CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

There were many synthesis method tested to produce forsterite powder successfully. Some of the common methods include sol gel method and solid state reaction method. Although both techniques are different, however there are similarities at the end stage of powder preparation such as ball milling of premix solution before being dried to obtain the powder form and options to include heat treatment before final sintering takes place. Previous results highlighted important points in optimizing forsterite synthesis process such as application of heat treatment before final sintering process and long ball milling time as high as 60 hours do not promise better mechanical properties.

With these known facts, it is feasible to determine the optimum synthesis condition to produce forsterite which have better mechanical properties. The first part of this chapter discussed the densification behavior of the synthesized forsterite and comparison with previous results using the conventional pressureless sintering. The second part of this chapter discussed microstructural and grain size analysis of the synthesized forsterite.

4.2 Powder Optimization Result – Phase Analysis

The following results present the application of different parameters that influence the formation of pure forsterite phase. This result will be used to identify the optimal condition to form pure forsterite.

4.2.1 Forsterite Powder Before Sintering

The forsterite powder was prepared by solid state reaction between magnesium oxide (MgO) and talc ($Mg_3SiO_4O_{10}(OH)_2$). The XRD result of forsterite powder before sintering is shown in Figure 4.1.

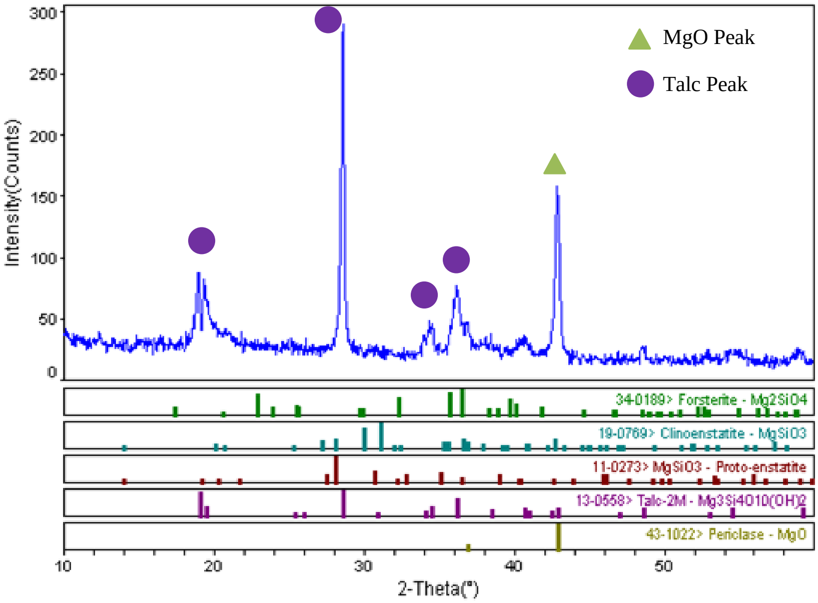

Figure 4.1: XRD traces of synthesized forsterite powder before sintering

The two starting precursors' individual phase, talc and perilcase can be distinguished clearly in the pre-sintered powder. The mixing ratio of talc and MgO, 1.88:1 resulting in recorded talc peaks at 2θ = 19°, 28.2°, 34° and 36° and perilcase at 2θ = 43°. No chemical reaction has occurred as no heat treatment was applied at this stage. Mechanical activation via ball milling alone was clearly not sufficient and thermal treatment was required to produce the forsterite phase (Kosanovic et al., 2005).

4.2.2 Effect of Direct Ultrasonification

The effect of ultrasonication on the forsterite formation was investigated by subjecting the powder mixture to direct ultrasonication for 2 hours with the amplitude of 30% and 50% (including pulse rate with interval of 1 minute on and 10 seconds off). This was followed with 2 hours heat treatment with ramp rate of 10˚C/min. The XRD result of forsterite powder was subjected to direct ultrasonification of 30% and 50% are shown in Figure 4.2 and 4.3 respectively.

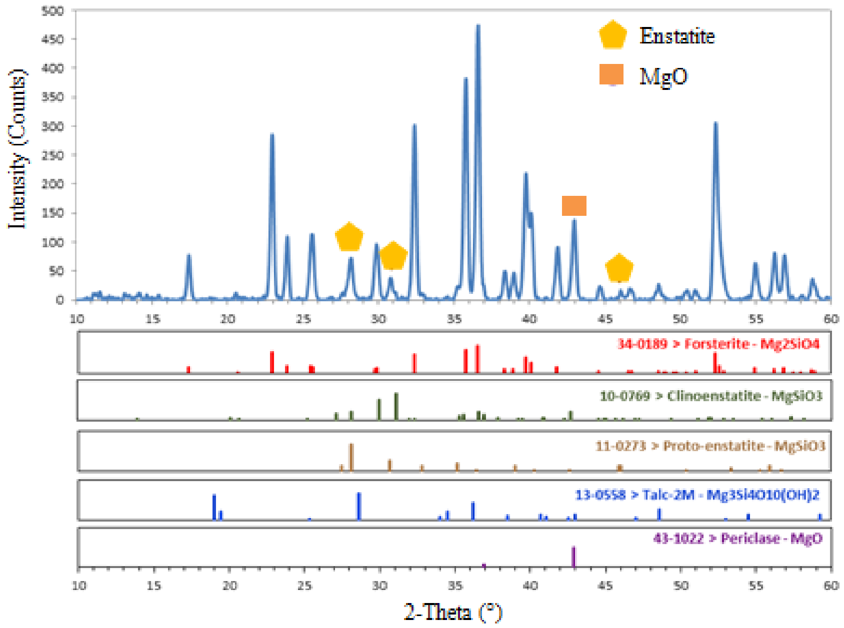

Figure 4.2: XRD traces of forsterite powder subject to 2 hours direct ultrasonification with 30% amplitude and 2 hours heat treatment at 1200˚C

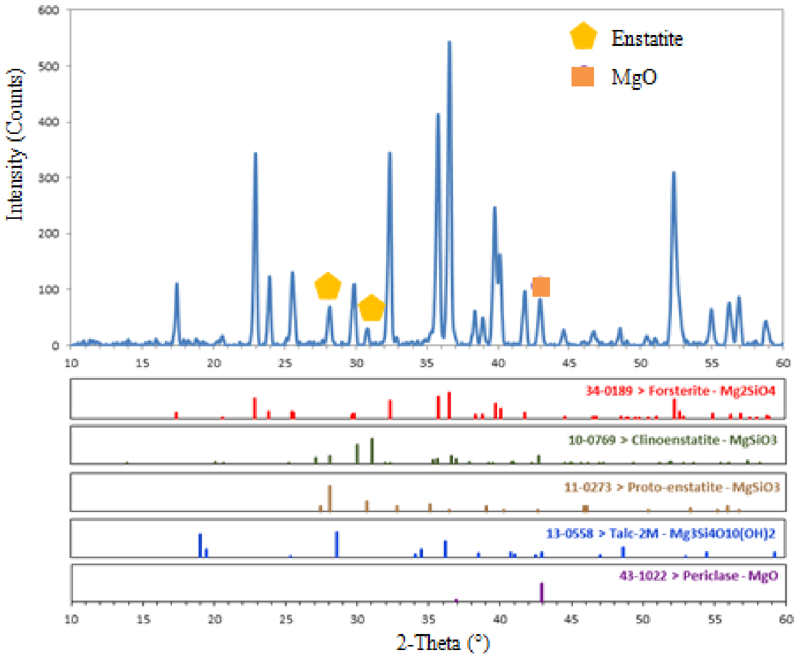

Figure 4.3: XRD traces of forsterite powder subject to 2 hours direct ultrasonification with 50% amplitude and 2 hours heat treatment at 1200˚C

Although forsterite peaks were detected as shown in Figure 4.2 and Figure 4.3, secondary phases such as enstatite and MgO were detected from the XRD trace which indicates incomplete reaction to form forsterite (Fathi & Kharaziha, 2008a). Enstatite peaks were detected at 2θ = 28.2°, 30.8° and 46°. MgO peak was detected at 2θ = 43° for both cases.

Direct ultrasonication with higher amplitude at 50% showed substantial reduction of the secondary phases as shown in Figure 4.2, which indicates faster reaction rate to form forsterite. The intensity of enstatite and MgO were also reduced from 29% to 15% and 15 to 13% respectively. The higher amplitude direct ultrasonification also promotes cavitations in the mixtures resulting in more homogenized mixture that lead to the formation of forsterite with higher crystallinity.

4.2.3 Effect of Ball Milling after Direct Ultrasonification

Direct ultrasonification with 50% amplitude helped in decreasing the formation of secondary phases, enstatite and MgO as shown in Figure 4.3 but was insufficient to form pure forsterite after heat treatment. Ball milling with duration of 1 hour and 3 hours respectively were applied on the two mixtures after direct ultrasonification followed by 2 hours heat treatment. The XRD results are shown in Figure 4.4 and 4.5 respectively.

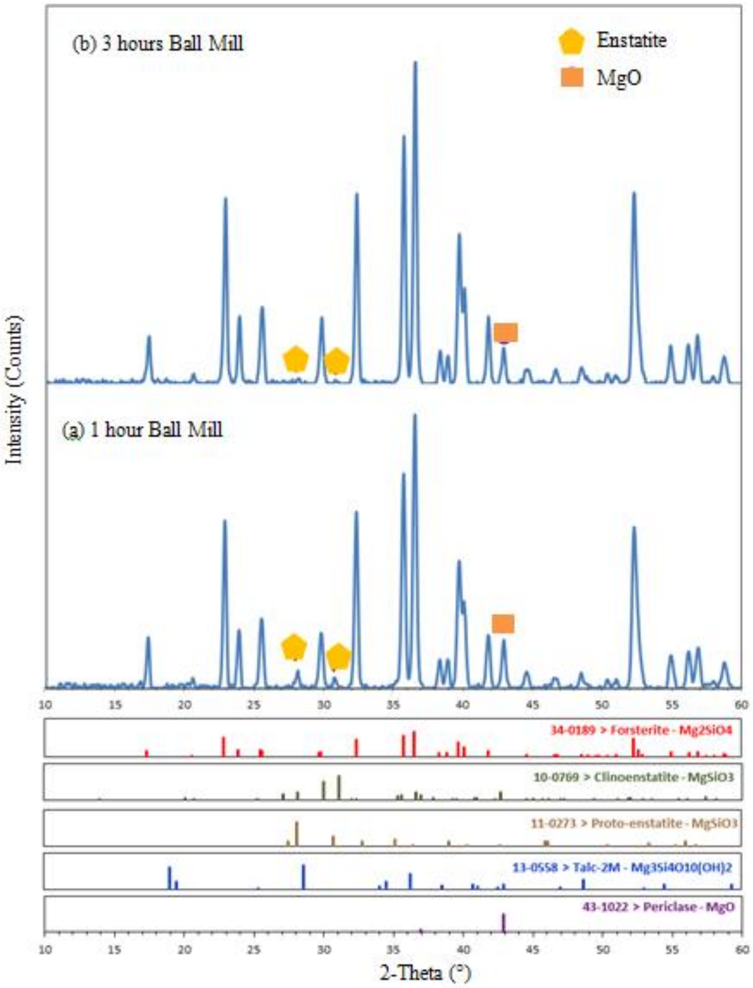

Figure 4.4: XRD traces of forsterite powder after direct ultrasonication with 30% amplitude and ball milling at various time after heat treatment

The intensity of enstatite and MgO reduced with the increasing ball milling duration from 1 hour to 3 hours for the mixture after direct ultrasonification with 30% amplitude as shown in Figure 4.4. The MgO peak reduced from 18% to 11%. The crystallinity of forsterite was also enhanced with the increasing ball milling duration. Figure 4.5 shows substantial reduction in secondary phases as ball milling duration increases from 1 hour to 3 hours for mixture with direct ultrasonification at 50% amplitude. The enstatite and MgO amounts with 50% amplitude were 4% and 5%, respectively. The MgO peak was reduced by 18%. However the reduction rate of enstatite peak for the 50% amplitude mixture was less than the 30% amplitude mixture with values of 3% and 5% respectively.

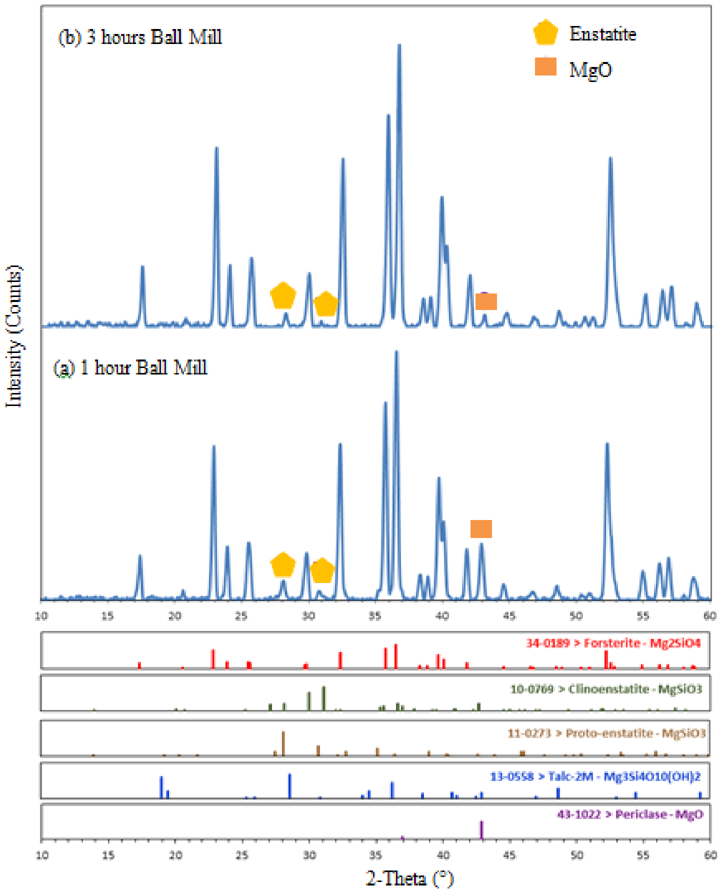

Figure 4.5: XRD traces of forsterite powder after direct ultrasonication with 50% amplitude and ball milling at various time after heat treatment

4.2.4 Effect of Heat Treatment Temperature on Direct and Indirect Ultrasonification

The samples were subjected to higher heat treatment temperature at 1250˚C as shown in Figure 4.6. The secondary phase of MgO and enstatite intensifies reduced to 3% and 2.5%, respectively. The peaks are lower compared to samples subjected to heat treatment temperature at 1200˚C as shown in Figure 4.5 (b).

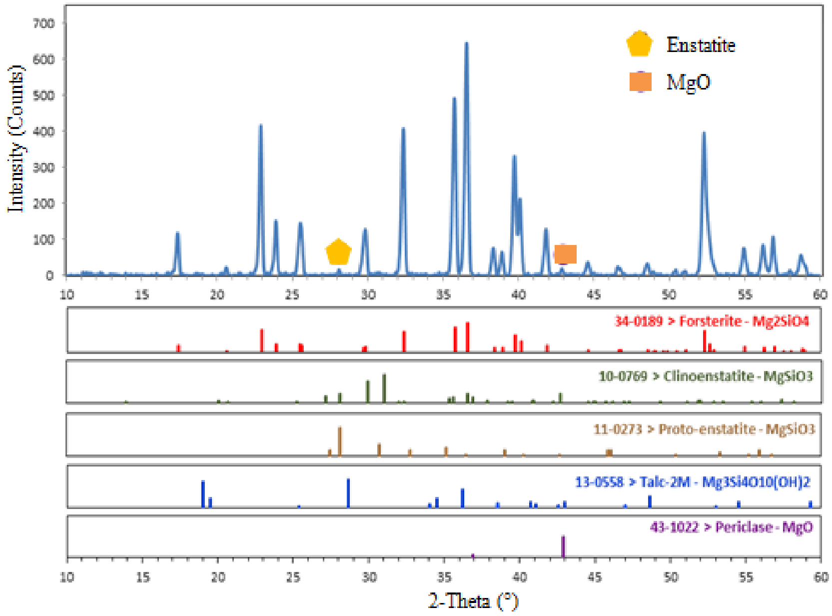

Figure 4.6: XRD traces of forsterite powder after direct ultrasonication with 50% amplitude, 3 hours ball milling and heat treatment 1250°C for 2 hours

The samples were subjected to two heat treatment temperatures, 1200˚C and 1250˚C after 3 hours ball milling only without ultrasonification. Figure 4.7 shows a drastic reduction in MgO peaks from 19% to 7% and enstatite from 13% to 5% for heat treatment temperature at 1250˚C. These results proved that heat treatment is more influencial compared to ultrasonification and ball milling duration in reducing the formation of secondary phases.

