

Solid State Synthesis, Characterization, and Nonlinear Optical Properties of a Monoclinic Tricalcium Silicate, Ca_3SiO_5

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Portland cement is widely used for the production of concrete that is a composite material in most construction industries such as buildings, roads, bridges, and runways in airports. A few main compounds found in cement clinker, a hard synthetic substance obtained by high-temperature calcination, are dicalcium silicate (Ca_2SiO_4 , C_2S), tricalcium silicate (Ca_3SiO_5 , C_3S), tricalcium aluminate ($\text{Ca}_3\text{Al}_6\text{O}_{12}$, C_3A), tetracalcium aluminoferrite ($\text{Ca}_4\text{Al}_8\text{Fe}_8\text{O}_{28}$, C_4AF), and some minor phases.¹ Depending on the composition of cement constituents, important physical properties such as fineness, stability, solidification, heat of hydration, and compressibility strength may vary.^{2,3} Among several compounds that consist of cement, we were very interested in the tricalcium silicate (C_3S). Cements containing high contents of C_3S are very effective to an urgent construction work mainly attributable to the manifestation ability of fast strength. In fact, Ca_3SiO_5 has been known to have seven polymorphs, *i.e.*, three triclinics, three monoclinics, and one rhombohedral.^{4,6} A monoclinic phase, "alite" is especially important, since the polymorph is the major component of Portland clinker.⁶ However, it is not easy to stabilize the high temperature monoclinic structure at room temperature. In order to stabilize the monoclinic phase at room temperature, foreign cations such as Mg^{2+} have been introduced to the structure.^{7,8} The added cations can stabilize the orientation of the silicate tetrahedra at room temperature. It has been also pointed out that thermal history of the sample during the synthesis is another important factor to stabilize the monoclinic phase at room temperature.⁹ Recent studies using the joint X-ray synchrotron and neutron powder diffraction suggest that the monoclinic alite material crystallizes in a noncentrosymmetric (NCS) space group, Cm .¹⁰ Therefore, the monoclinic Ca_3SiO_5 may be a potential interest in construction work of smart roads exhibiting some functional properties such as piezoelectricity, where crystallographic NCS is a very important and fundamental requirement. Interestingly, the symmetry requirements for piezoelectricity and second-harmonic generation (SHG) are identical, because the two phenomena are described by the same third rank tensor, d_{ijk} .¹¹ Thus, we decided to investigate more details of nonlinear optical properties and the structural origin of asymmetric environment for Ca_3SiO_5 . By doing so, we hope to suggest some background information to develop

an advanced functional road system. In this paper, we report the phase pure solid-state synthesis, infrared spectroscopy, elemental analysis, and nonlinear optical properties of Ca_3SiO_5 along with structure-property relationships.

Experimental Section

Synthesis. CaCO_3 (Shinyo Pure Chemicals, 98%) and SiO_2 (Aldrich, 99.6%) were used as received. Pure polycrystalline Ca_3SiO_5 was synthesized through a standard solid-state reaction technique. A stoichiometric mixture of CaCO_3 (0.901 g, 9.01 mmol) and SiO_2 (0.180 g, 3.00 mmol) was thoroughly ground with an agate mortar and pestle, and pressed into a pellet. The pellet was loaded in an alumina crucible and heated to 1350 °C for 18 h with an intermediate regrinding. The sample was cooled back, reground, and repelletized during the intermediate heating. The pellet was cooled down to room temperature at a rate of 5 °C min^{-1} . The powder X-ray diffraction pattern on the resultant white powder indicated the material was single-phase and in a good agreement with the reported pattern.¹⁰

Characterization. The X-ray powder diffraction data were collected on a Bruker D8-Advance diffractometer using $\text{Cu-K}\alpha$ radiation at room temperature with 40 kV and 40 mA in the 2θ range 10-100° with a step size of 0.02°, and a step time of 1 s. The diffraction pattern was analyzed using the LeBail method with the GSAS program.¹² The experimental, calculated, and difference diffraction plots with the refined unit cell parameters and refinement results for Ca_3SiO_5 were deposited to the Supporting Information. Refined unit cell parameters are $a = 33.2157(6)$ Å, $b = 7.0427(3)$ Å, $c = 18.6132(4)$ Å, and $\beta = 94.2933(18)^\circ$, which is slightly larger than those of reported values.^{7,8,10} The increased unit cell parameters may be attributable to the absence of small foreign cation, Mg^{2+} . Thermogravimetric analysis was performed on a Setaram LABSYS TG-DTA/DSC Thermogravimetric Analyzer. The polycrystalline Ca_3SiO_5 sample was contained within an alumina crucible and heated to 1000 °C at a rate of 10 °C min^{-1} under flowing air. Infrared spectrum was recorded on a Varian 1000 FT-IR spectrometer in the 400-4000 cm^{-1} range, with the sample embedded in a KBr matrix. SEM/EDX analyses have been performed using a Hitachi S-3400N/Horiba Energy EX-250 instruments. Powder

