Phase Analysis of Bio-Based Derived Tricalcium Disilicate From 2CaO:1SiO₂ By X-ray Diffraction

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Abstract. In this paper, tricalcium disilicate was formed from dicalcium silicate compound powder, synthesised via a mechanochemical technique using a stoichiometric 2CaO:1SiO₂. Compound CaO and SiO₂ were derived from the bio-waste of eggshell and rice husk at the calcination temperature of 900°C and 800°C, respectively. The dicalcium disilicate powder was sintered for 2 hours at different temperatures ranging from 1150°C to 1350°C. Using X-ray diffraction with Rietveld analysis, it was found that the amount of tricalcium disilicate with monoclinic (beta) crystal structure increases on sintering temperature at the expense of dicalcium silicate. The complete formation of single-phase tricalcium disilicate began at a sintering temperature of 1300°C. The effect of sintering temperatures on the crystallisation and phase transition of dicalcium silicate is reported. The size of crystallites depends on the sintering temperature. The finding of this study rebound to the benefit of society by reducing the risk-off pollution cause by excessive redundant bio-waste eggshell and rice husk and also reduced the amount of CaO and SiO₂ used in the fabrication of Ca₃Si₂O₇.

1. Introduction

Several compounds compose of calcium oxide (CaO) and silica (SiO₂) exists stably are known as calcium silicate (Ca₃SiO₄), dicalcium silicate (Ca₂SiO₄), tricalcium silicate (Ca₃SiO₅), and tricalcium disilicate (Ca₃Si₂O₇) [1]. Tricalcium disilicate or known as rankinite was recognised as a low-lime calcium silicate, and it has non-hydraulic nature, i.e., not prone to hydration [2]. Tricalcium disilicate compound has a structure array of silicate tetrahedral, Si₂O₇ group linked together by calcium atoms, each having seven coordinate oxygen atoms [3]. The reactivity of calcium silicate types is influenced by the kind and amount of foreign oxides [4].
Tricalcium disilicate is a building material, usually applied as binders, cement clinkers, and steel slag [2,5]. Besides, it is used as a host material for producing phosphor for lighting [6]. Also, tricalcium disilicate is applied to absorb carbon dioxide in the decarbonation process [7]. Its simple components and obvious advantages motivate the researchers to exploit its full potential to benefit all mankind. Since tricalcium disilicate contains CaO and SiO$_2$, it is feasible to use existing bio-wastes, for instance, eggshell and rice husk, as raw materials to synthesis ceramic.

Eggshell (ES) comprises more than 90% calcium carbonate (CaCO$_3$) [8,9], which could produce solid CaO through a calcination process [10,11]. SiO$_2$ can be obtained from rice husk (RH), mainly composed of SiO$_2$ [12]. The rice husk ash (RHA) produced by complete combustion contains about 90-98% of SiO$_2$, forming a porous structure of nano-silica with a particle size of about 5-60 nm [13-15]. Besides, SiO$_2$ synthesised from RHA is more sustainable than quartz sand and sodium carbonate, which require much energy at around 1300°C [16]. Nevertheless, these precious natural resources rich in minerals are underestimated and cause disposal and pollution problems. The best way to release the pressure of nature is to make full use of these bio-wastes to achieve sustainability.

The present work investigates the feasibility of deriving Ca$_3$Si$_2$O$_7$ using ES and RH in the ratio of 2 by applying the mechanochemical technique. The phase analysis was conducted using X-ray diffraction (XRD).

2. Materials and method

2.1. Material

ES was collected from the daily basis of food waste in Malaysia, while RH was obtained from the rice-growing region of Malaysia.

2.2. Preparation of calcium oxide

The ES was rinsed and cleaned to remove residue. The cleaned ES was dried in an electric oven and was ground manually using mortar and pestle. Finally, the powdered ES was calcined in a muffle furnace at 900°C for 4 hours with a heating rate of 10°C/min.

2.3. Preparation of silica

The RH was washed with tap water then dried at 110°C for 45 minutes in an electric oven. The dried RH was proceeded to calcination process in a muffle furnace at 800°C for 2 hours with a heating rate of 10°C/min. Lastly, white RHA was obtained and ground by using mortar and pestle.

2.4. Preparation of calcium orthosilicate, Ca$_2$SiO$_4$

Calcined RH and ES in powder form were mixed according to stoichiometric of 2:1 of 2CaO:1SiO$_2$ in an agate milling jar containing milling balls. The milling jar operated in planetary ball milling, PBM at 300 rpm for 10 hours. This method was relatively straightforward without using any filler or additional oxide matter. Next, the milled powder was pressed into pallet form and sintered in an electrical muffle furnace at different temperatures (1150°C, 1200°C, 1250°C, 1300°C, and 1350°C) for 2 hours with a heating rate of 5°C/min.

