β-Si₃N₄ Microcrystals Prepared by Carbothermal Reduction-Nitridation of Quartz

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Abstract: Single phase β-Si₃N₄ with microcrystals was synthesized via carbothermal reduction-nitridation (CRN) of quartz and carbon coke powder as starting materials. The effects of reaction parameters, i.e., heating temperature, holding time, C/SiO₂ ratio, Fe₂O₃ additive and β-Si₃N₄ seeds on the phase transformation and morphology of products were investigated and discussed. Rather than receiving a mixture of both α- and β- phases of Si₃N₄ in the products, we synthesized powders of β-Si₃N₄ single polymorph in this work. The mechanism for the CRN synthesis of β-Si₃N₄ from quartz and the formation mechanism of Fe₃Si droplets were discussed. We also firstly reported the formation of Fe₃Si Archimedean solids from a CRN process where Fe₂O₃ was introduced as additive. Comparing to the gear-like short columnar morphology observed in samples without β-Si₃N₄ seeding, the addition of β-Si₃N₄ seeds led to an elongated morphology of final products and much finer widths. In addition, the β-Si₃N₄ microcrystals exhibited a violet-blue spectral emission range, which could be highly valuable for their future potential optoelectronic applications.

Keywords: β-Si₃N₄ microcrystals; Fe₃Si archimedean solids; quartz; carbothermal reduction nitridation; seeding

1. Introduction

Silicon nitride (Si₃N₄) is an important high temperature structural material because of its excellent properties, including high strength, high decomposition temperature (1900 °C), good resistance to oxidation, thermal shock, corrosive environments, which have been investigated extensively over the past three decades [1–4].

The most prevalent methods for preparing Si₃N₄ powders include direct nitridation method, carbothermal reduction-nitridation (CRN) method and thermal decomposition method [5–7]. By CRN method, Si₃N₄ powders or columnar grains with excellent size distribution and physical properties could be synthesized and used as thermal conductive fillers or commercial applications for manufacturing engineering devices [8,9]. For example, Karakus et al. [9]. synthesized α-Si₃N₄ powders by CRN of synthetic silica and activated charcoal at 1470 °C, and then used the obtained α-Si₃N₄ powders as the raw materials to prepare the Si₃N₄ ceramic by a pressureless sintering method. Comparing the results with commercial Si₃N₄ powders, the resultant Si₃N₄ powders by CRN method indicated a similar or ever better density and β-phase conversion by the pressureless sintering. Yin et al. prepared ZrN–Si₃N₄ composite powders from natural zircon and quartz via CRN reaction at temperatures below 1600 °C [10]. Similarly, Arik prepared Si₃N₄ powders by CRN from diatomite
with C/SiO₂ molar ratio 4 at 1400 °C for 16 h [11]. Thus, it is feasible to prepare Si₃N₄ with quartz and carbon black. On the other hand, CRN method takes advantage from low-cost starting materials [8,9]. The high cost of raw materials is a primary limitation for large scale production of Si₃N₄ powders. Through the CRN method, it is possible to synthesize Si₃N₄ powders from low-cost quartz with abundant reserves in the world. It was reported that the same problem for the massive production of SiC powders was overcome by this way, and the product was much finer for achieving excellent flexural strength [12].

Grain size and shape of Si₃N₄ powders can influence some properties of Si₃N₄-based products such as varying electrical and optical properties and mechanical properties [13,14]. Apart from Si₃N₄ seeds, Fe and its oxides have been used as additives to change the morphology of a product or to promote nitriding process [15–18]. However, to the best of our knowledge, the crystal microstructure/morphology of Fe-containing compounds formed in the nitridation process while Fe or iron oxide being used as additive was rarely reported.

In this study, quartz and carbon coke powders were selected as raw materials to prepare Si₃N₄ powders via CRN method. The influence of temperature, holding times, C/SiO₂ molar ratio, additive amount of Fe₂O₃ and β-Si₃N₄ seeds were studied on the phase transformation and morphology of products. Faceted Fe₃Si Archimedean solids, a novel morphology of the iron silicide, were observed firstly which have the potential application in spintronics devices [19]. The formation mechanism of products from the nitridation reaction was discussed and photoluminescence (PL) properties of samples were also detected.

2. Experimental

2.1. Materials

Natural quartz powders (granularity ≤ 400 mesh, chemical composition (wt.%): SiO₂: 97.8, Al₂O₃: 0.63, Fe₂O₃: 0.13, CaO: 0.08, K₂O: 0.05, others: 1.31), and coke powders (granularity ≤ 200 mesh, carbon content = 88%) were used as the main starting raw materials. The crystalline phase of the natural quartz powders was hexagonal α-quartz (Figure 1). Fe₂O₃ (A.R. grade, Sinopharm Chemical Reagent Beijing Co., Ltd., Beijing, China) and Si₃N₄ (A.R. grade, ~800 nm, Shanghai Pantian powder material Co., Ltd., Shanghai, China) were used as additives. The starting compositions of all the samples are listed in Table 1.