The increase in heat treatment temperature from 1200˚C to 1250˚C has bigger effect in reducing the secondary peaks. The next study focuses on the effect of heat treatment on samples subjected to indirect ultrasonification and 3 hours ball milling. Heat treatment temperatures was studied and indicated that 1200˚C is the minimum temperature to form forsterite (Ni et al., 2007; Fathi & Kharaziha, 2009a; Tavangarian and Emadi, 2010a). The maximum heat treatment temperature is best set below 1500˚C mark which is below the melting point of enstatite. Therefore the samples were subjected to heat treatment temperatures of 1200˚C, 1300˚C and 1400˚C for 1 hour.

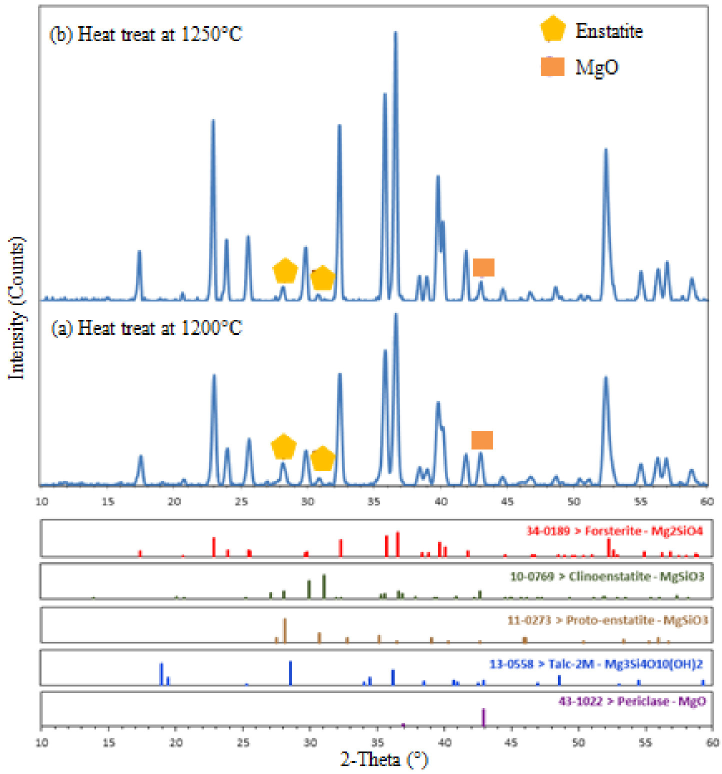

Figure 4.7: XRD traces of forsterite powder after 3 hours ball milling and heat treatment (1200°C & 1250°C) for 2 hours

MgO and enstatite were detected when the samples were subjected to heat treatment at 1200˚C for 1 hour as shown in Figure 4.8 (a). This result is agreeable with previous published result indicating enstatite and MgO peaks were detected in samples that were subjected to 1 minute ball milling or 1 hour heat treatment at 1200˚C (Tavangarian and Emadi, 2009). MgO peak intensity reduced and enstatite peaks disappeared when the heat treatment temperature increased to 1300˚C as shown in Figure 4.8 (b). These results proved that heat treatment temperature of 1200˚C may not be sufficient to form pure forsterite. Pure forsterite phase was detected with heat treatment temperature increased to 1400˚C as shown in Figure 4.8 (c). This result is encouraging because the ball milling duration is much shorter compared with previous results reported in Chapter 2. Previous study that resulted in successful formation of pure forsterite powder include 5 hours ball milling followed by 1 hour heat treatment at 1000˚C and 1200˚C (Tavangarian and Emadi, 2010a). Another example would be 10 hours ball milling followed by 10 minutes heat treatment at 1000˚C, 1200˚C, 1300˚C and 1400˚C (Tavangarian et al., 2010).

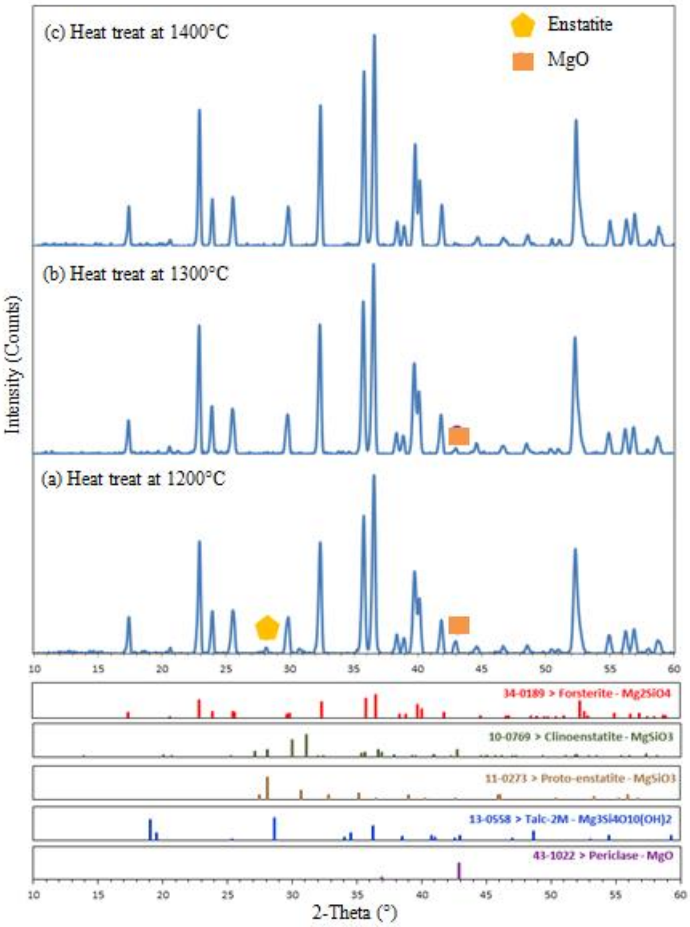

Figure 4.8: XRD traces of forsterite powder after ultrasonic bath, 3 hours ball milling and heat treatment at different temperature for 1 hour

4.2.5 Effect of Heat Treatment Dwell Time

The heat treatment dwell time of 1 minute, 1 hour and 2 hours were selected to study the effect on the sample subjected to heat treatment temperature of 1400°C. MgO was detected in the sample with 1 minute dwell time as shown in Figure 4.9 (a). Pure forsterite phase was successfully formed with 1 hour dwell time at 1400°C as shown in Figure 4.9 (b). However, the longer dwell time of 2 hours caused MgO peak to reappear as shown in Figure 4.9 (c).

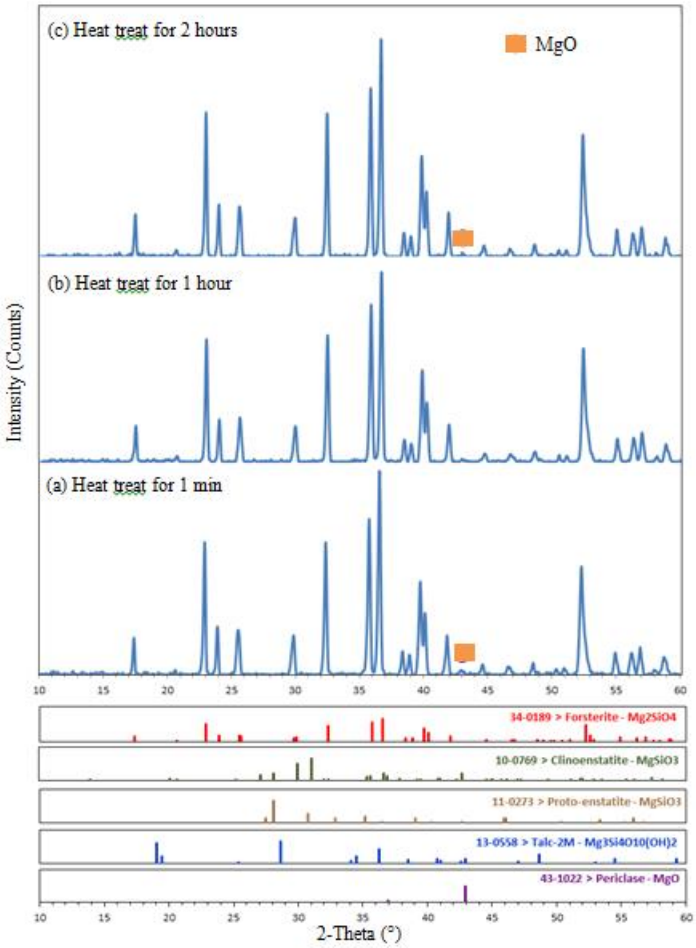

Figure 4.9: XRD traces of forsterite powder after 3 hours ball milling and 1 hour heat treatment at 1400°C with different holding time

These results are agreeable with previous published result (Tavangarian et al., 2010), that indicate heat treatment below 1 hour and longer duration for ball milling set at 10 hours followed by 1 hour heat treatment at 1000°C are insufficient to eliminate secondary phase, MgO. Longer dwell time of 2 hours with 1400°C does not guarantee a pure phase forsterite because the increasing heating time at elevated temperature increased the intensity of MgO peaks. Therefore, 3 hours ball milling with heat treatment at 1400°C for 1 hour was found to be the optimal condition to form pure forsterite in this study.

4.3 Sintering Profile Optimization Result

This section shows the result of the optimized sintering profile to produce pure phase forsterite with the least secondary phase peaks. Sample set no. 1 utilized forsterite powder that was subjected to 3 hours ball milling followed by 1 hour heat treatment at 1400˚C before compaction and sintering. Sample set no. 2 on the other hand, utilized forsterite powder without heat treatment for the compaction and sintering process.

4.3.1 Effect of Heat Treatment Powder on Phase Analysis

Figure 4.10 show the XRD signature for sample set no.1 that correspond to the JCPDS card number 34-0189 for forsterite throughout all sintering temperatures (1200˚C, 1300˚C, 1400˚C, 1500˚C). However, MgO peaks (JCPDS card number 43-1022) were identified at sintering temperatures; 1200˚C, 1300˚C and 1400˚C but disappear at sintering temperature 1500˚C. This result is agreeable with previous research finding that found forsterite thermally stable at 1450˚C and 1500˚C after heat treatment (Ni et al., 2007). MgO peaks appear at sintering temperature 1200˚C for sample set no. 2 and disappear as the sintering temperature increase to 1300˚C, 1400˚C and 1500˚C as shown in Figure 4.11. These results prove that forsterite is thermally stable at high temperature, when no heat treatment is applied on the starting powder. Furthermore, sintering temperature at 1200˚C was insufficient to eliminate secondary peaks of MgO. Lastly, it can concluded that sample set no. 2 is the optimal sintering profile because it is more energy efficient and will be used for densification behavior study.

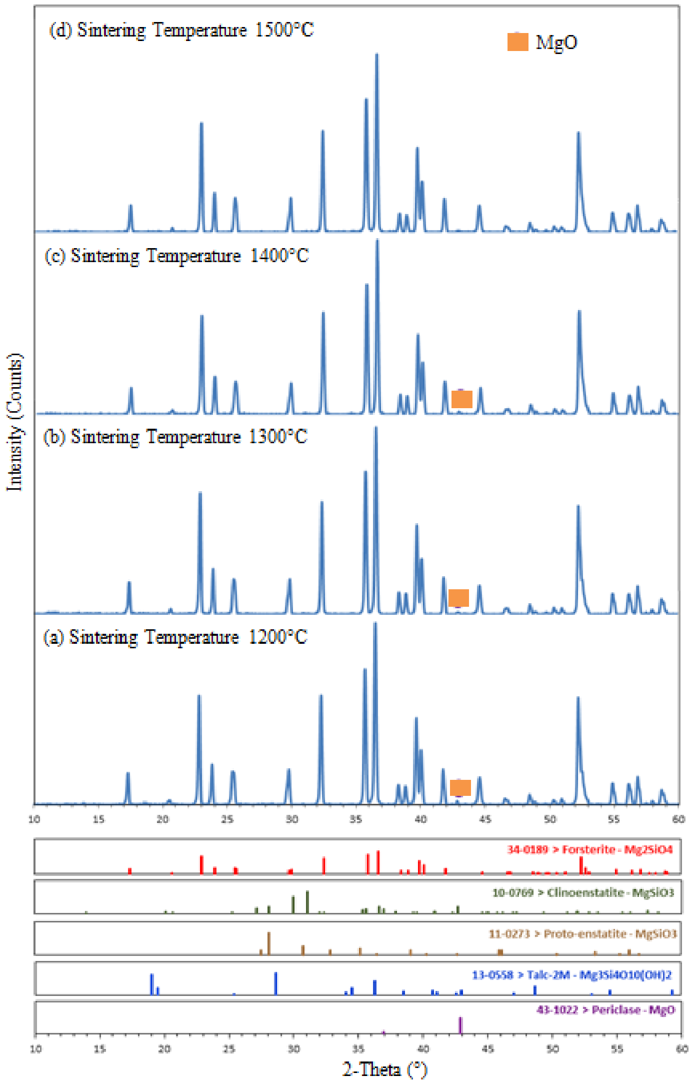

Figure 4.10: XRD traces sample set no.1 (3 hours ball milling and 1 hour heat treatment) after sintering at different temperatures (1200°C to 1500°C)

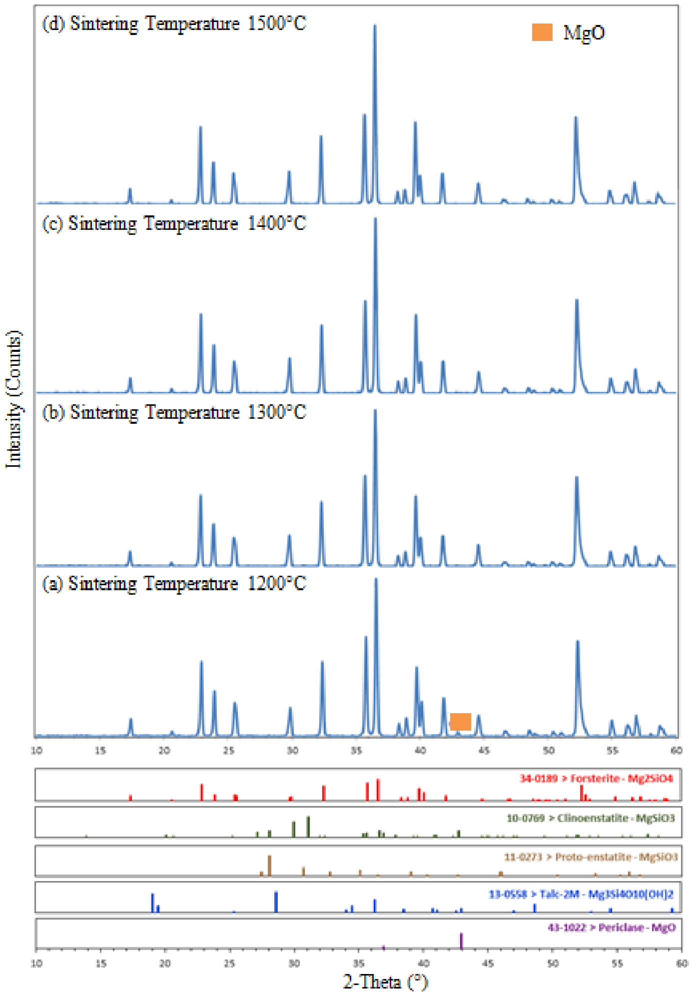

Figure 4.11: XRD traces sample set no.2 (3 hours ball milling and no heat treatment) after sintering at different temperatures (1200°C to 1500°C)

4.4 Densification Behavior of Sintered Forsterite Compacts

Based on the sintering profile optimization result in section 4.3, the optimal sintering profile employed for this experiment would utilize forsterite green body formed by forsterite powder without heat treatment and subjected to sintering temperature of 1200°C, 1300°C, 1400°C and 1500°C with 3 different holding time which are 1 hour, 2 hours and 1 minute respectively. The 3 different holding time will be known as Group 1: 2 hours, Group 2: 1 hour, Group 3: 1 minute. The densification behavior in terms of phase analysis, crystallite size, dimension & bulk shrinkage, bulk density, Vickers hardness, fracture toughness and Young's modulus were analyzed.