SHG measurements on polycrystalline Ca_3SiO_5 were performed on a modified Kurtz-NLO system¹³ using 1064 nm radiation. A DAWA Q-switched Nd:YAG laser, operating at 20 Hz, was used for all measurements. Since SHG efficiency has been shown to depend strongly on particle size, polycrystalline samples were ground and sieved (Newark Wire Cloth Co.) into distinct particle size ranges (20-45, 45-63, 63-75, 75-90, 90-125, > 125 μm). In order to make relevant comparisons with known SHG materials, crystalline $\alpha\text{-SiO}_2$ and LiNbO_3 were also ground and sieved into the same particle size ranges. Powders with particle size 45-63 μm were used for comparing SHG intensities. All of the powders were placed in separate capillary tubes. No index-matching fluid was used in any of the experiments. The SHG light, *i.e.*, 532 nm green light, was collected in reflection and detected by a photomultiplier tube (Hamamatsu). To detect only the SHG light, a 532 nm narrow band-pass interference filter was attached to the tube. A digital oscilloscope (Tektronix TDS 1032) was used to view the SHG signal. A detailed description of the equipment and the methodology used has been published.^{11,14}

Results and Discussion

We were able to synthesize successfully a phase pure monoclinic Ca_3SiO_5 through a standard solid state reaction technique. In order to obtain a pure monoclinic form of Ca_3SiO_5 , thorough and intermediate grindings of the mixture of starting materials would be necessary. As can be seen in the Figure 1, the experimental diffraction pattern and the parameters are in good agreement with those of the calculated. Since the crystal structure of Ca_3SiO_5 has been reported earlier,¹⁰ only a brief description will be provided here. Ca_3SiO_5 crystallizes in a noncentrosymmetric monoclinic space group Cm (No. 8). There are eighteen unique Si^{4+} cations that are exhibiting tetrahedral geometries with coordinated oxygen atoms. Among 18 tetrahedra, five SiO_4 are disordered. More specifically, three SiO_4 tetrahedra [$\text{Si}(9)$, $\text{Si}(10)$, and $\text{Si}(14)$] are disordered with fractional up

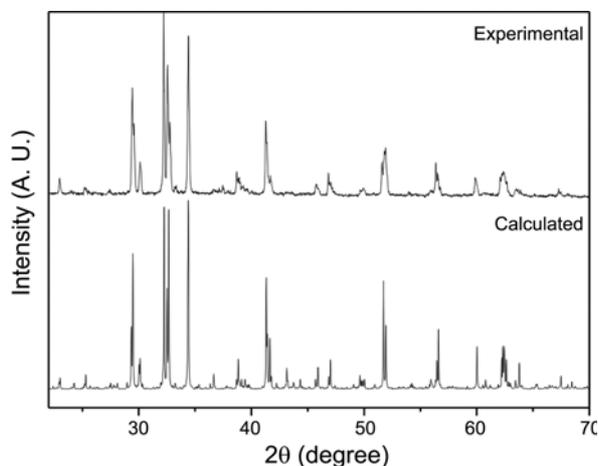


Figure 1. Experimental and calculated powder X-ray diffraction patterns for Ca_3SiO_5 .

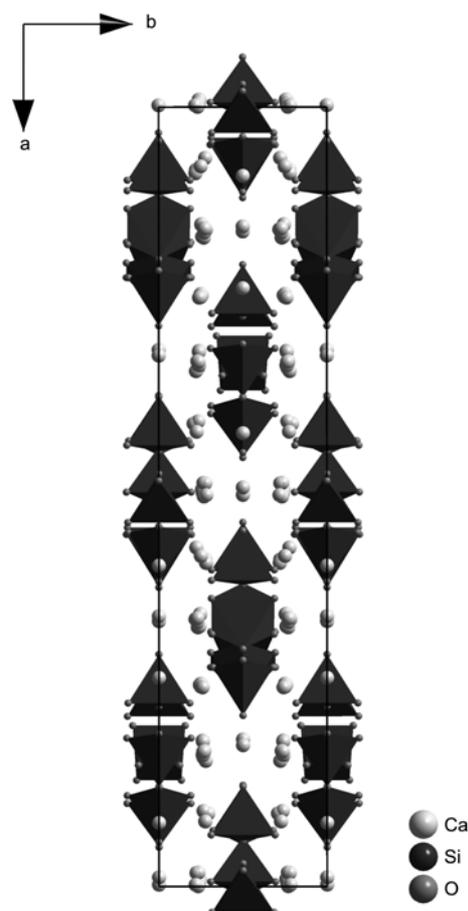


Figure 2. Ball-and-stick and polyhedral representation of Ca_3SiO_5 in the ab -plane. Eighteen unique Si^{4+} cations and fifty four unique Ca^{2+} cations are residing.

