

Study of Crystal Growth Phenomenon During the Synthesis of Wollastonite Utilizing Amorphous Silica

M. Sharif Nizami^{a*}, K. Hussain^b

^aPCSIR Laboratories Complex, Ferozepur Road, Lahore-54600, Pakistan

^bDepartment of Physics, Punjab University, Lahore, Pakistan

(received July 19, 2005; revised May, 27, 2007; accepted June 5, 2007)

Abstract. Wollastonite (CaSiO_3), a mineral of wide industrial application, was synthesized under solid state conditions. Starting materials for the synthesis were CaO resulting from the in-situ thermal decomposition of limestone and amorphous silica obtained by controlled pyro-processing of rice husk. A mineralizer having glass like composition was prepared and intermixed with the raw materials pulverized to 75μ particle size. The compact powder batches were sintered at $900\text{-}1300^\circ\text{C}$ for 1 h in order to grow wollastonite crystals from matrix of the reacting oxides. The reaction was monitored simultaneously by specific chemical analysis and XRD techniques. Solid state reactions, involving orientation and geometrical reshuffling of the interacting and newly produced phases, require special considerations for the product crystal growth. Three possible reaction models, under which the wollastonite crystals may grow in reacting solids were considered and the generated data treated according to the laid down criteria. The nuclei growth model was consequently found to be promising as the route adopted by the present solid state reaction yielding wollastonite.

Keywords: crystal growth, wollastonite, silica

Introduction

Wollastonite, chemically CaSiO_3 , is a naturally occurring mineral found in several countries of the world. However, the demand for this raw material of wide industrial application is not being fulfilled from its available deposits (Nizami *et al.*, 1999; Rieger, 1991, Sainamthip and Reed, 1987). On the other hand, rice husk (RH) is an abundant and cheaper agricultural waste, ash of which yields 88-96% SiO_2 if prepared under proper thermal treatment (Bui, 2001). This SiO_2 is amorphous in nature and several times more reactive than its common source quartz (Bui, 2001). It was prepared from RH under controlled pyro-processing conditions and reacted with CaO of the limestone to synthesize wollastonite. Solid state (SS) reaction was carried out for growing wollastonite crystals from intermixed and compact powders of reactants. Simultaneously, chemical analysis (CA) and XRD were carried out since the former technique can only predict the formation of CaSiO_3 giving no information about the developed mineral phase (Ibnez *et al.*, 1990). It is notable here that there exist 121 calcium silicates but out of these a few are wollastonite. As synthesis of a mineral (wollastonite) by utilizing silica obtained from an abundant agricultural waste product is unique in nature, therefore, it was imperative to investigate this under different aspects. One of the authors studied it from the point of view of chemical kinetics and concluded that the said

synthesis required almost one third energy of activation than that consumed using quartz as a source of silica (Nizami and Iqbal, 2001).

Solid State (SS) reactions involve breaking of chemical bonds and their rearrangement is not so simple. In fact, these involve geometrical reshuffling of the consumed and newly produced phases which diffuse with one another and propagate within the reaction mixture. Consequently, the space coordinates cannot be ignored while studying the above mentioned SS reaction. Considering this aspect, the formation of product consisting of crystals grown from matrix of solid reacting species may take place through a number of possible routes. Hence, the nature of crystal growth phenomenon taking place during SS synthesis of wollastonite was studied and is reported comprehensively as below.

Materials and Methods

Amorphous silica was obtained from RH by its proper thermal treatment at 500°C for 8 h and purified by applying different physicochemical techniques reported elsewhere (Nizami *et al.*, 1992). Its complete chemical analysis has been recorded in Table 1.

Limestone containing 55.91% CaO was used as another raw material. A mineralizer composed of: CaCO_3 , Na_2CO_3 , H_2BO_3 and CaF_2 was prepared to affect the chemical combination

*Author for correspondence; E-mail: pesir@brain.net.pk

Table 1. Chemical composition of rice husk silica used in synthesis of wollastonite

Constituents	Weight (%)
L.O.I.	0.08
SiO ₂	98.50
Al ₂ O ₃	0.91
Fe ₂ O ₃	0.06
TiO ₂	Traces
P ₂ O ₅	Traces
CaO	Traces
MgO	Traces
Na ₂ O	0.19
K ₂ O	0.21

between the reacting oxides. Its raw batch was thoroughly mixed, melted at 1100 °C, quenched in cold water and pulverized. All of the chemicals required for mineralizer preparation were A.R. grade reagents.

Stoichiometrically calculated amounts of the raw materials in 1:1 molar ratio, along with 2% mineralizer were mixed and pulverized to 75 μ particle size. All of the raw batches were pelletized by compressing under 1000 psi pressure. The dried pellets were placed in separate platinum crucibles and sintered in an electric furnace at 900-1300 °C for 1 h under the average heating rate of 10 °C per minute. The temperatures at which individual batches were sintered are given in Table 2.