4.4.1 Phase Analysis

The forsterite compacts were divided into 3 groups with each group having different holding time. Group 1: 2 hours, Group 2: 1 hour and Group 3: 1 minute. In each group, there were four sintering temperature profiles of 1200°C, 1300°C, 1400°C and 1500°C respectively using the same ramp rate of 10°C/minute. All groups included pre-sintering steps which was subjected to 22 minutes of ultrasonification and 3 hours ball milling using zirconia balls as the milling media.

Figure 4.12 indicates no secondary phase was developed with sintering temperature of 1200°C with holding time and ramp rate in Group 1. Sintering temperature above 1000°C was the ideal temperature required to eliminate secondary phase even though longer holding time was applied. Secondary phase consisting of spinel was observed to form when sintering temperature and holding time of 974°C and 3 hours respectively were applied (Kosanovic et al., 2005).

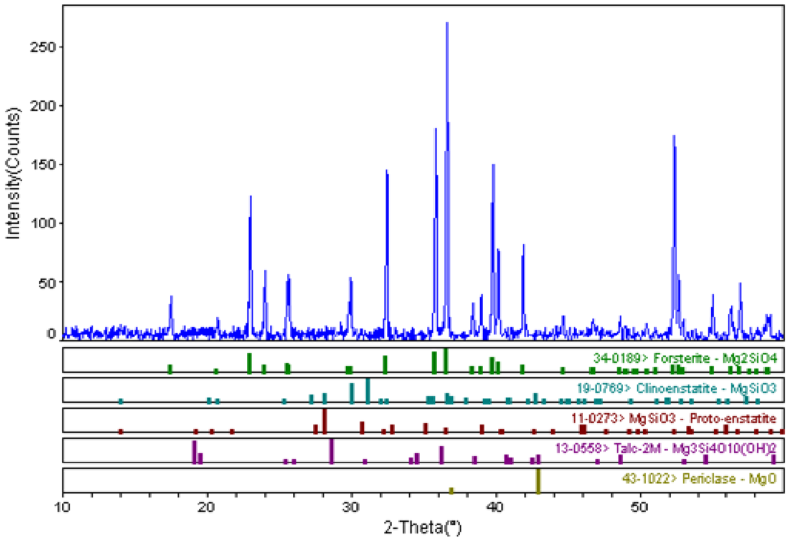

Figure 4.12: XRD traces of sintered forsterite compacts with 1200°C for 2 hours at 10°C/min

In current experimental setup, the additional mechanical activation procedure which was the 22 minutes of ultrasonification bath increased the homogenization effect (Sakka et al., 2001). Thus, no secondary phase was formed even though reduced ball milling and sintering holding time were applied. The combination of 2 hours ball milling in water, heat treatment at 900°C for 3 hours and sintering temperature between 1200°C to 1250°C with 2 hours holding time were successful in forsterite synthesis but there was still small amount of perilcase observed (Afonina et al., 2005).

Typical pattern of forsterite without secondary phase were observed with higher sintering temperature (1300°C 1400°C and 1500°C) as shown in Figure 4.13, 4.14 and 4.15.

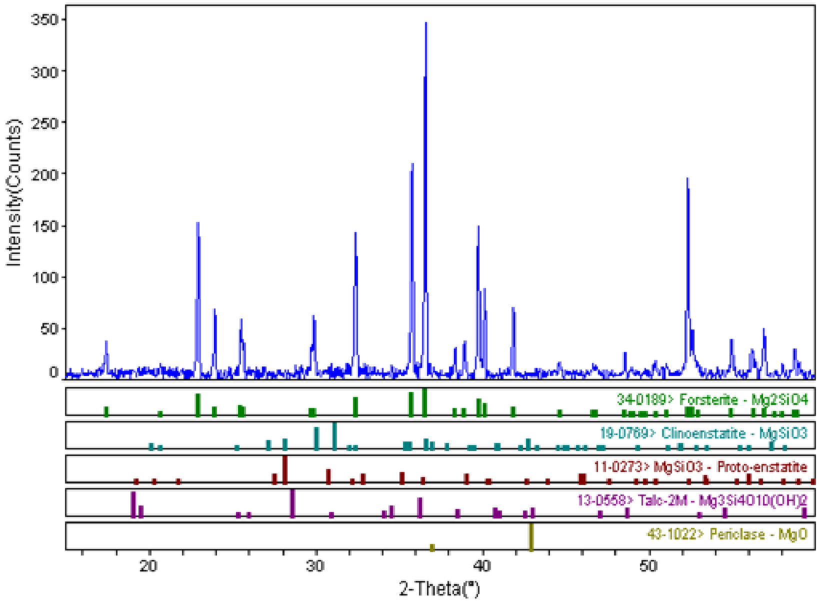

Figure 4.13: XRD traces of sintered forsterite compacts with 1300°C for 2 hours at 10°C/min

This is similar to the result obtained from previous setup which included milling for 24 hours, calcined at 1200°C for 3 hours and sintering temperature of 1350°C, 1450°C and 1550°C with holding time of 8 hours (Ni et al., 2007). The combination of talc and calcined magnesite which were ball milled for 1 hour and fired at 1450°C with ramp rate of 5°/minute for 2 hours produced forsterite with the presence of spinel as secondary phase (Mustafa et al., 2002).

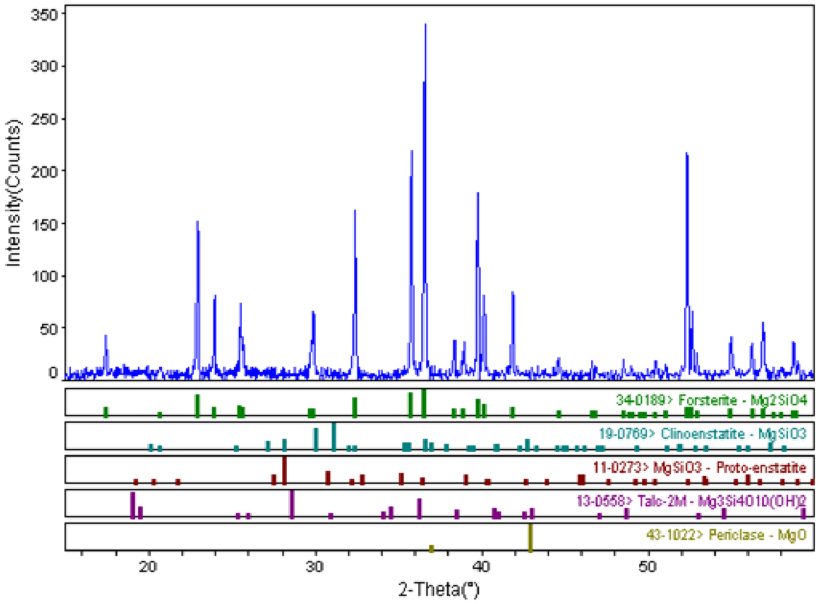

Figure 4.14: XRD traces of sintered forsterite compacts with 1400°C for 2 hours at 10°C/min

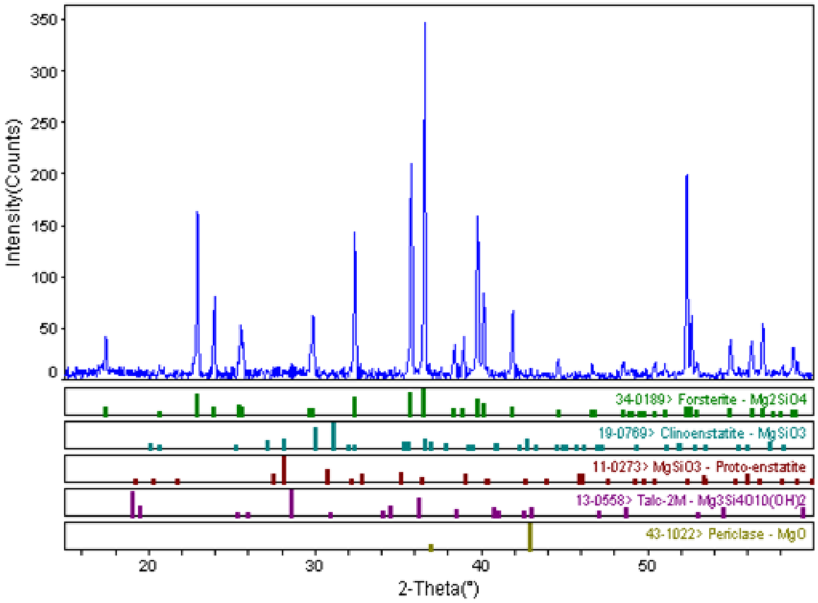

Figure 4.15: XRD traces of sintered forsterite compacts with 1500°C for 2 hours at 10°C/min

No secondary phase was detected in all four temperature profiles in Group 2. The result in Figure 4.16 is an improvement over previous findings where enstatite phase was still present even after 10 hours of planetary ball mill for 10 hours and fired at 1200°C with 1 hour holding time (Tavangarian & Emadi, 2011).

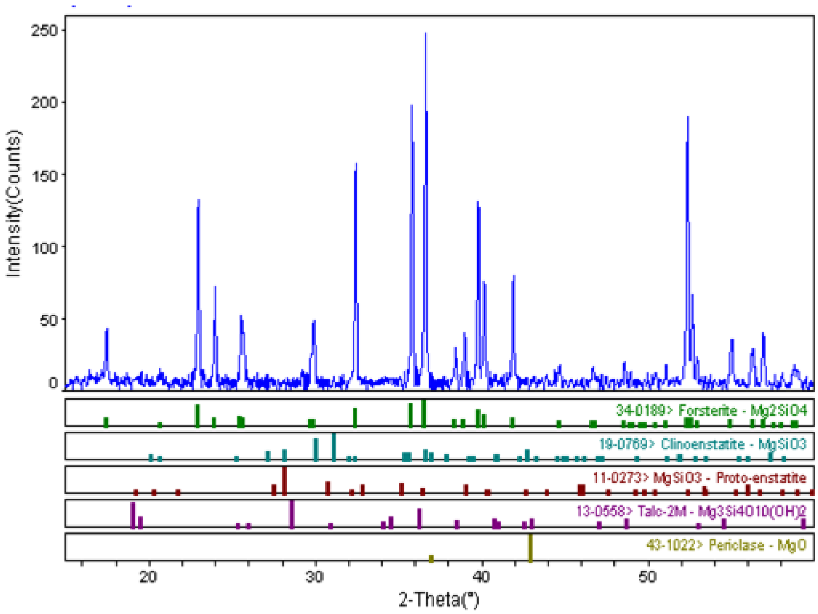

Figure 4.16: XRD traces of sintered forsterite compacts with 1200°C for 1 hour at 10°C/min

No secondary phase was observed as sintering temperature increased as shown in Figure 4.17 (1300°C), Figure 4.18 (1400°C) and Figure 4.19 (1500°C). These results are in agreement with previous setup which applies the same sintering temperature profile as Group 2 with holding time of 2 hours which indicates forsterite has high degree of resistance towards phase decomposition at elevated sintering temperature (Tan et al., 2015). However the result obtained in Group 2 has improvement because the holding time was only 1 hour.

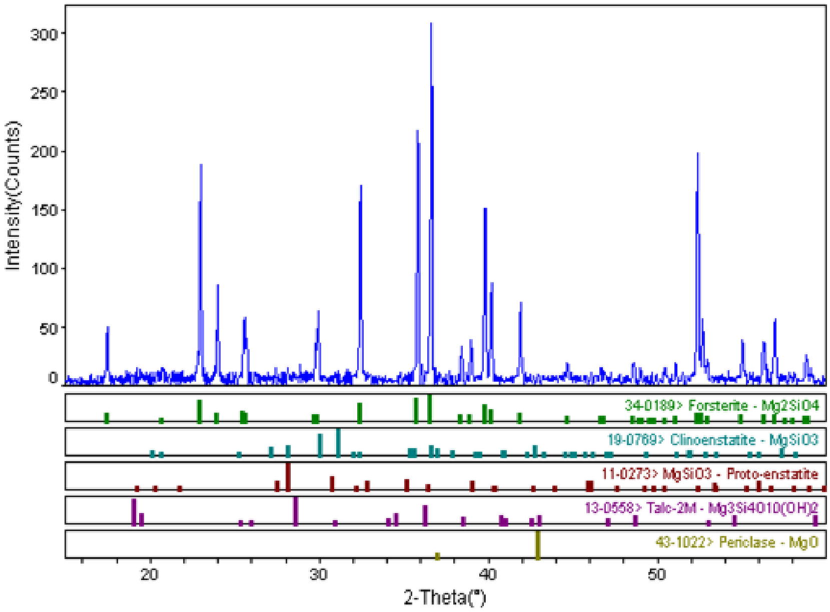

Figure 4.17: XRD traces of sintered forsterite compacts with 1300°C for 1 hour at 10°C/min

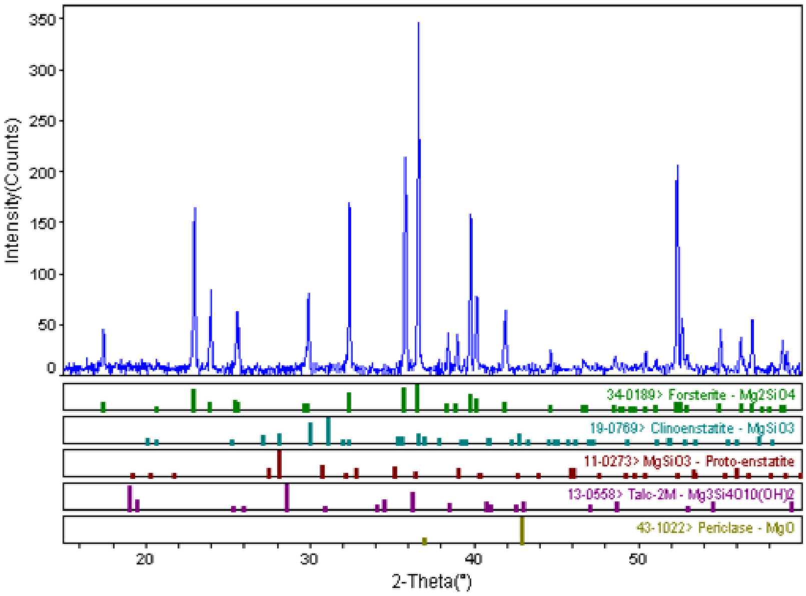

Figure 4.18: XRD traces of sintered forsterite compacts with 1400°C for 1 hour at 10°C/min

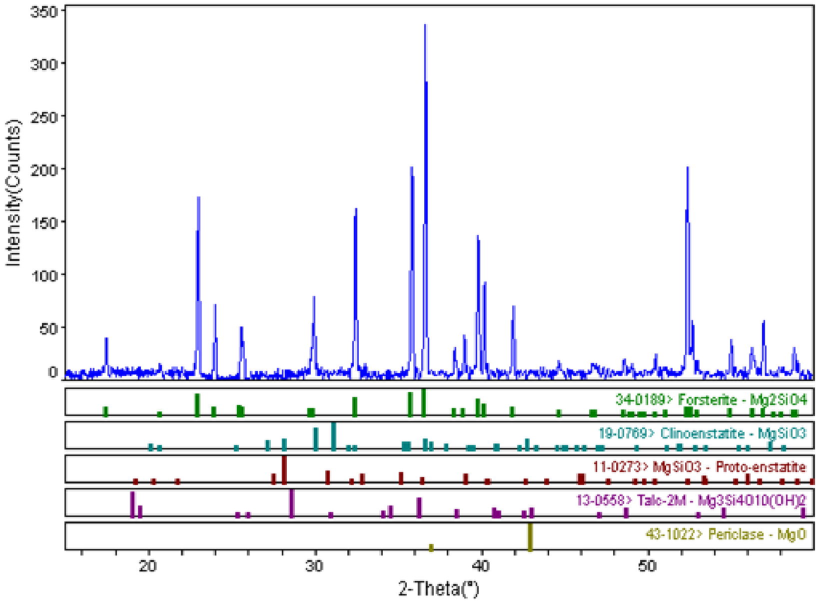

Figure 4.19: XRD traces of sintered forsterite compacts with 1500°C for 1 hour at 10°C/min

Secondary phase peaks were detected in Group 3. MgO and talc peaks were detected in Figure 4.20 (1200°C) while enstatite and talc peaks were detected in Figure 4.21 (1300°C). The combination of 1200°C sintering time with 1 minute holding time was not sufficient for the diffusion process to occur. That is the reason for the two precursors, MgO and talc still being detected in the sample.