(U) and down (D) orientations along the pseudo-three-fold axis, $[-207]$. However, the other two SiO_4 [$\text{Si}(8)$ and $\text{Si}(17)$] are out of the pseudo-three-fold axis (G); thus they are disordered as well. As we will discuss more in detail later, the remaining 13 ordered SiO_4 tetrahedra that are oriented differently are responsible for the NCS structure and the subsequent nonlinear optical properties of Ca_3SiO_5 . Total fifty four unique Ca^{2+} cations are residing in the crystal structure to maintain the charge balance (see Figure 2).

The infrared spectrum of Ca_3SiO_5 revealed the presence of Si-O vibrations. Bands occurring in the region *ca.* 890-940 and 449-522 cm^{-1} can be attributed to the Si-O stretching and bending vibrations, respectively. The assignments are consistent with those previously reported.¹⁵ The thermal behavior of Ca_3SiO_5 was investigated using thermogravimetric analysis (TGA). As expected from the synthesis condition, Ca_3SiO_5 is stable at high temperature. No weight change has been observed up to 1000 $^\circ\text{C}$. As seen in the Figure 3(a), well crystalline samples of Ca_3SiO_5 are observed in the Scanning Electron Microscope (SEM) picture. Energy Dispersive Analysis by X-ray (EDAX) for Ca_3SiO_5 provided a Ca:Si ratio of 3:1, which is in a very good agreement with the stoichiometry of the reported material (see Figure 3(b)).

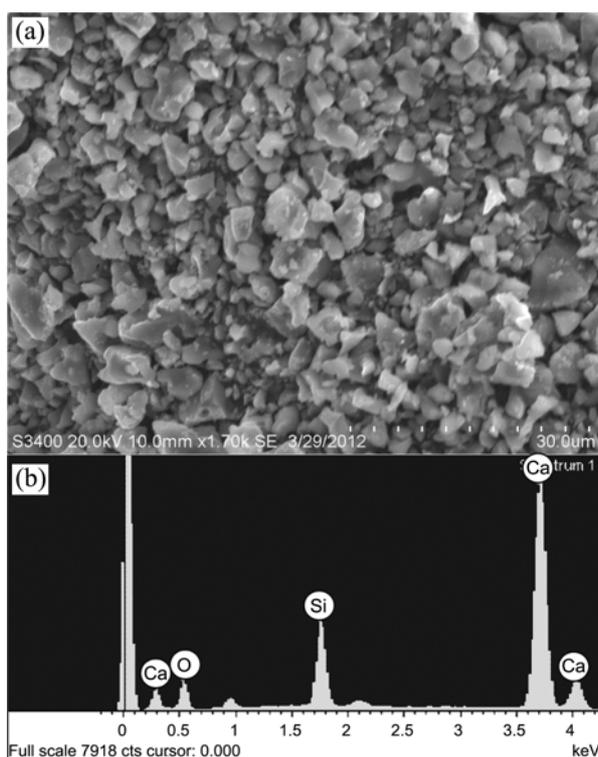


Figure 3. (a) SEM image exhibiting a high crystallinity of Ca_3SiO_5 . (b) EDAX spectrum shows a Ca:Si ratio of 3:1.

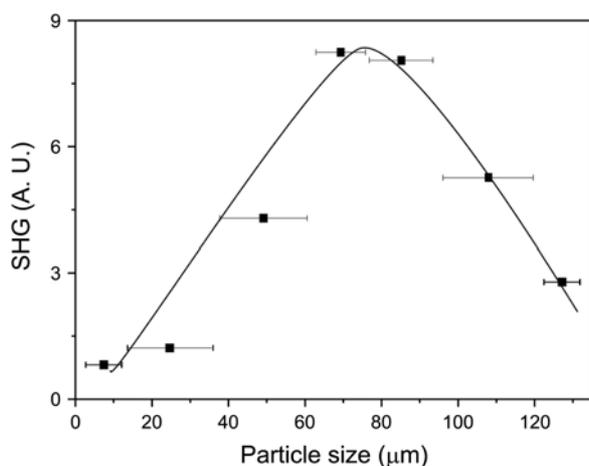


Figure 4. Phase matching curve (Type 1) for Ca_3SiO_5 . The curve is drawn to guide the eye and is not a fit to the data.