All of the resulting products were first identified by applying analytical methods specific for wollastonite, while crystal growth was monitored by XRD during whole of the experimentation. Specimens from sintered batches were powdered to fine particle size (45 μ) and investigated on computer controlled powder X-ray diffractometer (D-Max/II-A, Rigaku) with CuKα radiations. The 2θ values were scanned from 20 °C to 50 °C and the resulting data was analysed by Hannawalt method. File of Joint Committee on Powder Diffraction Standards was consulted as standard document to identify different batch products (JCPDS, 1984).

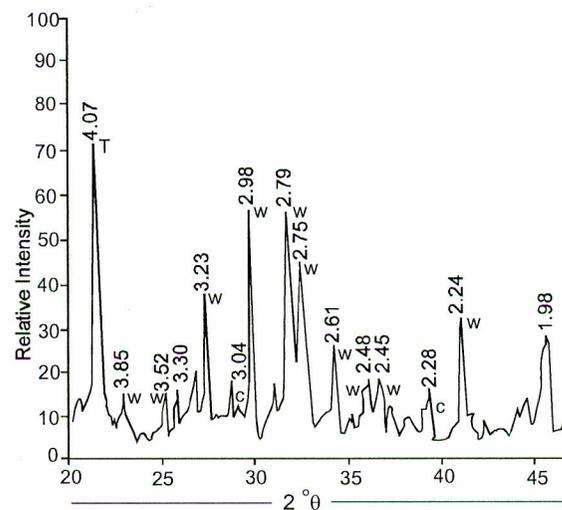
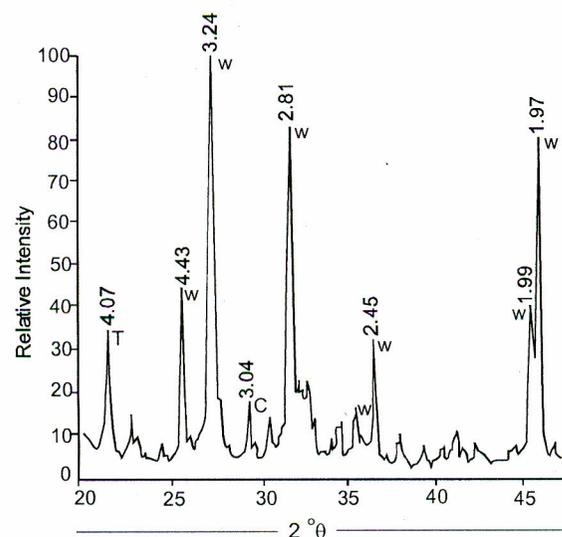
Table 2. Sintering temperature of individual raw batches for solid state synthesis

Batch no.	Temperature (°C)
RB*-1	900
RB-2	1000
RB-3	1100
RB-4	1200
RB-5	1300

RB* = Raw batch

Results and Discussion

XRD analysis data of RB-1 product revealed that wollastonite crystals co-existed with the raw materials, while diffractogram for RB-2 product showed that SS reaction progressed here considerably. Similarly, data relating to RB-3 product clearly indicated that amount of wollastonite synthesized in this batch was appreciably larger than the previous two batches. It was further observed in the diffractogram of RB-4 product, that there existed only two peaks (Fig. 1) due to unreacted tridymite and calcite, while all other peaks belonged to wollastonite. Similarly, the XRD pattern (Fig. 2) also showed that RB-5 batch product mainly consisted of wollastonite. Sharpness and intensity of the X-ray peaks present in both of the diffractograms (Fig. 1 and 2) gave clear indication of good crystallinity of the products obtained from RB-4 and RB-5.

**Fig. 1.** XRD data (cuk α) on batch RB-4 (1200 °C).**Fig. 2.** XRD data (cuk α) on batch RB-5 (1300 °C).

Probable explanation of the crystal growth in SS reactions, provided by all the described models, were considered to study the phenomenon of synthesis under discussion.

Diffusion model. As chemical combination of solids usually occurs at the area of their contact, therefore, it is necessary to generate such interfaces for propagation of SS reaction. This process is sometimes very difficult to start, however once formation of the product crystallite, embedded in the matrix of reactants, starts the required chemical change propagates further. Consequently, reactants diffuse more and more into the product layer for sustaining the on-going growth of the product crystals. Fundamental assumption of this model, regarding wollastonite formation, has been depicted in Fig. 3. However, only planner surfaces, instead of three-dimensional view of CaO, SiO₂ and the resulting product, could be seen here.