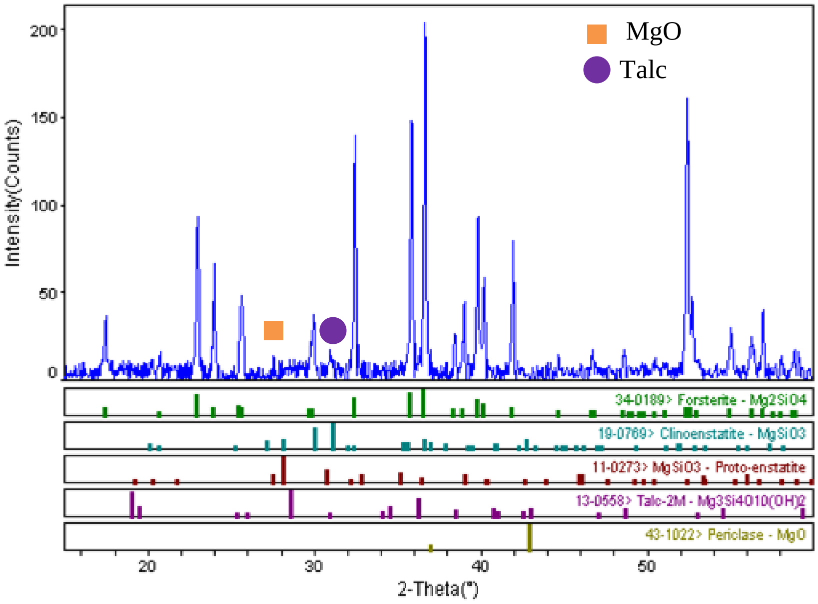

Figure 4.20: XRD traces of sintered forsterite compacts with 1200°C for 1 minute at 10°C/min

However as the sintering temperature was increased to 1300°C, the diffusion process did take place but short holding time of 1 minute was not enough to eliminate the secondary phase, enstatite and talc. These findings are agreeable with earlier findings where secondary phase peaks cannot be eliminated because the applied holding time was less than one hour (Tavangarian et al., 2010).

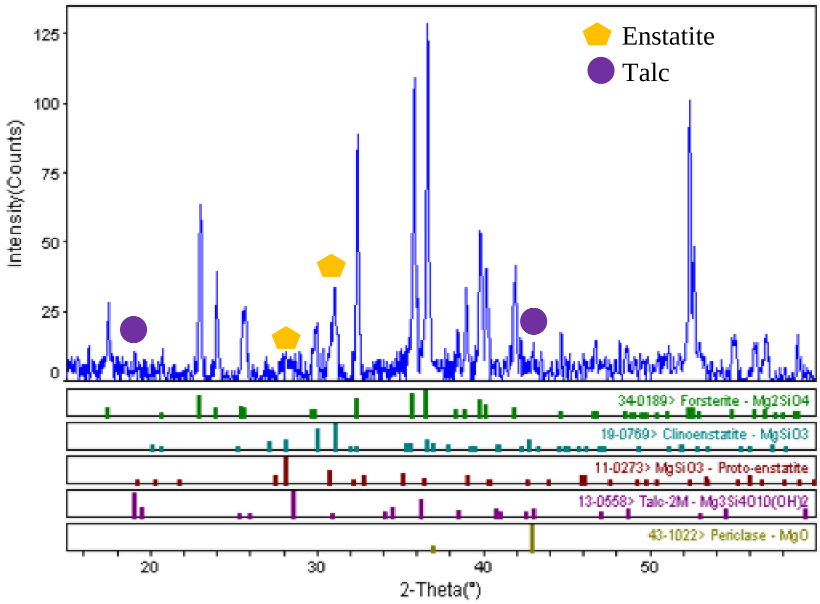

Figure 4.21: XRD traces of sintered forsterite compacts with 1300°C for 1 minute at 10°C/min

Only enstatite peak was detected as the sintering temperature was increased to 1400°C as shown in Figure 4.22. This result is consistent with the theory of higher sintering temperature enabling diffusion process leading to the elimination of talc but still not enough to form pure forsterite due to the short holding time of 1 minute.

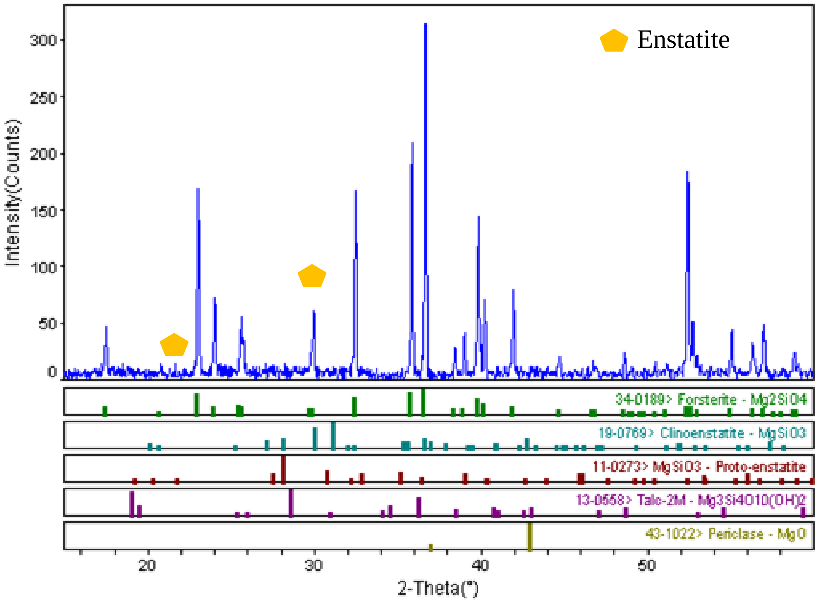

Figure 4.22: XRD traces of sintered forsterite compacts with 1400°C for 1 minute at 10°C/min

The highest sintering temperature within Group 3, at 1500°C with holding time of 1 minute was enough to eliminate all secondary phase to produce pure forsterite as shown in Figure 4.23. It will be interesting to compare the mechanical properties of the produced forsterite in Group 1, 2 and 3.

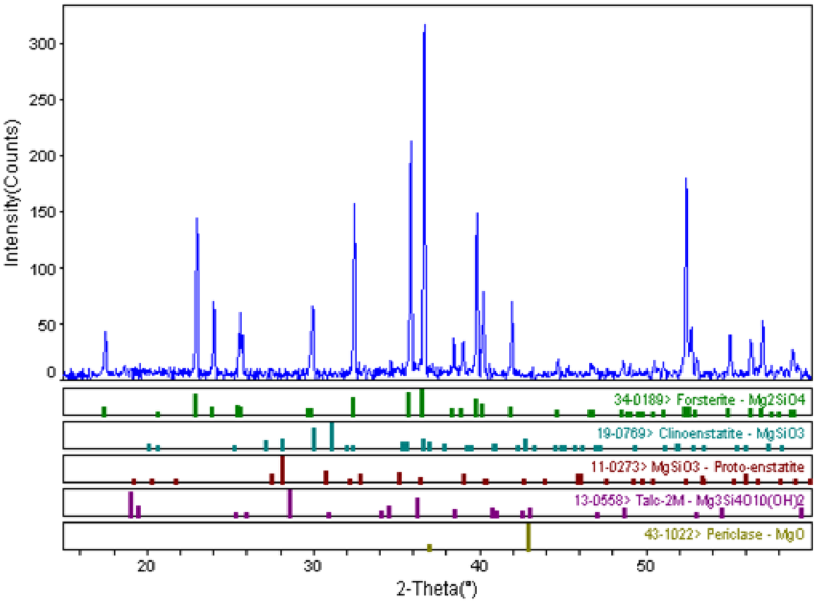

Figure 4.23: XRD traces of sintered forsterite compacts with 1500°C for 1 minute at 10°C/min

4.4.2 Crystallite Size

The crystallite size of forsterite compacts produced with four different sintering temperatures (1200°C, 1300°C, 1400°C, 1500°C) and 3 different holding time, 2 hours (Group 1), 1 hour (Group 2) and 1 minute (Group 3) are shown in Figure 4.24.

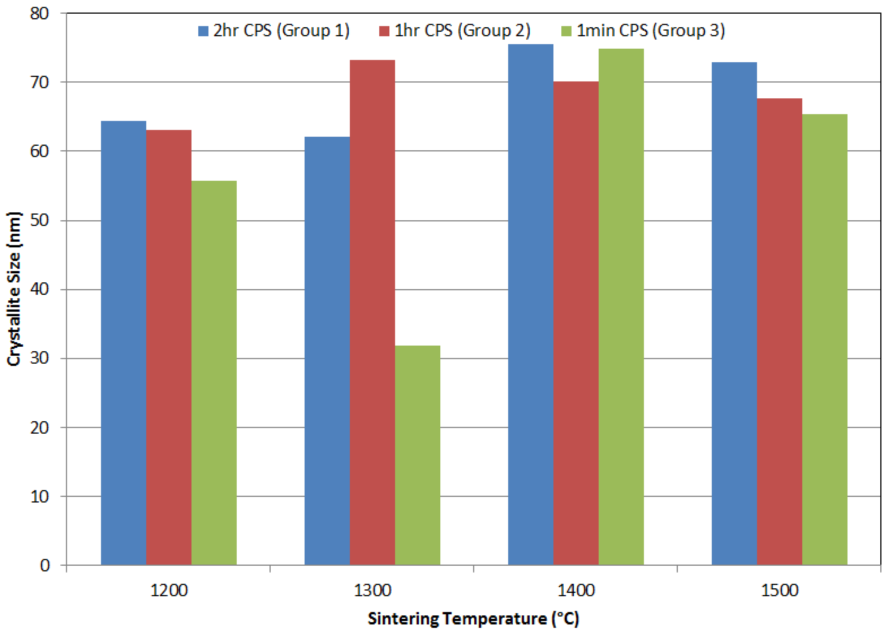

Figure 4.24: Crystallite size of forsterite produced with different sintering temperatures and holding times

Group 1 result showed slight decrease by 3.5% in crystallite size from 64.4 nm to 62.1 nm for sintering temperature of 1200°C and 1300°C respectively. However there was 21.7% jump to 75.6 nm when the sintering temperature increased to 1400°C and settled down at 72.9 nm with highest sintering temperature at 1500°C. The result in Group 2, showed increasing trend in crystallite size as the sintering temperature increased from 1200°C to 1300°C with 63.1 nm and 73.3 nm respectively. However, as the sintering temperature increased to 1400°C and 1500°C, the crystallite size decreased by 4.2% and 7.6% to 70.2 nm and 67.7 nm respectively. The pattern displayed in the result of Group 3 was similar with Group 1 but with bigger change in crystallite size as the sintering temperature increased. The crystallite size decreased by 42.7% from 55.7 nm to 31.9 nm followed by a huge increase to 74.8 nm and finally decreased slightly to 65.4 nm.

The increasing trend of crystallite size with increasing sintering temperature as shown in Group 1 is due the crystallization of forsterite at higher temperature exceeding 1200°C which caused grain growth (Fathi & Kharaziha, 2009a). This is proven in the result showing crystallite size reducing with increasing ball milling time from 1 hour up to maximum 100 hours and sintering temperature of 1200°C. However there was no change in crystallite size when sintering temperature of 1000°C was applied with similar ball milling time (Tavangarian et al., 2010). Another similar finding showed increasing crystallite size from 40 nm to 138 nm after 5 hours of ball milling and 1 hour heat treatment at 1000°C and 1200°C respectively (Tavangarian et al., 2010a).

The results in Group 1 and 3 have similar reducing crystallite size pattern at sintering temperature 1300°C and 1500°C. There was a significant increase in crystallite size at 1400°C. The big gap in the two holding time (1 minute and 2 hours) played a big factor resulting in the increasing and decreasing pattern in crystallite size. Sintering temperature of 1300°C was able to suppress grain growth with holding time of 1 minute and 2 hours respectively but sintering temperature above 1350°C was considered over heating resulting in over crystallization and facilitates an increase in porosity and formation of slot-shaped pores (Andrainov et al., 2004) which was shown in the result here for 1400°C. The result in Group 2 with holding time of 1 hour show consistent result where the crystallite size increased at sintering temperature 1200°C and 1300°C but reduced at 1400°C and 1500°C. 1 hour holding time managed to eliminate over crystallization which attributed to decreasing crystallite size pattern.

The combination of 3 hours ball milling and no pre thermal treatment of fosterite powder was able to produce phase pure forsterite with crystallite size below 80 nm is more cost effective and energy efficient compared to previous setup discussed above that required heat treatment before sintering process. 60 hours ball milling to produce forsterite with crystallite size 33 nm is not feasible and contamination of ball milling media, Fe and Cr were detected (Tavangarian et al., 2010). However there was another setup with additional step on top of 5 hours ball milling followed by 2 min and 2 hours sintering in the presence of chloride ion were able to obtain crystallite size of 20 nm and 31 nm respectively. The additional step was adding NH_4Cl powder to the ball milled mixture and ball milled for another extra 5 minutes (Tavangarian & Emadi, 2011). The increase in crystallite size was due to the increasing the holding time at elevated temperature, which contributed to grain growth.

4.4.3 Bulk Shrinkage

The dimensions of the forsterite disc compacts were measured before and after sintering process using the conventional pressureless sintering technique (CPS). The result of shrinkage versus sintering temperature for 3 different holding times is shown in the Figure 4.25.

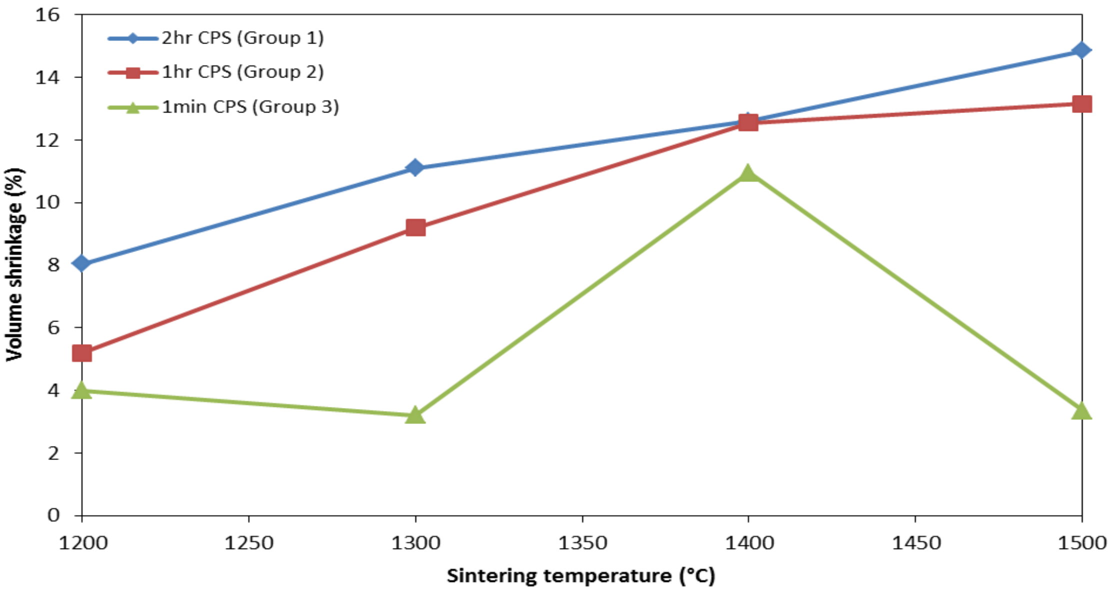

Figure 4.25: The effect of sintering temperatures and holding times on forsterite volume shrinkage

The results in Group 1 and Group 2 show linear pattern of increasing volume shrinkage with increasing sintering temperature which means densification occurred as porosity residual was removed during sintering process (Bernard-Granger et al., 2007). The difference of volume shrinkage between Group 1 (2 hours holding time) and Group 2 (1 hour holding time) decreased as sintering temperature was increased. The biggest difference was observed at sintering temperature of 1200°C, with 35.4% difference between Group 1 and Group 2 volume shrinkage of 8.05% and 5.20% respectively. Both Group 1 and Group 2 shared the same shrinkage slope as sintering temperature increased from 1200°C to 1300°C. This is agreeable with XRD result shown in Figures 4.12, 4.13, 4.16 and 4.17 which showed no secondary phase detected. Group 2 showed higher volume shrinkage than Group 1 at sintering temperature of 1200°C to 1300°C respectively because the longer holding time enabled further removal of residual porosity hence higher densification. At 1300°C, the recorded volume shrinkage of Group 1 and Group 2 were 11.1% and 9.2% respectively which showed difference of 17.1%. Almost similar volume shrinkage of 12.60% and 12.55% respectively was recorded at 1400°C with difference of 0.39%. Here, Group 2 showed higher shrinkage slope as sintering temperature increased from 1300°C to 1400°C. Group 1 recorded the highest volume shrinkage at 14.85% with the longer holding time at 1500°C followed by Group 2 and Group 3 at 13.15% and 3.35% respectively. 1400°C was the optimal sintering temperature for 1 hour holding time because it was more efficient to obtain similar volume shrinkage as Group 1 which required longer holding time of 2 hours.