| Samples C/SiO₂ Molar Ratio Coke Quartz Fe₂O₃ (Extra) β-Si₃N₄ (Extra) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| wt.%            | wt.%            | wt.%            | wt.%            | wt.%            |
| S1              | 2               | 30.77           | 69.23           | 0               | 0               |

Figure 1. X-ray diffraction (XRD) pattern of natural quartz.
Table 1. Compositional design of the samples (wt.%).

| Samples | C/SiO₂ Molar Ratio | Coke | Quartz | Fe₂O₃ (Extra) | β-Si₃N₄ (Extra) |
|---------|---------------------|------|--------|--------------|----------------|
| S1      | 2                   | 30.77| 69.23  | 0            | 0              |
| S2      | 2.2                 | 32.84| 67.16  | 0            | 0              |
| S3      | 3                   | 40.00| 60.00  | 0            | 0              |
| S4      | 4                   | 47.06| 52.94  | 0            | 0              |
| S5      | 2                   | 30.77| 69.23  | 4            | 0              |
| S6      | 2                   | 30.77| 69.23  | 0            | 2              |

2.2. Methods

The starting materials were ball-milled together for 2 h. Then, 2 g of the mixed powders were die-pressed under 20 MPa into a specimen of 10 mm in diameter. The specimens were placed in a graphite crucible and heated in flow nitrogen (purity 99.999%) in the reaction chamber of a tube furnace at temperatures in the range of 1450–1600 °C. A two stage heating schedule was used, i.e., heating up from ambient temperature to 1000 °C at 10 °C·min⁻¹, then raising to the final temperature at 5 °C·min⁻¹ and held for 3 h. The final temperatures were set as 1470 °C, 1500 °C, 1530 °C, 1550 °C, 1570 °C, and 1600 °C, respectively. In addition, in order to study the effect of holding time to the CRNed product, S1 sample was synthesized at 1600 °C and held for 1 h, 2 h, and 3 h, respectively. The fired samples were furnace-cooled to room temperature, and then reheated in air at 700 °C for 2 h to remove the residual carbon.

2.3. Characterization

The crystalline phases of the synthesized products were identified by X-ray diffraction (XRD; D8 Advance diffractometer, Bruker, Rheinstetten, Germany), using Cu Kα₁ radiation (λ = 1.5406 Å) with a step of 0.02° (2θ) and a scanning rate of 4° min⁻¹. The microstructures and morphologies of the products were observed by scanning electron microscopy (SEM; JEM-6460LV microscope, JEOL, Tokyo, Japan) and high-resolution transmission electron microscopy (HRTEM, JEM2010, JEOL, Tokyo, Japan). The energy dispersive X-ray spectroscopies (EDS) linked with the SEM and the HRTEM were employed to assist the micro-area chemical analysis of the products. FT-IR spectra were collected at room temperature using a FT-IR Spectrometer (FT/IR-4000 JASCO, Tokyo, Japan) equipped with a Michelson 28° interferometer with corner-cube mirrors, covering a range between 250,000 and 5 cm⁻¹. Photoluminescence emission (PL) spectra were measured by F-7000 fluorescence spectrophotometer (Eppendorf, Shanghai, China) with a photomultiplier tube functioning at 700 V, and a 150 W Xe lamp as the excitation source.

3. Results and Discussion

3.1. Influence of Synthetic Schedule on the Phase Composition and Morphology of Products

3.1.1. Influence of Temperature on the Phase Composition and Morphology of Products

Figure 2 shows XRD patterns of sample S1 nitrided at different temperatures for 3 h. As can be seen, cristobalite was the dominant phase at 1470 °C, which was phase transition from quartz. In additional, some SiC, Si₂N₂O and residual quartz were present in the products (Figure 2a). With nitriding temperature being gradually elevated from 1470 °C to 1550 °C, intensity of β-SiC and Si₂N₂O diffraction peaks increased and that of cristobalite decreased (Figure 2a–d). After further increasing the temperature to 1570 °C, β-Si₃N₄ had just emerged while its diffraction intensity was much lower than that of β-SiC and Si₂N₂O; in the meantime, the peaks of cristobalite disappeared, and no other silica phases were detected (Figure 2e). By applying a higher temperature of 1600 °C, β-Si₃N₄ was formed in a relatively high purity (Figure 2f). The intensity of the secondary phase β-SiC was very weak. The
β-Si₃N₄ synthesized at 1570 & 1600 °C (Figure 2e,f) in S1 crystallized as a hexagonal structure and their lattice parameters and cell volumes are listed in Table 2. They were increased from 1570 to 1600 °C. The weight fraction of each phase in S1 at 1570 & 1600 °C is shown Table 3, the weight fraction was remarkable increased from 32.30 to 91.52 with the increased of temperature to 1600 °C. Upon the above observation, it is clear that in this work, the effect of temperature on the phase formation from quartz by CRN is very significant. For the holding period of 3 h, the temperature 1570 °C was critical for the transformation of cristobalite into Si₃N₄, whereas it cannot be formed at a lightly lower temperature of 1550 °C. Moreover, a temperature of 1600 °C, 30 °C higher than 1570 °C contributed to the formation of high-purity Si₃N₄ powders.