Since Ca_3SiO_5 crystallizes in a noncentrosymmetric space group Cm , we investigated the nonlinear optical properties of the material. Powder SHG measurements, using 1064 nm radiation, indicated that Ca_3SiO_5 has a SHG efficiency of approximately 2 times that of $\alpha\text{-SiO}_2$. By sieving Ca_3SiO_5 powder into various particle sizes, ranging from 20–150 μm , and measuring the SHG as a function of particle size, we were able to determine the Type 1 phase-matching capability of the material. Similar to that of $\alpha\text{-SiO}_2$, the phase-matching experiments show that Ca_3SiO_5 is nonphase-matchable (see Figure 4). On the basis of the SHG efficiency and phase-matching measurements, Ca_3SiO_5 falls into the Class

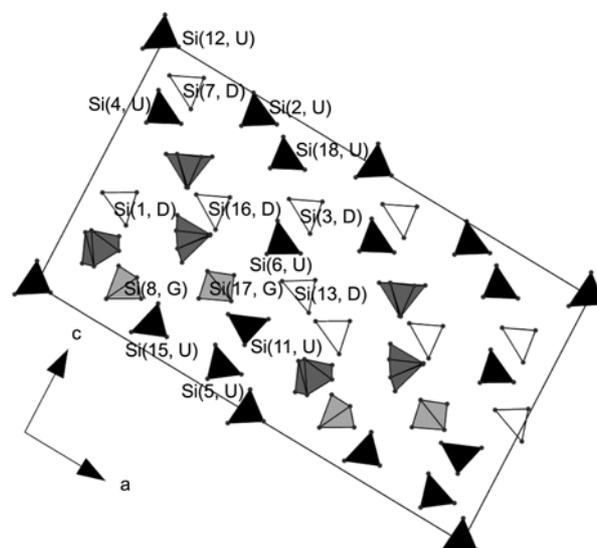


Figure 5. Polyhedral representation of Ca_3SiO_5 in the ac -plane. Eight tetrahedra [Si(2), Si(4), Si(5), Si(6), Si(11), Si(12), Si(15), and Si(18)] are pointing toward up (U) and five tetrahedra [Si(1), Si(3), Si(7), Si(13), and Si(16)] are pointing toward down (D). Three SiO_4 [Si(9), Si(10) and Si(14)] are disordered with fractional U and D orientations and two tetrahedra [Si(8), Si(17)] are out of the pseudo-threefold axis (G).

D category of SHG materials, as defined by Kurtz and Perry.¹³ Once the SHG efficiency and the phase-matching capability of a material are known, the bulk SHG efficiency, $\langle d_{\text{eff}} \rangle_{\text{exp}}$, can be estimated.¹⁶ With Ca_3SiO_5 , $\langle d_{\text{eff}} \rangle_{\text{exp}}$ is approximately 0.78 pm V^{-1} . The observed SHG efficiency attributable to the crystallographic NCS can be understood by analyzing the polarization of the asymmetric polyhedra. In Ca_3SiO_5 , macroscopic NCS can be obtained by the net moment arising from the alignment of the SiO_4 tetrahedra. Among thirteen ordered SiO_4 tetrahedra, eight tetrahedra [Si(2), Si(4), Si(5), Si(6), Si(11), Si(12), Si(15), and Si(18)] are pointing toward up (U) and five tetrahedra [Si(1), Si(3), Si(7), Si(13), and Si(16)] are pointing toward opposite direction (D) (see Figure 5). As seen in Figure 5, the three SiO_4 [Si(9), Si(10) and Si(14)] are disordered with fractional U and D orientations and the other two tetrahedra [Si(8), Si(17)] are out of the pseudo-threefold axis (G). Once the directions of ordered SiO_4 are taken as a whole, a net alignment of SiO_4 tetrahedra pointing toward up is observed (see Figure 5). The net direction obtained from the alignment of tetrahedra is responsible for the crystallographic NCS and subsequent SHG response.

Pure polycrystalline NCS tricalcium silicate, Ca_3SiO_5 (C_3S) was successfully synthesized by the standard solid-state reaction technique. The synthesized material is stable at room temperature and crystallizing in the monoclinic NCS space group, Cm . Full characterization including powder XRD, Infrared spectroscopy, thermogravimetric analysis, SEM/EDAX, and second-harmonic generating properties have been successfully demonstrated.

Supporting Information. Detailed experimental data for

the reported materials are available from the authors upon request.

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