The volume shrinkage for Group 3 was inconsistent because of the short holding time of 1 minute. The shrinkage was reduced from 4% to 3.2% as sintering temperature has increased from 1200°C to 1300°. The short holding time caused grain growth due to incomplete thermal reaction to form forsterite resulted in the formation of secondary phase, enstatite as shown in Figure 4.11. The volume shrinkage at 10.95% which was also the highest shrinkage slope because talc and MgO were eliminated as sintering temperature increased from 1300°C to 1400°C. However, enstatite remained until eliminated as the sintering temperature increased to 1500°C but recorded drop in volume shrinkage to 3.35%.

Overall, the results obtained here is agreeable that shrinkage is linearly proportionate with increasing sintering temperature regardless of heat treatment temperature (Andrianov et al., 2004). The absence of secondary phase show higher shrinkage rate. At 1500°C, the longer holding time of 2 hours produced higher shrinkage at 14.85% but 1400°C was the optimal temperature for 1 hour holding time.

4.4.4 Relative Bulk Density

The effect of sintering temperature with three different holding times 2 hours (Group 1), 1 hour (Group 2), 1 minute (Group 3) on relative bulk density is shown in Figure 4.26.

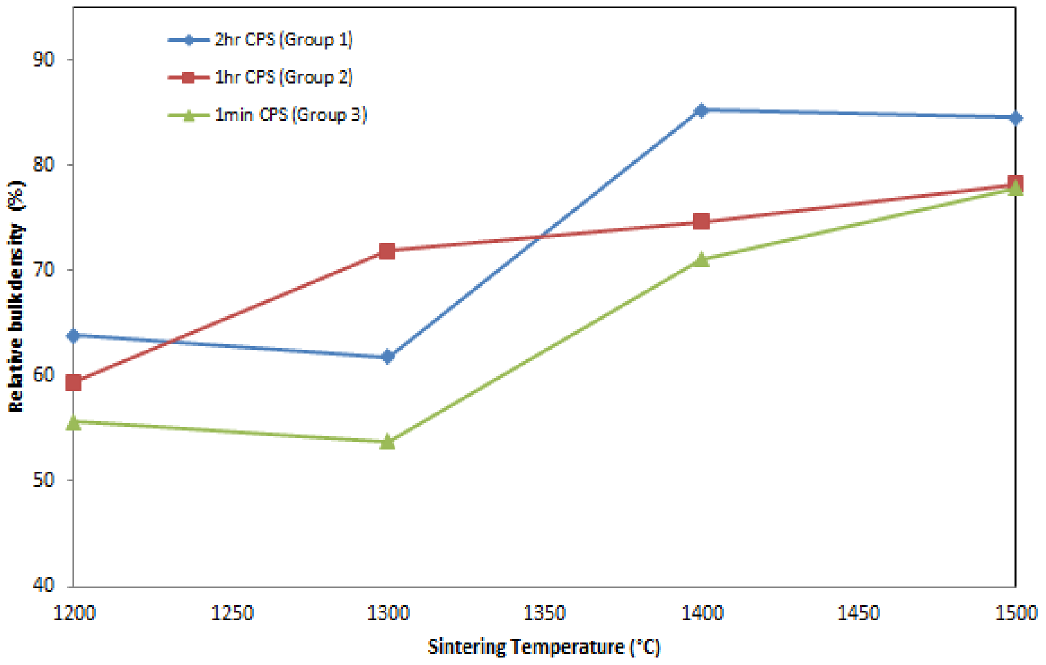

Figure 4.26: The effect of sintering temperatures and holding times on forsterite relative bulk density

The relative bulk density calculation was based on forsterite theoretical density of 3.221 g/cm^3 (Ghomi et al., 2011). Overall results indicate that the relative bulk density increased with increasing sintering temperature. Group 1 recorded the highest value of 85.2% at 1400°C and dropped slightly at 1500°C with 84.5%. Group 2 and 3 recorded highest value at 1500°C with 78.2% and 78.8% respectively. In this setup, Group 1 showed better result than Group 2 and Group 3 in terms of improved densification and shrinkage. This is in agreement with a setup which obtained higher relative bulk density of 92.5% by applying longer holding time of 8 hours with sintering temperature at 1450°C (Ni et al., 2007). There was also another setup that obtained relative bulk density of 80.7% by applying sintering temperature of 1550°C for 2 hours after ball milling for 1 hour (Mustafa et al., 2002). Similarly like the volume shrinkage graph in Figure 4.25, Group 3 showed a drop in volume shrinkage from sintering temperature 1200°C to 1300°C due to the formation of secondary phase enstatite. Overall, the result here is agreeable that relative bulk density will increase together with increasing sintering temperature as porosity reduced.

4.4.5 Vickers Hardness

The diagonal length of diamond impression resulted from Vickers pyramidal diamond hardness test were measured and then used in the calculation of Vickers hardness. Figure 4.27 shows an example of diamond shaped Vickers indentation of forsterite samples sintered at 1200°C, 1300°C, 1400°C and 1500°C with 1 hour holding time.

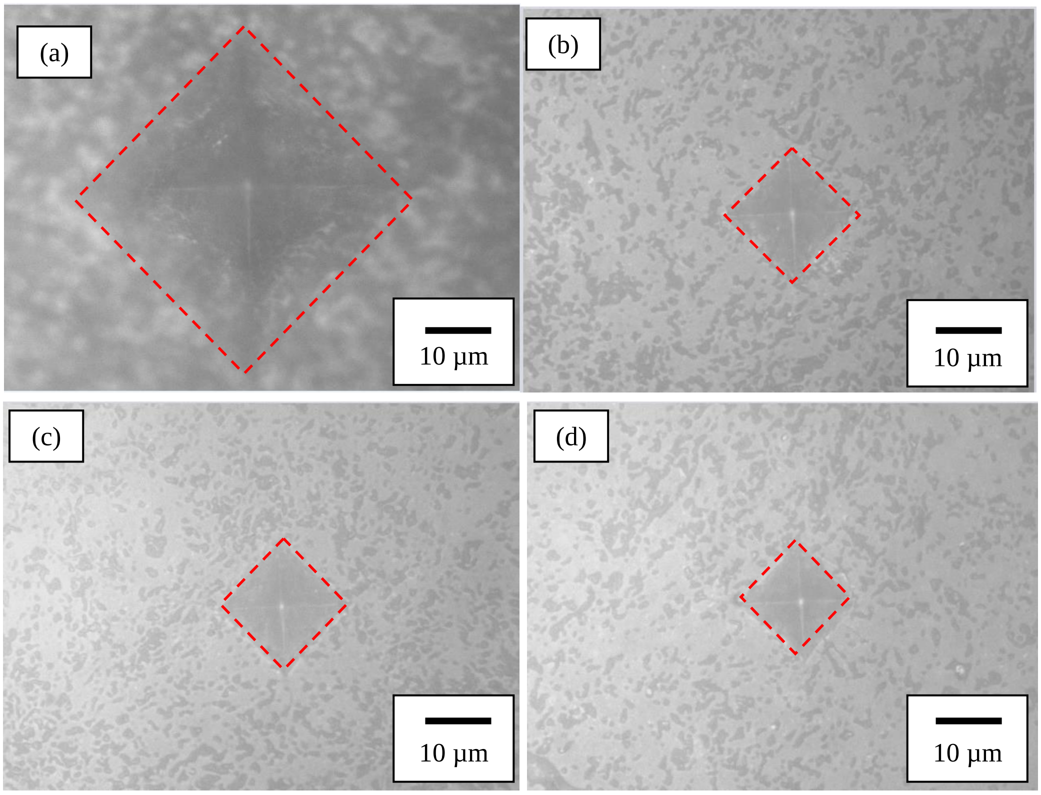

Figure 4.27: Diamond shaped Vickers indentation of forsterite sample sintered at 1200°C, 1300°C, 1400°C and 1500°C with 1 hour holding time

The diamond shaped indentations became smaller as the sintering temperature increases from 1200°C to 1500°C. There were no cracks observed on the corners of the indentations as commonly found in Vickers hardness test on ceramic material (Anstis et al., 1981). This result suggests Vickers hardness is inversely proportional to the square of average diagonal length which means shorter diagonal length equals higher hardness.

Figure 4.28 shows an example of diamond shaped Vickers indentation of forsterite sample sintered at 1500°C with 3 different holding times, Group 1: 2 hours, Group 2: 1 hour and Group 3: 1 minute.

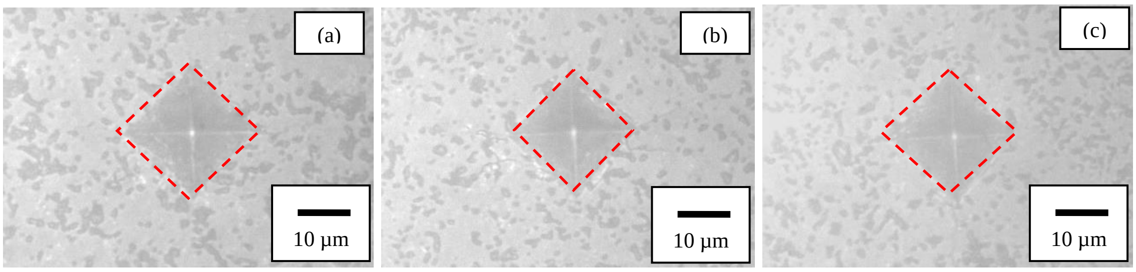

Figure 4.28: Diamond shaped Vickers indentation of forsterite sample sintered at 1500°C with 3 different holding times; (a) 2 hours, (b) 1 hour, (c) 1 minute

It is interesting to observe that Group 2 has produced the smallest diamond shaped Vickers indentation followed by Group 3 and Group 1. The result shown in Figure 4.27 and 4.28 are reflected in Figure 4.29 which shows the effect of sintering temperature and holding time on Vickers hardness of forsterite samples. The three highest Vickers hardness value were recorded at sintering temperature of 1500°C. The 1 hour holding time sample produced the highest Vickers hardness value at 5.01 GPa followed by 4.79 GPa with 1 minute holding time and lastly 4.4 GPa with 2 hours holding time.

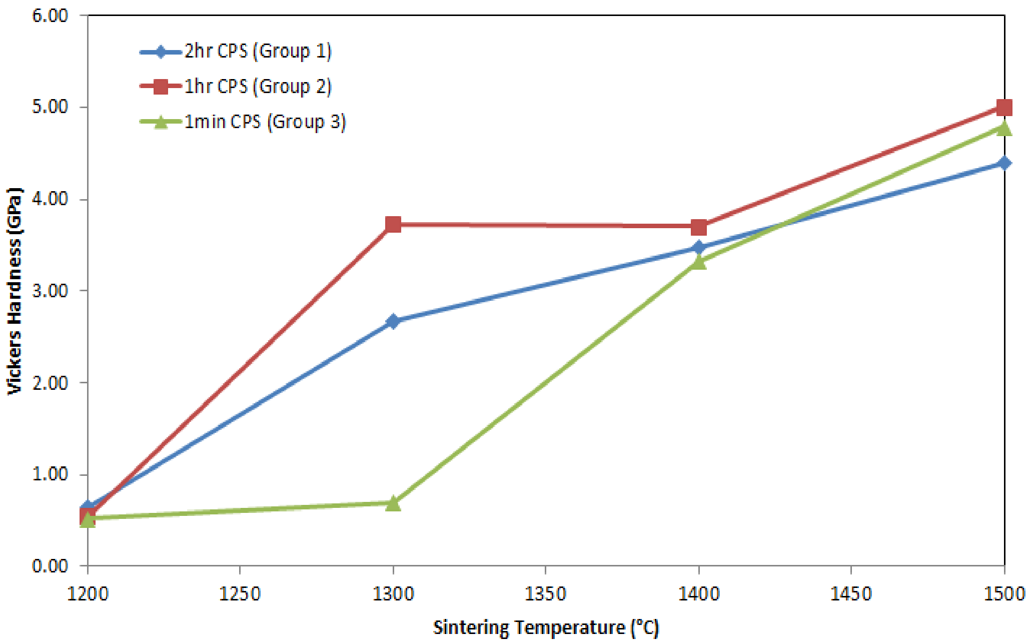

Figure 4.29: The effect of sintering temperature and holding time on Vickers hardness of forsterite samples

The big jump in Vickers hardness from 0.55 GPa to 3.73 GPa at sintering temperature 1300°C with holding time of 1 hour can be related with the increasing relative density recorded from 59.3% to 71.9% as shown in Figure 4.30.

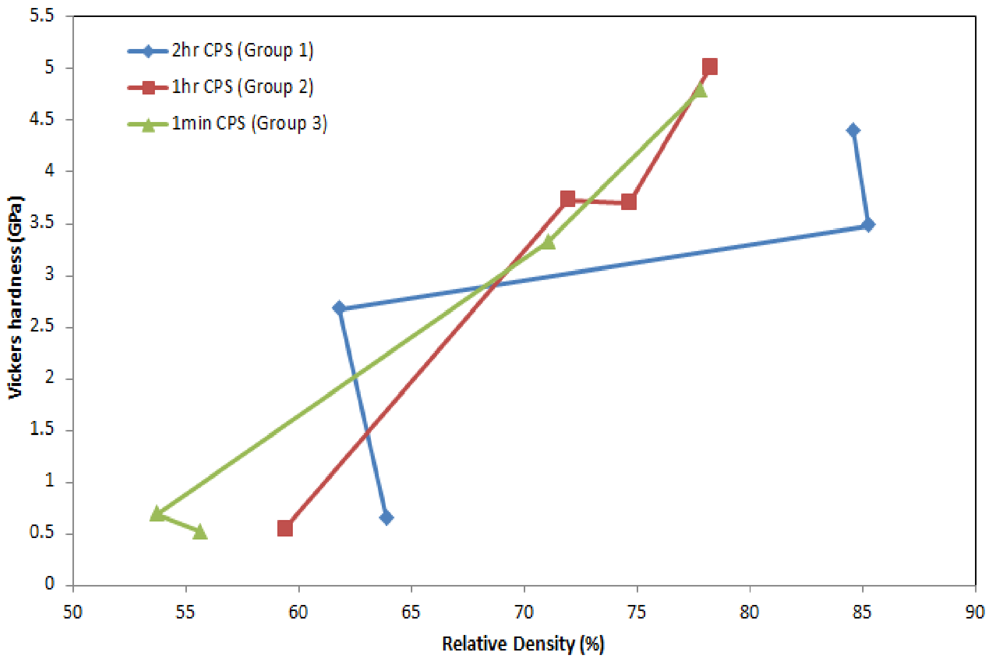

Figure 4.30: The effect of relative density on Vickers hardness with different sintering temperature and holding time

It can be observed that the relative density for Group 1 and Group 3 were the lowest at 61.8% and 53.7% respectively. However Vickers hardness for both Group 1 and Group 3 were observed with an increasing trend at 2.67 GPa and 0.69 GPa respectively. Among the 3 holding times at 1300°C, Group 3 has the lowest Vickers hardness value of 0.69 GPa because secondary phases talc and enstatite were present. However, the relative density and Vickers hardness in Group 3 increased linearly as the secondary phase were eliminated at 1400°C and 1500°C. The results indicated hardness is governed by relative density. Longer holding time may lead to over firing thus reducing the toughness property. Other than that, it is important to note that the highest Vickers hardness obtained from this experiment, 5.01 GPa is higher than the cortical bone lower limit which is about 0.2 GPa (Pramanik et al., 2005). Therefore, forsterite has the potential for biomedical application.

4.4.6 Fracture Toughness

The effect of sintering temperature with three different holding times (Group 1: 2 hours, Group 2: 1 hour, Group 3: 1 minute) on fracture toughness is shown in Figure 4.31.