2.5. Experimental analysis

The phase analysis of the green body and sintered samples was analysed with XRD (Bruker D2 Phaser Model) from 5° to 90° and 10° to 90° at a scan speed of 2° 2θ/min and a step size of 0.02° 2θ with CuKα radiation (Kα = 1.5406 nm) at 10 mA and 30 kV. Rietveld refinement was performed using structure models of known crystalline phases from the Inorganic Crystal Structure Database (ICSD) database (ICSD 2008). Crystallite size was determined using the well known Scherrer Equation, as presented in Equation (1) [17]:

\[ D = \frac{K\lambda}{\beta \cos \theta} \] (1)
where $D$ is the crystallite size, $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum (FWHM) of the intense peak, $\theta$ is the Bragg angle, and $K$ is the Scherrer constant, which was taken as 0.9.

3. Result and Discussion

3.1. Phase analysis

Figure 1(a) shows the XRD pattern of calcined RH at 800°C. A broad peak ranging from 15° to 30° in 2θ angle confirms the amorphous nature of silica [18]. A diffused peak at about 23° indicates an incipient crystallisation process that leads to disorder cristobalite [19,20]. The presence of cristobalite phase corresponds to crystallisation phenomena of silica, SiO$_2$ during the heating or calcination process [13]. Furthermore, the absence of peaks of possible impurities affirmed the purity of the as-derived silica.

Figure 1(b) shows the XRD pattern of calcined ES at 900°C for 2 hours. The occurrence of intense and narrow peaks in calcined solid is defined as a good crystallinity of the material [21]. The pattern with sharp peaks indicated crystalline structure and comprised calcium oxide, CaO, and portlandite, Ca(OH)$_2$. Calcium carbonate present in the ES gone through decarbonation process that transforms into calcium oxide and carbon dioxide. Calcium oxide evolved into calcium hydroxide, Ca(OH)$_2$ due to the exposure to moisture from the atmosphere through the reaction of CaO + H$_2$O $\rightarrow$ Ca(OH)$_2$ [22]. There was no observation of calcite phase in the XRD pattern of calcined ES, showing that calcium carbonate phase was completely transformed to calcium oxide during the calcination process at 900°C.

Figure 1. XRD pattern of (a) calcined rice husk, RH. (b) calcined eggshell, ES.

XRD pattern of green body sample is shown in Figure 2(a). The figure clearly illustrated the presence of sharp diffraction peaks in the pattern indicates the powder composes of crystalline and getting to an amorphous state after about 2θ = 60°. The analysis of XRD pattern peaks reveals that the main phase is dicalcium silicate, accounting for 93.5%, with chemical formula of Ca$_2$SiO$_4$. Also, there is a small amount of (6.5%) silicon oxide (SiO$_2$). The pattern reveals the presence of Ca$_2$SiO$_4$ (ICSD: 98-011-2218) has a monoclinic (beta) crystal structure, and its crystallite size [Å] calculated by Scherrer equation is 209. The phase of SiO$_2$ (ICSD: 98-010-6054) has a hexagonal crystal structure with the calculated crystallite size [Å] is 171. There is also a small amount of unreacted SiO$_2$ and an absence of unreacted CaO. During the milling process, a chemical reaction occurred between 2CaO and 1SiO$_2$, which was directly converted into Ca$_2$SiO$_4$ without sintering or heating. This shows that the application mechanochemical route at a higher speed and longer duration can improve and increase the reactivity of CaO and SiO$_2$. Composite material produces by mechanochemical treatment resulted in a very fine homogenised powder, thereby improving the reactivity between the corresponding single-phase compound of 2CaO and 1SiO$_2$ to form Ca$_2$SiO$_4$ [1]. Under the dry milling condition at about 300 rpm for 8 hours, particle size was reduced to below 10 μm [22-23], and the interaction between particles was enhanced. The milling process during the mechanochemical treatment may
cause some disturbances in the crystal structure formed that gradually influence the reactivity of the composite compound [4].