Nuclei growth model. It is based upon the supposition that nucleation of the product or products at active sites, within the reaction mixture, is responsible for the propagation of a reaction yielding product crystals. This depends on ever growing nuclei under optimal conditions and ultimately results in entire conversion of reactants into the product. There are a number of possibilities regarding the shapes, dimensions and orientation of the said nuclei in place and their distribution within the volume of reacting masses. At the same time, their growth rate and important influencing factors are to be necessarily considered. Fig. 4 is a two dimensional representation of probable reaction between CaO and SiO₂ propagating under this model.

Phase boundary model. It is the concept dealing with a situation where diffusion through the product layer is too fast to combine the reactants chemically for growth of the product crystals. Consequently, equilibrium cannot be established at the reaction interface. It has been proposed in this regard that the effective step may be the chemical process occurring at the boundary of a discontinuous product phase. Such reactions are generally referred to as topochemical and phase boundary controlled processes. Several aspects about spatial

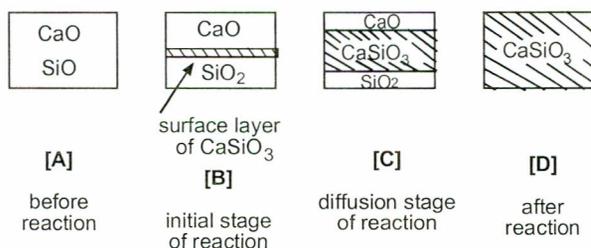


Fig. 3. Solid-solid reaction between CaO and SiO₂ under diffusion model.

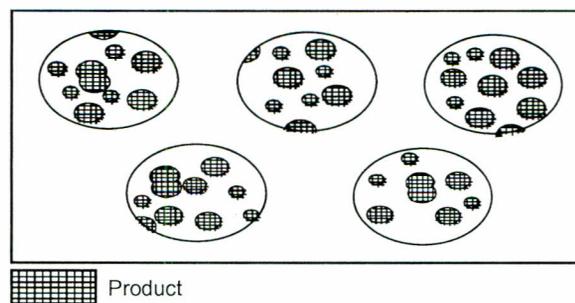


Fig. 4. Schematic representation of nuclei growth model.

positions of reactants and products have been taken into account in this regard.

In order to determine the correct growth model of the wollastonite crystals, the method of Janders's analysis was adopted (Nizami, 1993). It was first of all applied to testify whether or not the diffusion model could be suggested for synthesized wollastonite. However, this did not seem to be followed during the course of this reaction. The possibility of phase boundary model was also explored but the criterion specific for this one did not support it as the adopted path. The experimental data were finally treated according to the criterion laid down for nuclei growth model, which was found to be a promising route for the growth of wollastonite crystals.

Galwey stated that the growth of nuclei results in an increase in the contact area of the product nuclei-reactant surface, increasing the final product formation as shown in Fig. 5 (Nizami, 1993).

It is evident from the curve given in this figure that the reaction is first accelerated by the interaction of the reaction interfaces of different nuclei and then reaches a maximum. Almost similar situation was observed during the present synthesis. Comparison of this experimental observation with the results obtained by Galwey also favoured the above proposed crystal growth model. Similarly, the suggested model also finds support from the work carried out by Chang and

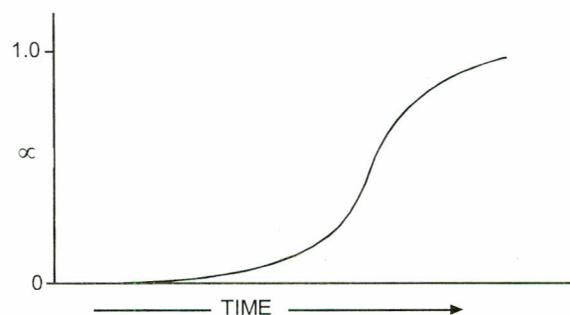


Fig. 5. Progress of product formation (x) with time under nucleation and growth process.

co-workers, who obtained grains of β -dicalcium silicate surrounded by an amorphous phase from which wollastonite crystals nucleated and grew completely at the final stage (Chang *et al.*, 1988).

Conclusion

The trend of wollastonite crystal growth enhanced with rise in temperature. It was also noted that β -polymorph of wollastonite was produced during SS reaction at 1200 °C while such reaction at 1300 °C resulted in α -polymorph of the same. The batch products obtained at 1200 °C and 1300 °C showed good crystallinity in comparison with the remaining batches. The crystal growth phenomenon seems to take place following the 'nuclei growth model' pertaining to the category of SS reactions.

Acknowledgement

Dr. Saadat Siddiqui, Professor, Centre of Excellence for Solid State Physics, Punjab University, Lahore, Pakistan, extended the facility of X-ray Diffractometer in order to study different batch products of the carried out synthesis. Authors are highly thankful to him in this regard.

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