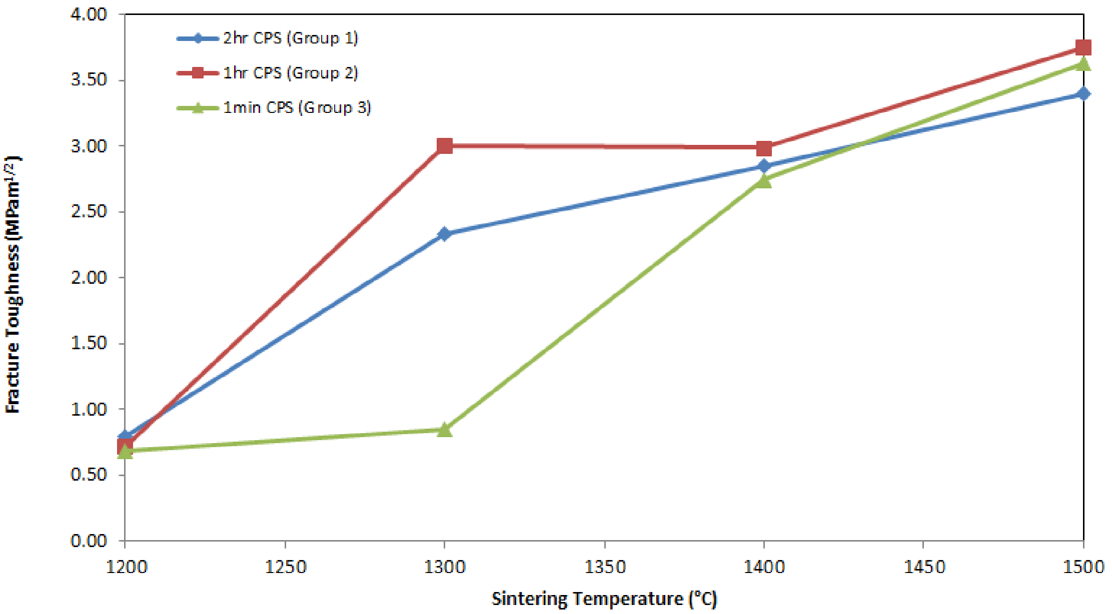

Figure 4.31: The effect of sintering temperatures and holding times on fracture toughness of forsterite compacts

The highest fracture toughness was achieved at sintering temperature of 1500°C. Group 2 achieved the highest value at 3.75 MPam$^{1/2}$ followed by Group 3 with 3.63 MPam$^{1/2}$ and Group 1 with 3.4 Mpam1/2. Figure 4.33 shows the effect of different sintering temperatures and holding times on Young's Modulus of forsterite. This result displayed similar trend as Vickers hardness in Figure 4.30 which showed Group 2 was the optimized holding time that produced the highest fracture toughness at sintering temperature 1500°C. The maximum fracture toughness value of 3.75 MPam$^{1/2}$ is 36% higher than the setup by Ni et al., 2007, which applied sintering temperature of 1450°C with holding time of 8 hours. However the setup by Tan et al., 2013 which applied ball milling for 10 hours followed by sintering temperature of 1500°C with holding time of 2 hours and 10°C/minute ramp rate managed to produce fracture toughness of 4.88 MPam$^{1/2}$. The experiment by Kharaziha & Fathi, 2010, managed to obtained fracture toughness of 4.3 MPam$^{1/2}$ with the powder calcined at 800°C for 2 hours followed by two step sintering. In this experiment, step 1 involved of sintering the sample at 600°C with 1 hour holding time and 10°C/minute ramp rate followed by 50°C/minute cooling rate. Next, for step 2 the sample was sintered at 900°C with similar ramp rate and holding time of 6 minutes. Lastly, the sample was kept on hold at 850°C for 2 to 15 hours followed by cooling at a rate of 10°C/minute.

Relative density of 78.2% produced maximum fracture toughness of 3.75 MPam$^{1/2}$ through 1500°C sintering temperature with 1 hour holding time as shown in Figure 4.32. The maximum relative density achieved at 84.5% produced the lowest fracture toughness in this experimental setup equivalent to 3.4 MPam$^{1/2}$. The maximum fracture toughness of 3.75 MPam$^{1/2}$ is 46.6% higher than the cortical bone lower limit at 2.0 MPam$^{1/2}$. The results here proved that other than the density property of the sintered forsterite compacts, the holding time of the sintering process is a contributing factor to improved hardness and fracture toughness properties.

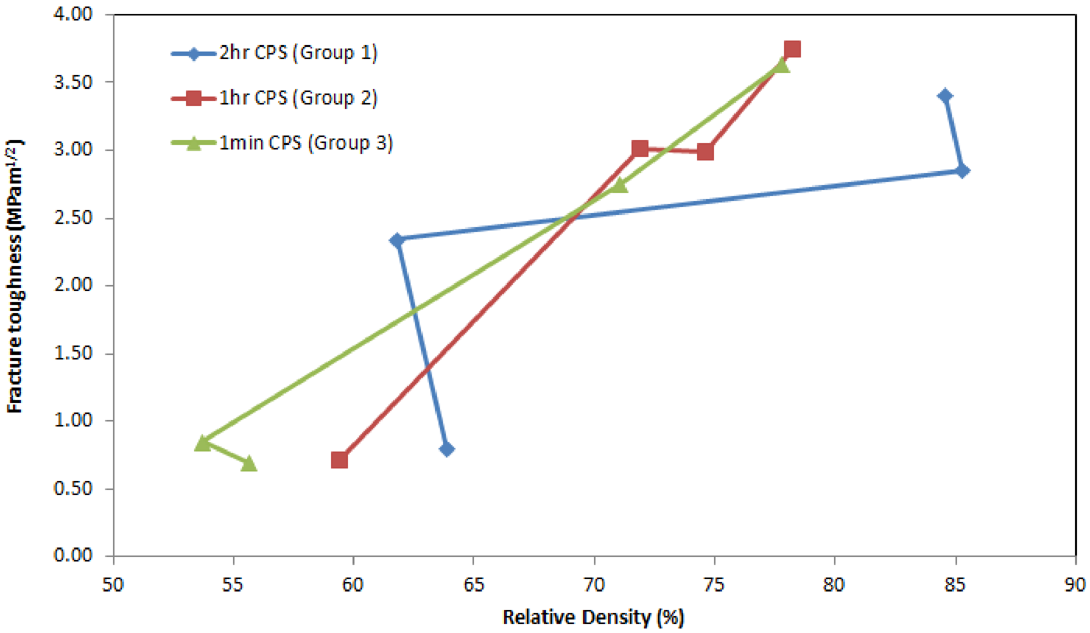

Figure 4.32: The effect of relative density on fracture toughness with different sintering temperature and holding time

4.4.7 Young's Modulus

Figure 4.33 shows the effect of different sintering temperatures and holding times on Young's modulus of forsterite. In general, Young's modulus was proportional with increasing sintering temperature for Group 1 and Group 2 respectively. However the maximum stiffness for Group 1 were recorded at sintering of 1300°C with 73.84 GPa and for Group 2 at sintering temperature 1400°C with 90.46 GPa. The decreasing trend after the maximum stiffness was due to the large growth in grain size which resulted in deterioration of Young's modulus.

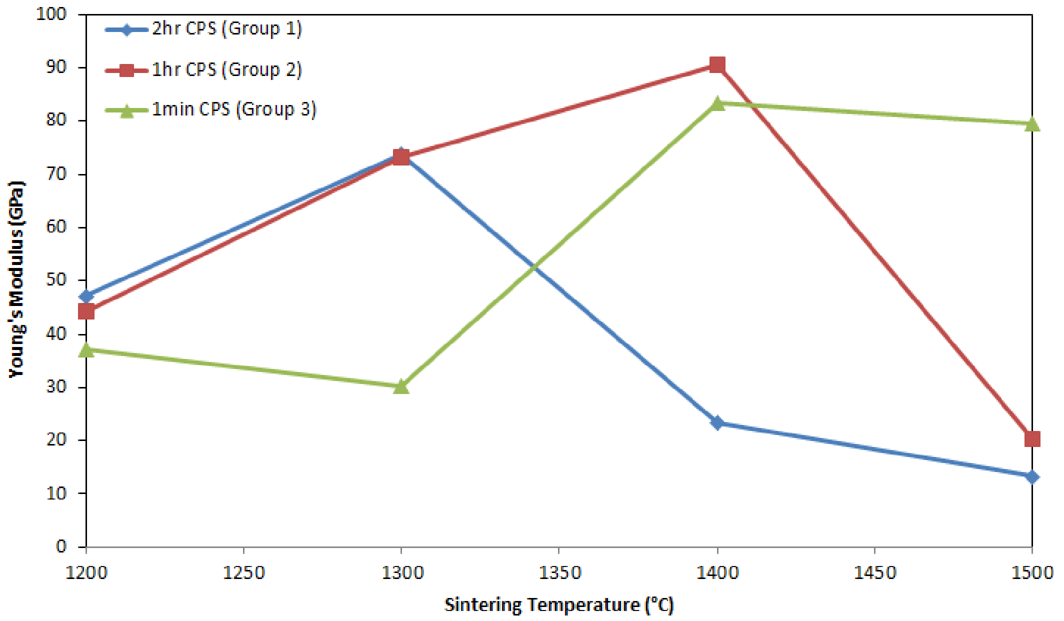

Figure 4.33: The effect of different sintering temperatures and holding times on Young's Modulus of forsterite

The presence of secondary phase (MgO and talc) for Group 3 resulted in low Young's modulus values of 37 GPa and 30.2 GPa at 1200°C and 1300°C respectively as shown in Figure 4.33 (Siebert et al., 1999). The sharp increase in stiffness from 1300°C to 1400°C was due to the elimination of secondary phase (talc) as reflected in Figure 4.22. The increasing Young's modulus is also related to reducing porosity (Radovic et al., 2004).

4.5 Microstructural and Grain Size Analysis

4.5.1 Forsterite Powder Morphology

Figure 4.34 shows the FESEM micrographs of forsterite powder that was produced after going through the synthesis process described in Chapter 3 including 22 minutes of ulrasonification and 3 hours ball milling. The starting powder elements of talc and MgO were clearly shown in XRD result for producing forsterite powder as shown in Figure 4.1. The micrographs show characteristic of both MgO which show flake like morphology (Díez et al., 2006) and talc with lamellar shape (Tavangarian & Emadi, 2009).

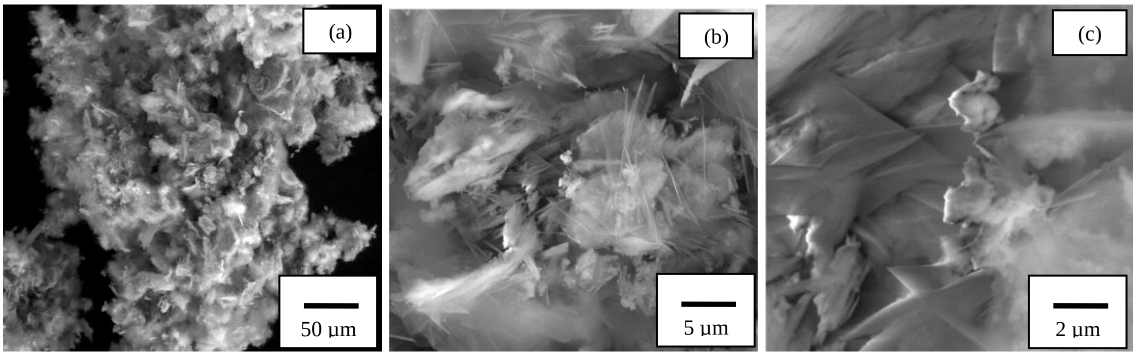

Figure 4.34: FESEM micrographs of forsterite powder prepared by 22 minutes ultrasonification and 3 hours ball milling

This result shows the original elements of the starting powders, talc and MgO were well preserved after the synthesis process to form forsterite powder. Another contributing factor would be the abstinence of heat treatment process.

4.5.2. Microstructure of Sintered Forsterite Compacts

Figures 4.35, 4.36 and 4.37 show FESEM micrographs of forsterite compacts sintered at 1200°C, 1300°C, 1400°C and 1500°C with 2 hours holding time (Group 1), 1 hour holding time (Group 2) and 1 minute holding time (Group 3) respectively.

Overall, it was observed that the porosity was reduced as sintering temperature increased for Group 1, 2 and 3. This is significantly evident at sintering temperature 1400°C and 1500°C. There was no secondary phase detected in Group 1 and Group 2 as shown in Figure 4.12 to Figure 4.19. However the porosity for Group 1 has higher reduced porosity than Group 2 at 1500°C because of the longer holding time which resulted in higher shrinkage at 14.85% and relative density at 84.5% as shown in Figures 4.25 and 4.26 respectively.

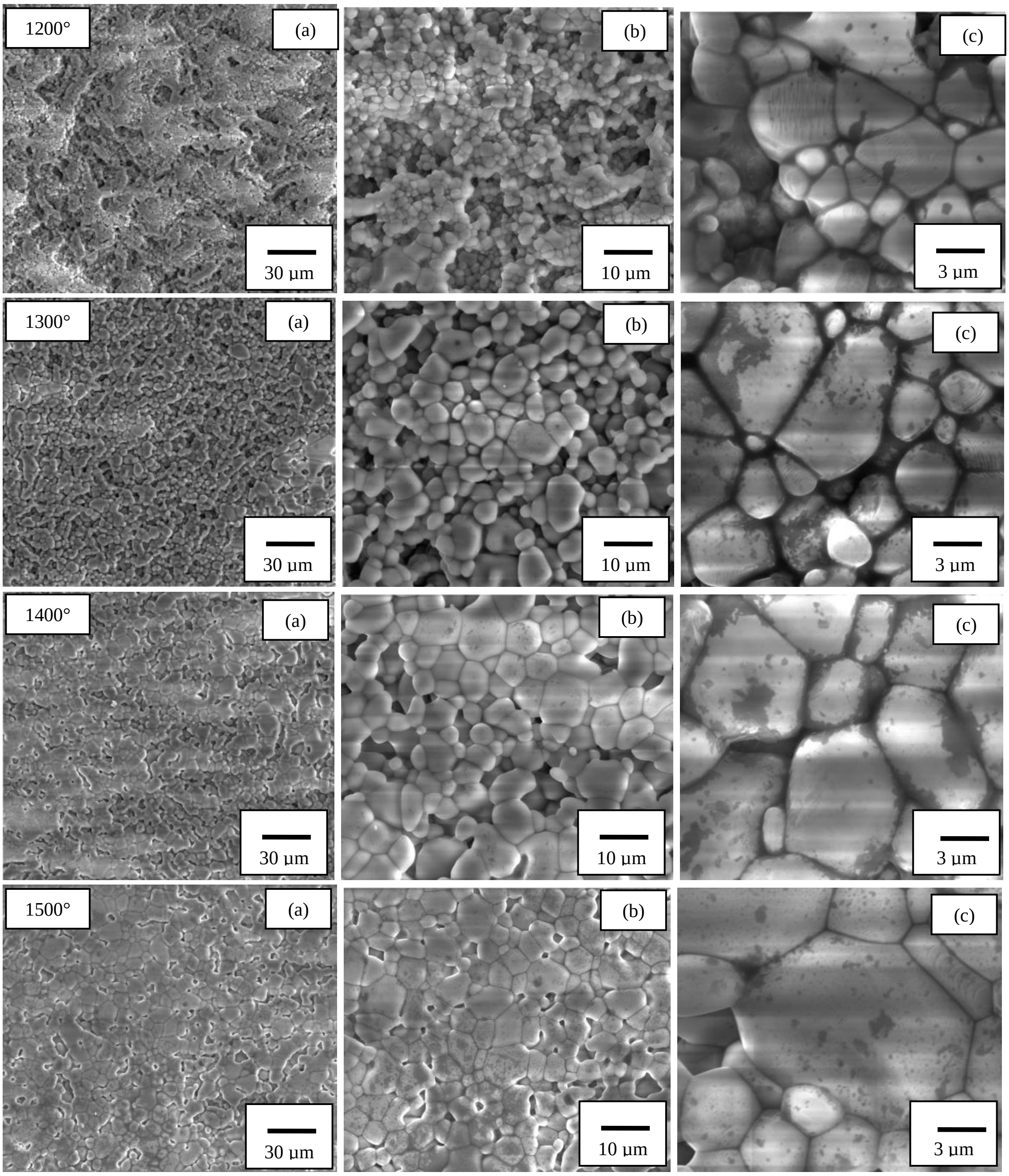

Figure 4.35: FESEM micrographs of forsterite compacts sintered at 1200°C, 1300°C, 1400°C and 1500°C with 2 hours holding time (Group 1)