XRD pattern of the sample sintered at 1150°C for 2 hours was illustrated in Figure 2(b). The obtained diffractograms verified that the sample is composed of crystalline material because of the sharp diffraction peaks. Among these peaks, there were 78.2% of larnite (Ca2SiO4) according to ICSD: 98-000-5670 with the monoclinic (beta) crystal structure and crystalline size [Å] calculated is 486. The observed 19.2% of rankinite (Ca3Si2O7) according to ICSD: 98-000-5769 is monoclinic (beta) crystal structure, and it has a crystalline size [Å] of 298. There is 2.6% of dicalcium silicate-gamma (Ca2SiO4), according to ICSD: 98-003-7851, in the orthorhombic crystal structure with crystal size [Å] of 744. Since the reactivity of the pre-sintered powder was improved during the milling process, the reaction is easier and faster than usual under heat energy. Therefore, high-temperature treatment can damage the pore structure and generate a new Ca3Si2O7 phase by transforming the already formed Ca2SiO4 phases into a different Ca3Si2O7 phase composition [1]. This finding is exciting because it can form Ca3Si2O7 from a stoichiometric 2CaO:1SiO2 at a relatively low operating temperature.

XRD data of the sample sintered at 1200°C is shown in figure 2(c). XRD pattern shows dual-phase and slightly amorphous in nature. From the analysis, there is 96.6% of rankinite (Ca3Si2O7) according to ICSD: 98-000-5769 with monoclinic (beta) crystal structure and the crystallite size is 796Å. Moreover, there is 3.3% moissanite 39R (C1Si1) according to ICSD: 98-004-8379 of trigonal (hexagonal axes) crystal structure with a crystallite size of 835Å. Also, a tiny amount of 0.2% zeolite (SiO2) presence in the sample according to ICSD: 98-009-3687 and crystallite size is 799Å. As the sintering temperature increases, the phase change from Ca2SiO4 to Ca3Si2O7 corresponds to the mixed crystal structure in the sample. For this reason, the percentage of rankinite increased dramatically at the expense of the dicalcium silicate phase.

XRD analysis of the sintered sample pallet at 1250°C is shown in figure 2(d). The pattern identified that the major crystalline phase in the sintered sample is rankinite (Ca3Si2O7) with 99.2% of intensity. Besides, there is a small amount of 0.8% zeolite (SiO2). Ca3Si2O7 (ICSD: 98-000-5769) present in monoclinic (beta) crystal structure with crystallite size 740 Å. The phase of SiO2 (ICSD: 98-009-3688) has a trigonal (hexagonal axes) crystal structure, and the crystallite size is 25Å. The amount of Ca3Si2O7 increases with increasing sintering temperature, and the amount of unreacted SiO2 starting to diminish.

Figure 2(e) shows the XRD pattern of the sample sintered at 1300°C. The pattern revealed the presence of 100% rankinite (Ca3Si2O7) according to ICSD: 98-000-5769 of space group P 1 21/C1 having monoclinic (beta) crystal structure with crystallite size of 655 Å, calculated from Scherrer Equation. It can be concluded that sintering temperature at 1300°C achieved the single phase of Ca3Si2O7 from a stoichiometric ratio of 2 CaO and 1 SiO2 without any other phases or impurities. This finding is in parallel agreement with [25], where sintering or heating treatment up to 1300°C can generate single-phase Ca3Si2O7. However, the present work used a single heating step for 2 hours under air atmosphere, which is much energy saver compared to [24] for 6 hours under 4% H2–96% N2 gas to complete the reaction.

Figure 2(f) shows the XRD pattern of the sample sintered at 1350°C. From the riveted refinement, the main phase identified in the sample is 100% rankinite, Ca3Si2O7. According to ICSD: 98-000-5769, it is a monoclinic (beta) crystal structure of space group P 1 21/C1, and its crystallite size is 797Å. For the sample sintered at 1300°C, the phase is similar to that sample sintered at 1350°C, where only peaks belonging to the Ca3Si2O7 single phase were detected, without any extraneous phases.
Figure 2. XRD pattern of (a) green body sample, (b) sample sintered at 1150°C. (c) sample sintered at 1200°C. (d) sample sintered at 1250°C. (e) sample sintered at 1300°C. (f) sample sintered at 1350°C.

4. Conclusion

Pure amorphous silica and calcium oxide was successfully extracted from rice husk ash and chicken eggshell, respectively, by a calcination process. Mechanochemical treatment at 300 rpm and 10 hours on the mixture of 2CaO and 1SiO₂ powder developed the formation of dicalcium silicate without sintering and heating process. Using XRD with Rietveld analysis, the progress of phase formation during sintering of the sample, as well as crystallite size was studied. The XRD results pointed out that the amount of tricalcium disilicate increases on sintering temperature at the expense of dicalcium silicate. During the sintering process, the heat treatment interferes with the formed crystals, resulting in phase transformation to the monoclinic (beta) crystal structure of tricalcium disilicate. The formation of single-phase rankinite has been formed completely onset at sintering temperature of 1300°C. The size of crystallites was found to be dependent on the sintering temperature.
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