample.

2. Research Methods
This article is a type of experimental research using high energy milling method to make nanoparticles, then investigated the effect of milling time on grain size of forsterite nanoparticles from serpentine mineral found in Jorong Sungai Padi Nagari Lbuak Gadang Sangir, South Solok District. The elements contained forsterite are analyzed using x-ray diffraction, while the grain size using scanning electron microscope. This research will perform several steps, namely: making nanoparticle, characterization, and data analysis.

3. Results
Table 1 Forsterite test results that have been milled with variations of time 5, 10, 20, and 40 hours using XRD detected elements detected silicon elements, Pericles compounds, and forsterite. The result is obtained by using High score Plus software with ICDD database. The x-ray Diffraction test can be used to determine the crystalline size of the test sample. Table 2 can be seen the crystalline size of the serpentine forsterite mineral samples with various time variations of milling on forsterite compounds can be determined using high score plus software.

The result of the measurement is obtained by crystalline size from forsterite phase, for the time of milling for 5 hours up to 10 hours crystalline size of forsterite is increasing, this is because the samples have agglomeration in milling process. The forsterite particles are broken or broken by the balls so that small size then occurs grouping until the time of milling 10 hours this occurs due to the powder that has been solved and small sized compaction which resulted in the powder together and resulted in crystalline from forsterite become large, but at the time milling for 20 hours up to 40 hours of
crystalline size from the forsterite shrank back this because the forsterite sample with a milling time variation of 5 hours to milling time for 40 hours of powder has a collision force with balls that have strong energy so that the powder becomes eroded again and become small. In addition to the collision style the powder also experiences other styles such as friction and compression. So at the time of milling for 40 hours from forsterite has reached the point of fracture and the size is smaller again. Grain size can be known by surface morphology obtained from SEM tool on forsterite with variation of milling time 5, 10, 20, and 40 hours. SEM is used to see grain size and surface morphology after milling process.

| Milling time | Mineral | a (Å)  | b (Å)  | c (Å)  | α     | β     | γ     | Space group | Crystal system |
|--------------|---------|--------|--------|--------|-------|-------|-------|-------------|----------------|
| 5 hours      | Forsterite | 10.219 | 5.99   | 4.758  | 90    | 90    | 90    | Pnma        | Orthorombic    |
|              | Periclase | 4.42   | 4.42   | 4.42   | 90    | 90    | 90    | Fm-3m       | Cubic          |
|              | Silicon  | 6.636  | 6.636  | 6.636  | 90    | 90    | 90    | Ia-3        | Cubic          |
|              | Forsterite | 10.219 | 5.99   | 4.758  | 90    | 90    | 90    | Pnma        | Orthorombic    |
| 10 hours     | Periclase | 4.42   | 4.42   | 4.42   | 90    | 90    | 90    | Fm-3m       | Cubic          |
|              | Silicon  | 6.636  | 6.636  | 6.636  | 90    | 90    | 90    | Ia-3        | Cubic          |
|              | Forsterite | 10.219 | 5.99   | 4.758  | 90    | 90    | 90    | Pnma        | Orthorombic    |
| 20 hours     | Periclase | 4.42   | 4.42   | 4.42   | 90    | 90    | 90    | Fm-3m       | Cubic          |
|              | Forsterite | 10.219 | 5.99   | 4.758  | 90    | 90    | 90    | Pnma        | Orthorombic    |
| 40 hours     | Forsterite | 10.219 | 5.99   | 4.758  | 90    | 90    | 90    | Pnma        | Orthorombic    |

**Table 1.** Fosterite structure with variation of milling time

| Milling time | Crystalline size (nm) |
|--------------|-----------------------|
| 5 hours      | 22.43                 |
| 10 hours     | 28.72                 |
| 20 hours     | 28.32                 |
| 40 hours     | 17.76                 |

The result of characterization using SEM for several time milling can be seen in Figure 1. Figure 1 shows that grain sizes of 5, 10, 20, and 40 h of milling time are 579 nm, 478 nm, 451 nm and 385 nm, respectively.

### 4. Discussion

The milling time affects the size of the crystal grains in the forsterite, this is because during the milling process, the powder particles will undergo repeated welding and repeating process when the ball collides with each other, the powder will be trapped between the two spheres and will result in deformed powder and then disintegrate. The surface of the newly formed powder particles allows the process of cold welding back between fellow particles to form new particles of larger size than their original size. Then the particle will again experience a collision and eventually re-destroyed, and so on until it reaches the nano size.

The morphology of forsterite for all samples is generally the same i.e uneven rounded shape. The results of the research were obtained for forsterite samples whose grain size was smaller than the previous study, which obtained a nanocrystalline grain size of 500 nm [4]. The morphology of the forsterite surface is indicated by the SEM of the forsterite grain size, the smoother as the milling time increases. Forsterite forms for all samples are generally equally spherical, this is because forsterite comes from anthropogenic processes. Naturally, anthropogenic processes occur at high temperatures.
in the process and production of Mg-related materials, in these high-temperature processes typically producing rounded minerals.

Figure 1. Comparison of SEM forsterite results of various time variations with magnification 33000x
a) 5 hours, b) 10 hours, c) 20 hours, and d) 40 hours

5. Conclusion
The grain size of 5, 10, 20, and 40 hour milling time is 579, 478, 451, and 385 nm, respectively. Based on the research that has been done can be drawn conclusion Time milling effect on the grain size of forsterite mineral serpentine from South Solok District, the longer milling time the size of forsterite grains smaller. Optimum milling time to produce nano forsterite is 40 hours with a grain size of 385 nm.

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