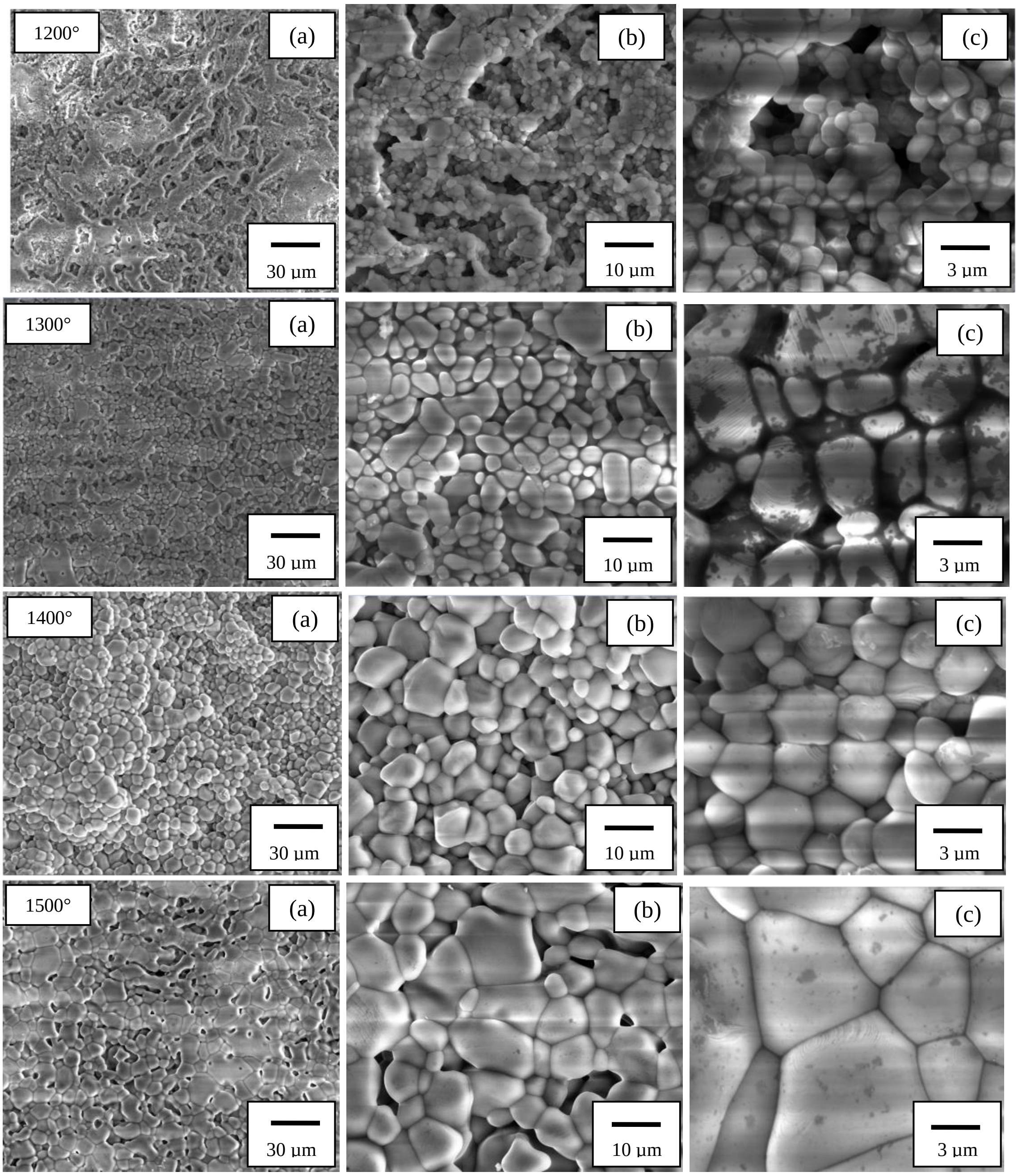

Figure 4.36: FESEM micrographs of forsterite compacts sintered at 1200°C, 1300°C, 1400°C and 1500°C with 1 hours holding time (Group 2)

The shorter holding time of 1 minute with sintering temperature 1200°C proved partial densification occurred as flaky like MgO trace was observed in Figure 4.37. This is in agreement with the presence of secondary phases, MgO and talc detected in Figure 4.20. However higher sintering temperature at 1500°C resulted in big improvement for Vickers hardness and fracture toughness at 4.79GPa and 3.63 MPam$^{1/2}$ respectively which were 8.1% and 6.3% higher than Group 1 results. The elimination of secondary phase and reduction in porosity are contributing factor in higher hardness (Hoepfner & Case, 2003; Siebert et al., 1999).

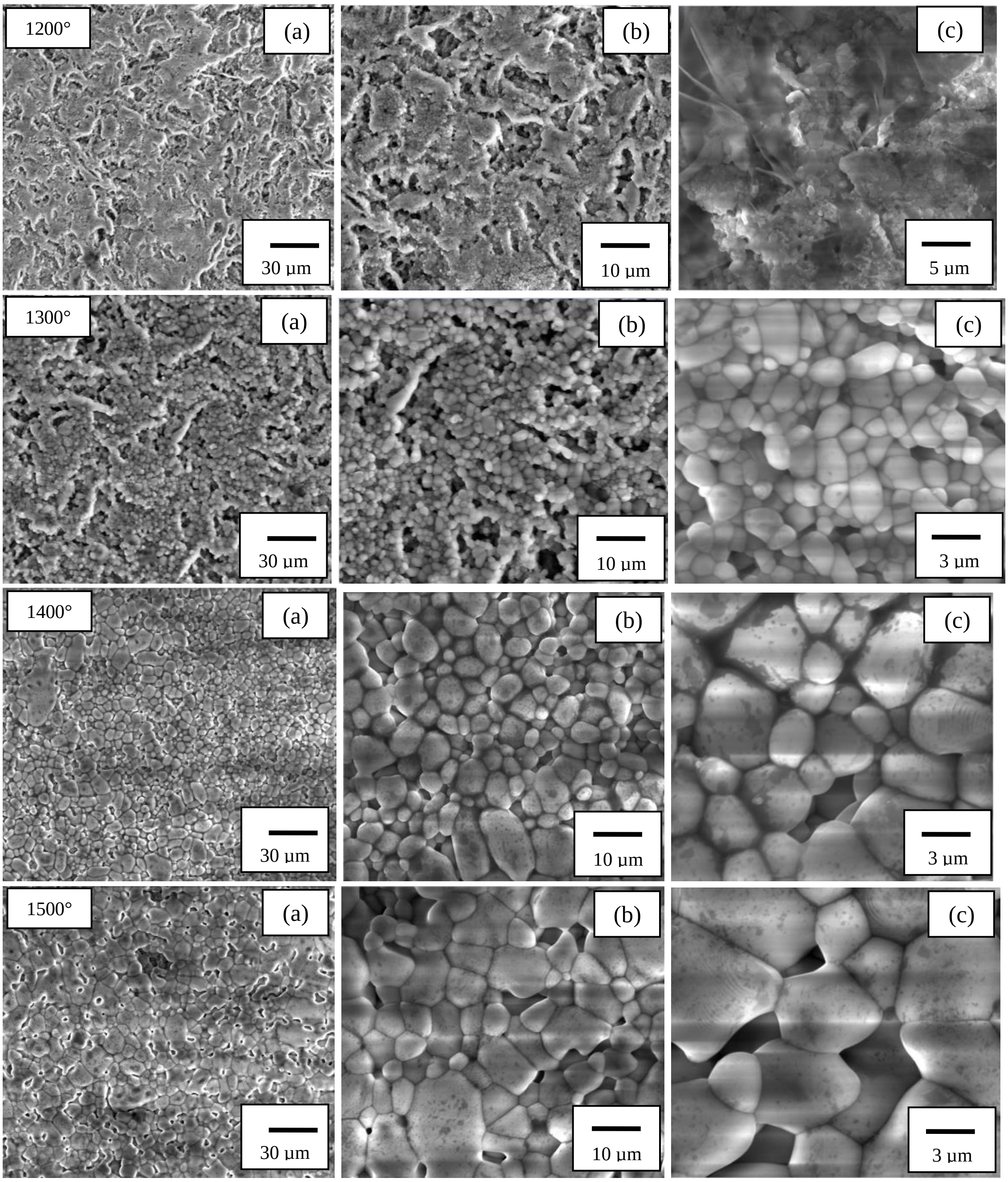

Figure 4.37: FESEM micrographs of forsterite compacts sintered at 1200°C, 1300°C, 1400°C and 1500°C with 1 minute holding time (Group 3)

The elimination of secondary phase and porosity are visually significant in Figure 4.38 for Group 3 with increasing sintering temperature 1200°C to 1500°C. Group 2 has lower bulk density than Group 1 by 14.2% and 8.1% at 1400°C and 1500° respectively as shown in Figure 4.26 which were reflected in the FESEM micrographs indicating Group 1 with less porosity than Group 2. However, the Vickers hardness and fracture toughness for Group 2 were higher than Group 1 by 4.9% and 4.7% at 1400°C and 12.2% and 9.3% at 1500°C respectively. These results were reflected in Figure 4.29 and 4.31 respectively which concluded Group 2 was the optimal holding time that resulted in highest Vickers hardness and fracture toughness properties. Over firing due to longer holding time in Group 1 was the probable cause that resulted in lower toughness properties.

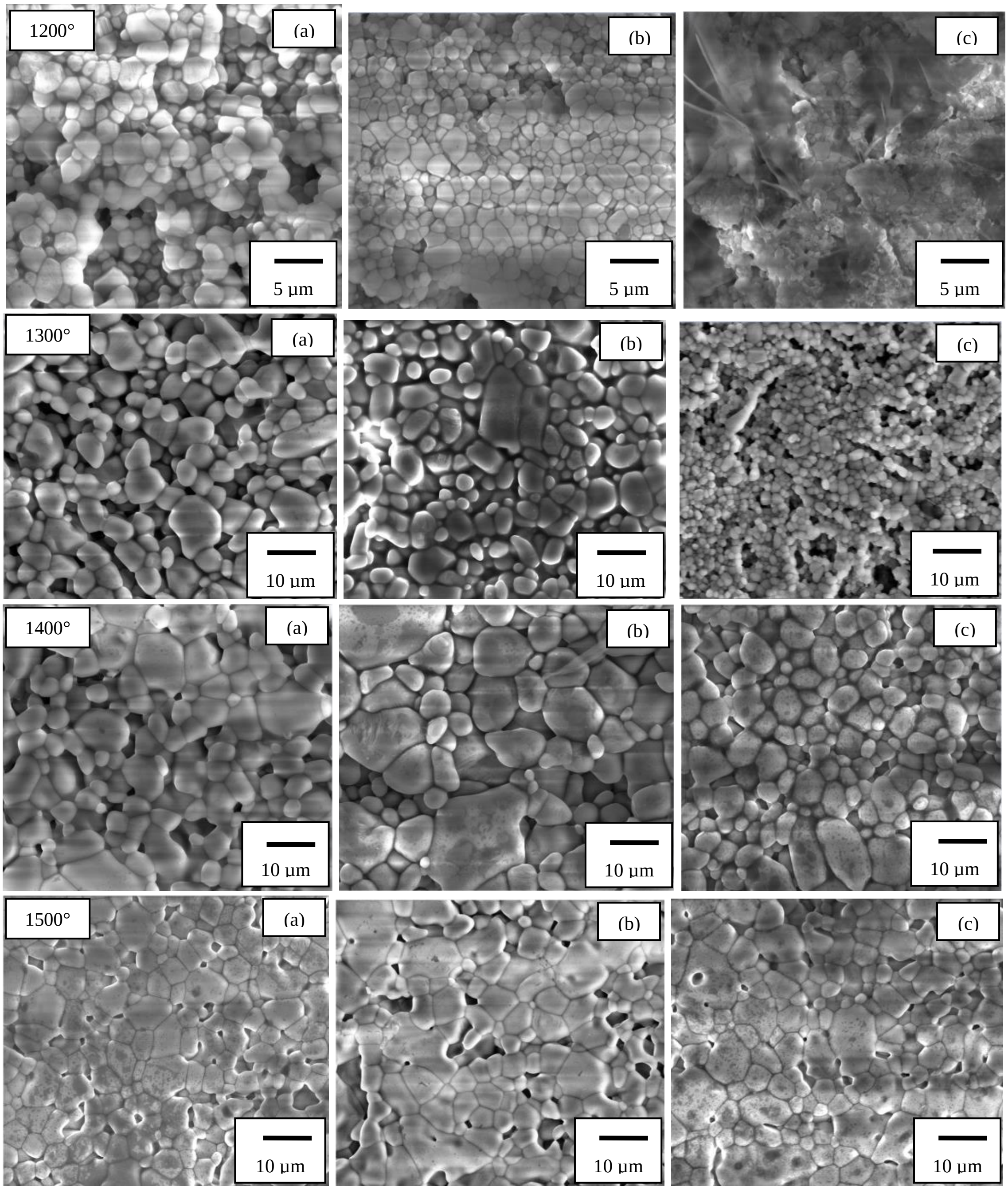

Figure 4.38: FESEM micrographs of sintered forsterite compacts sintered at 1200°C, 1300°C, 1400°C &1500°C with 3 different holding times; (a) 2 hours (Group 1), (b) 1 hour (Group 2), (c) 1 minute (Group 3)

Figure 4.39 show the FESEM micrographs of cracked surface resulting from quenching after sintered at 1000°C, 1200°C, 1400°C, 1500°C with ramp rate of 10°C/min.

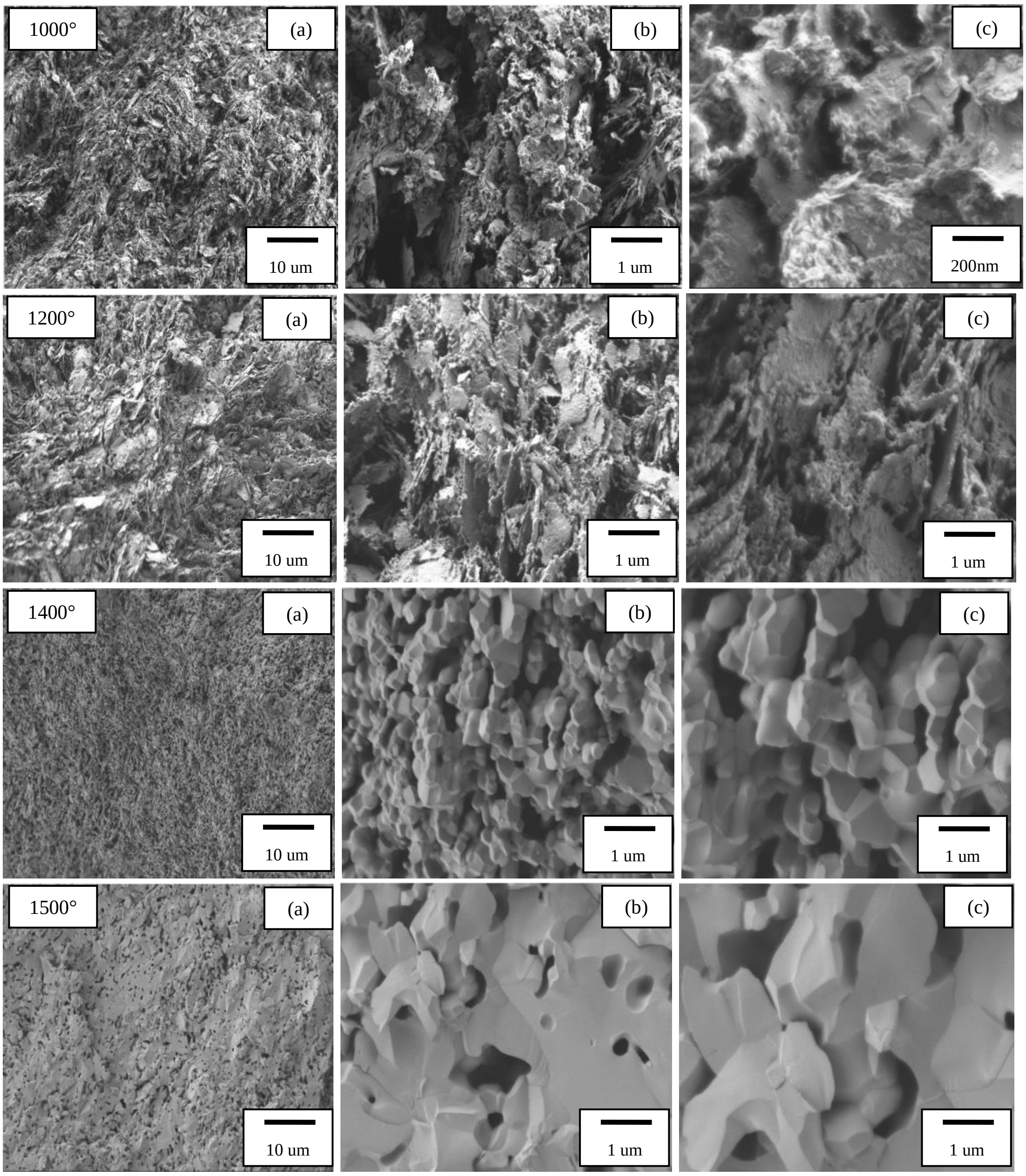

Figure 4.39: FESEM micrographs of cracked surface resulting from quenching after sintered at 1000°C, 1200°C, 1400°C, 1500°C with ramp rate of 10°C/min

The forsterite compacts cracked naturally after it was submerged into ice cold water. In general there are no unusual microstruture. The cracked surface of forsterite compact sintered at 1000°C are flaky-like as per Figure 4.34 which was an evident of partial densification took place. The microstructure was denser at sintering temperature 1200°C than 1000°C as partial densification occurred with presence of secondary phases MgO and talc as per Figure 4.20. Signicant densification and porosity reduction were observed as sintering temperature increased to 1400°C. However, secondary phase enstatite was still present as shown in Figure 4.22. The elimination of secondary phase at 1500°C resulted in maximum densification with minimum porosity. Figure 4.40 shows the closed up FESEM micrographs of forsterite compact sintered at 1500°C

.

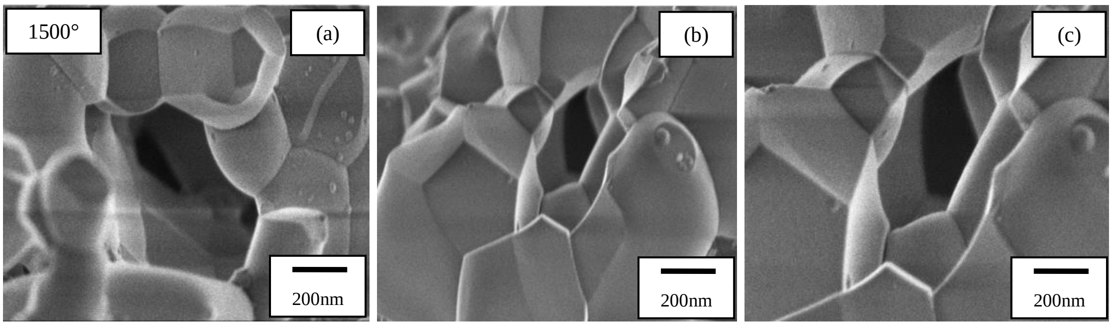

Figure 4.40: Closed up FESEM micrographs of forsterite compact sintered at 1500°C

The grain boundary diffusivity was enhanced at 1500°C, hence promoting particles consolidation that formed rounded pore with rounded grain boundary. However there was no sign of liquid phase sintering. The effect of sintering temperature with three different holding times (Group1: 2 hours, Group 2: 1 hour and Group 3: 1 minute) on grain size of sintered forsterite compacts are shown in Figure 4.41.

The grain size increased as sintering temperature increased for all 3 holding times in different rate. Group 1 initially recorded largest grain size at 1200°C followed by Group 2 and 3 with 1.22 µm, 0.53 µm and 0.31 µm respectively. However starting from 1300°C onwards, grain size in Group 2 overtook Group 1 to record largest grain size at 1500°C followed by Group 1 and Group 3 with 4.21 µm, 3.05 µm and 3.01 µm respectively.

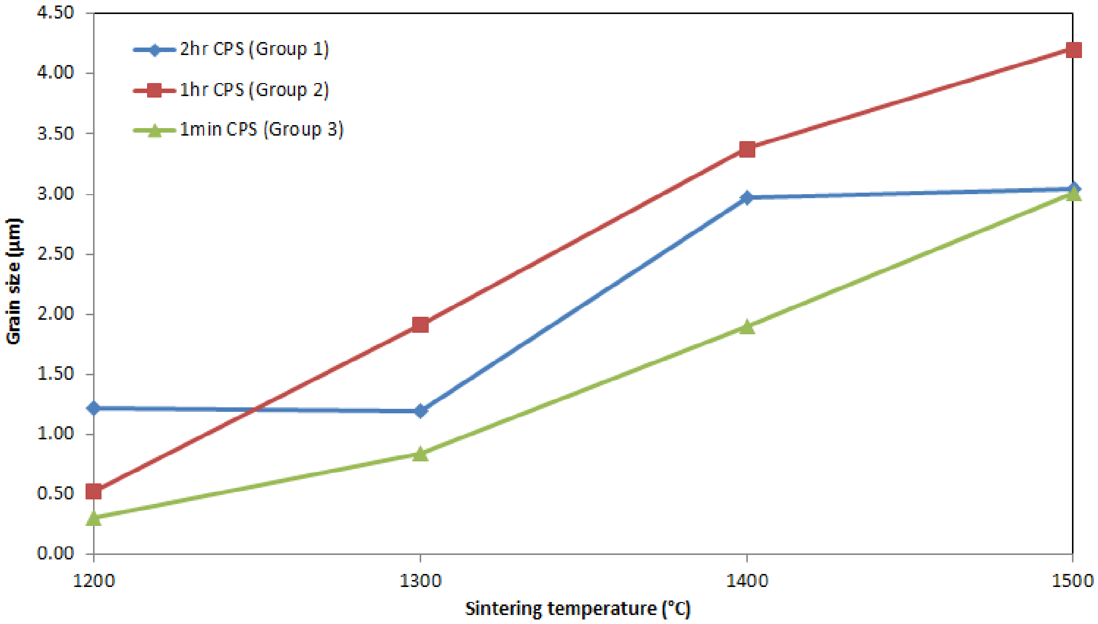

Figure 4.41: The effect of sintering temperature with three different holding times (Group1: 2 hours, Group 2: 1 hour and Group 3: 1 minute) on grain size of sintered forsterite compacts

4.5.3 Grain Size Analysis

The effect of relative density, Vickers hardness and fracture toughness on grain size of sintered forsterite compacts are shown in Figures 4.42, 4.43 and 4.44 respectively.

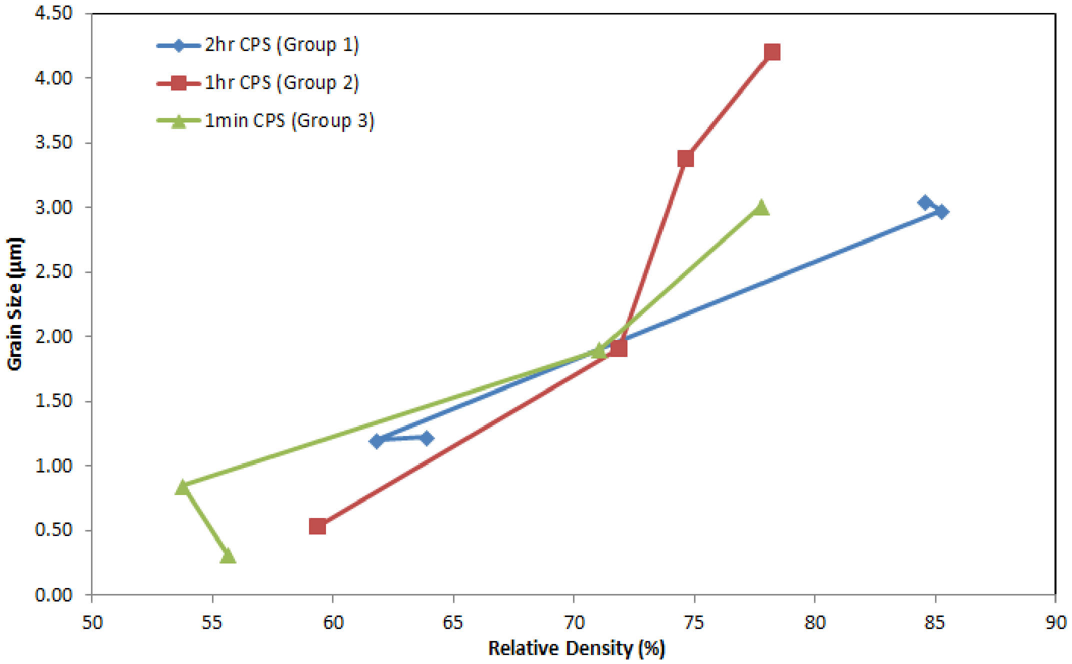

Figure 4.42: The effect of relative density on grain size of sinterered forsterite with

Group 2 was the only trend showing grain size increasing exponentially with increasing relative density. The maximum grain size recorded was 4.21 µm with relative density of 78.2% at 1500°C. There was slight decrease in relative density from 55.6% to 53.7% for Group 3 at sintering temperature of 1300°C due to the formation of secondary phases talc and enstatite respectively. However, the grain size increases at this point from 0.31 µm to 0.84 µm and continued to increasing as the secondary phases are fully eliminated at 1500°C resulted with grain size of 3.01 µm. There were slight decrease in both relative density and grain size at 1300°C for Group 3 by 3.1% (63.8% to 61.8%) and 1.6% (1.22 µm to 1.20 µm). However, the highest relative density among the 3 groups was recorded for Group 1 at 85.2% together with grain size of 2.98 µm in the steep increase at 1400°C. At 1500°C, the grain size continued to increase to 3.05 µm with slight dip in relative density to 84.5%.

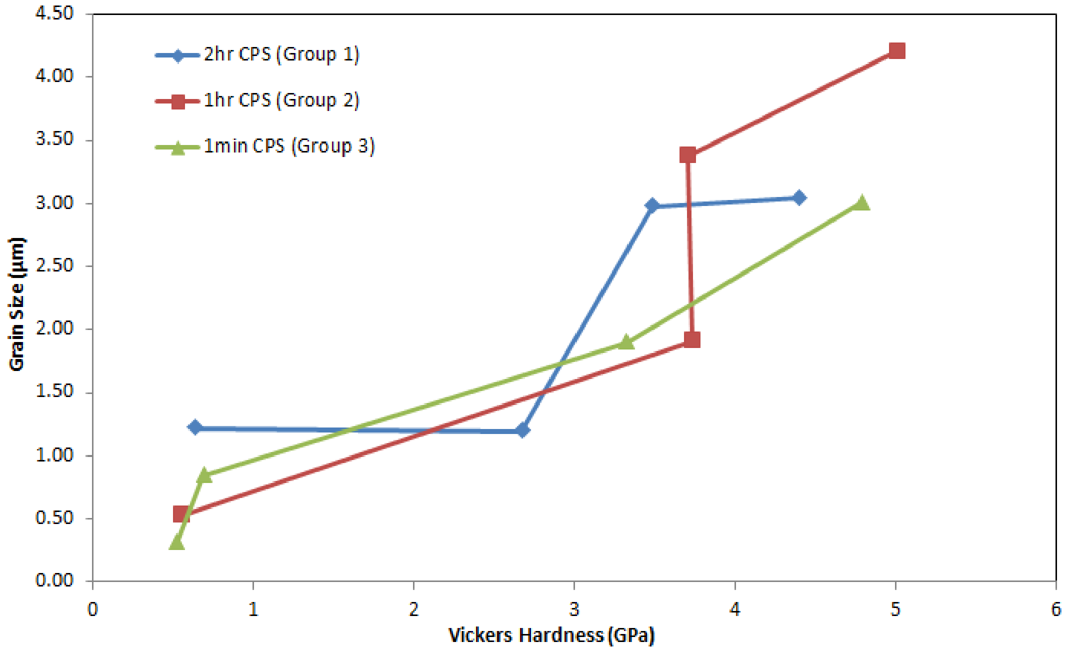

Figure 4.43: The effect of Vickers hardness on grain size of sinterered forsterite

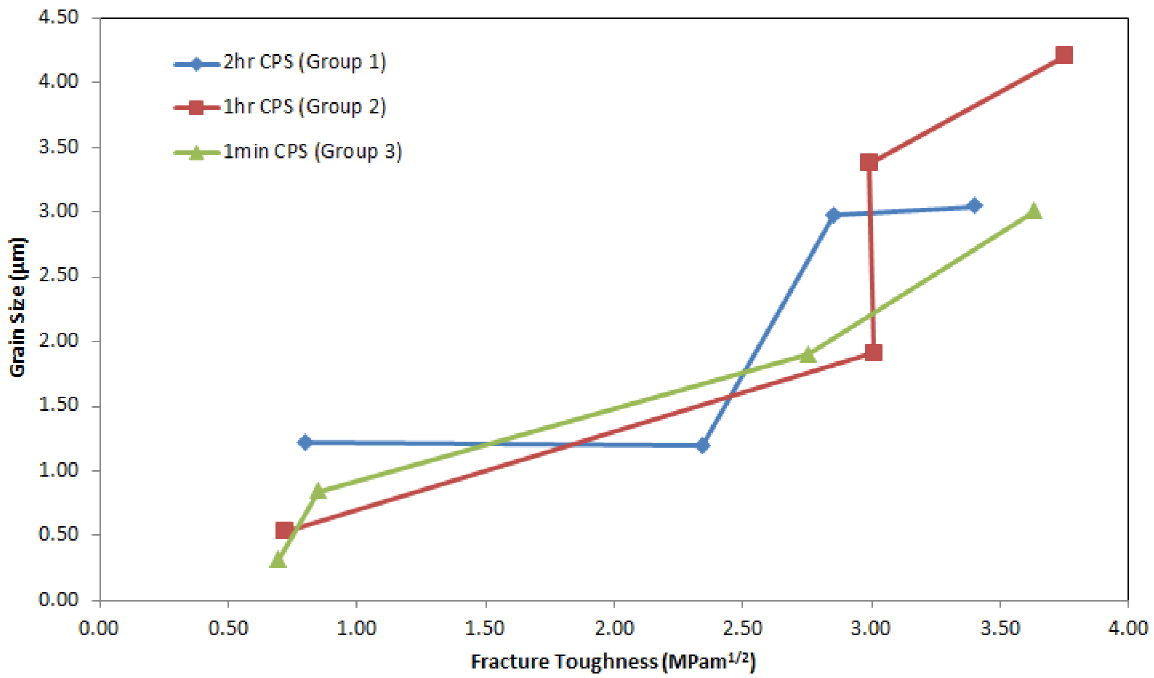

Figure 4.44: The effect of fracture toughness on grain size of sinterered forsterite

Both Figures 4.43 and 4.44 showed the same trend characteristics. Highest grain size of 4.21 µm was recorded with highest Vickers hardness and fracture toughness of 5.01 GPa and 3.75 MPam$^{1/2}$ respectively at 1500°C. Group 3 recorded the lowest grain size 3.01 µm with Vickers hardness and fracture toughness of 4.79 GPa and 3.63 MPam$^{1/2}$ respectively. The presence of secondary phases talc and enstatite for Group 3 at 1300°C limit the Vickers hardness and fracture toughness enhancement but it has improved as the increasing of sintering temperature to 1500°C eliminated secondary phases. Grain size was observed decreasing at 1300°C for Group 1 only, even though the Vickers hardness and fracture toughness were increasing.

The results at 1300°C and 1500°C shown for Group 1 were agreeable with Hall-Petch relationship indicating hardness and fracture toughness are inversely proportional to grain size (Hall, 1951; Petch, 1953; Milman et al., 1999; Kumar et al., 2003). However results in Group 2 and Group 3 were agreeable with most results indicating the inverse of Hall-Petch relationship which means hardness and fracture toughness increase with increasing grain size (Ramesh, 2001; Conrad et al., 2005; Ramesh et al., 2007; Shen et al., 2007, Péron-Lührs et al., 2013). An hour holding time in Group 2 proved to be the ideal duration which produced the highest Vickers hardness (5.01 GPa) and fracture toughness (3.75 $MPam^{1/2}$) even though the highest relative density was recorded in Group 1.