![Figure 2. XRD patterns of sample S1 nitrided at different temperatures for 3 h: (a) 1470 °C; (b) 1500 °C; (c) 1530 °C; (d) 1550 °C; (e) 1570 °C; (f) 1600 °C.](image)

Table 2. Lattice parameters and cell volume of β-Si₃N₄ in S1 & S5.

| Samples               | Lattice Parameters   | Cell Volume(Å³) |
|-----------------------|----------------------|-----------------|
|                       | a(Å) = b(Å)          | c(Å)            |                   |
| S1, 1570 °C, Figures 2e and 7c | 7.6351               | 2.8867          | 145.7343          |
| S1, 1600 °C, Figures 2f and 7e | 7.8607               | 2.9139          | 155.9293          |
| S5, 1570 °C, Figure 7d | 7.7205               | 2.8695          | 148.1248          |
| S5, 1600 °C, Figure 7f | 7.7753               | 2.8993          | 151.7952          |

Table 3. Weight fraction of each phase in S1 and S5 at 1570 and 1600 °C (wt. %).

| Samples               | β-Si₃N₄ | SiC | Si₂N₂O | Fe₃Si |
|-----------------------|---------|-----|--------|-------|
| S1, 1570 °C, Figures 2e and 7c | 32.20   | 36.06 | 31.74  | 0     |
| S1, 1600 °C, Figures 2f and 7e | 91.52   | 8.48  | 0      | 0     |
| S5, 1570 °C, Figure 7d  | 57.46   | 13.41 | 20.74  | 9.39  |
| S5, 1600 °C, Figure 7f  | 85.47   | 6.85  | 4.22   | 3.46  |

Morphological variation of sample S1 after being nitrided at different nitriding temperatures was investigated by SEM observation, and the elemental composition was performed by EDS analysis (Figure 3). There were many independent SiO₂ particles with size of 20 µm, covered by some Si₂N₂O and SiC fibers at temperatures of 1500–1550 °C, confirmed by EDS (Figure 3a–d). Some Fe element in the fibers was detected in the EDS, which should be from original quartz raw material (Figure 3e,f). In the sample synthesized at 1600 °C, short columnar grains with diameters of about 2 µm were dominant throughout the sample, which is the typical morphology of β-phase Si₃N₄. The trace amounts of Al and O was detected in the grains; this might come from impurity of original quartz or ball milling.
were evidently weakened with increasing the holding time to 2 h (Figure 4f) even almost disappeared penetration of N₂ after 3 h (Figure 2f). Since the permeation of N₂ in samples was from outside to inside, the external region with holding time of 1 h (Figure 4d,e). The diffraction peaks of SiC in interior region were evidently weakened with increasing the holding time to 2 h (Figure 4f) even almost disappeared after 3 h (Figure 2f). Since the permeation of N₂ in samples was from outside to inside, the external N₂ of samples was more abundant than that of internal. Increasing holding time allowed complete penetration of N₂ into the inner pellets, leading to the fully nitridation of the entire pellets.

![Figure 3](image-url)  
**Figure 3.** SEM images and X-ray spectroscopies (EDS) patterns of sample S1 nitrided at different temperatures for 3 h: (a,b) 1500 °C, (c,d) 1550 °C, (e,f) 1570 °C (g,h) 1600 °C.

3.1.2. Influence of Holding Time on the Phase Composition of Products

In order to elucidate the effect of holding time, the samples synthesized at 1600 °C for different holding times were compared. Figure 4a–c present the digital photos of three samples, which clearly demonstrated the degree of nitridation from the change in the nitridized area. As seen from the digital photos, 2 h was insufficient for CRN of quartz at 1600 °C. There were two different zones on the cross section of products (Figure 4a,b). The interior portion of pellets had a darker color while the exterior part was greenish gray. Interior regions of product narrowed down when holding time was 2 h and disappeared when 3 h. A longer holding time of 3 h enabled the complete nitridation of the entire pellet with diameter of <10 mm. The XRD patterns of them are depicted in Figure 4d,f. It is revealed that phase compositions were Si₃N₄, SiC, and Si₂N₂O for exterior region as well as SiC and Si₃N₄ for interior region with holding time of 1 h (Figure 4d,e). The diffraction peaks of SiC in interior region were evidently weakened with increasing the holding time to 2 h (Figure 4f) even almost disappeared after 3 h (Figure 2f). Since the permeation of N₂ in samples was from outside to inside, the external N₂ of samples was more abundant than that of internal. Increasing holding time allowed complete penetration of N₂ into the inner pellets, leading to the fully nitridation of the entire pellets.

![Figure 4](image-url)  
**Figure 4.** Digital photos of sample S1 nitrided at 1600 °C with different holding time: (a) 1 h, (b) 2 h, (c) 3 h; and XRD patterns of sample S1 in different regions: (d) exterior region and (e) interior region of pellet reacted for 1 h, (f) interior region of the pellet reacted for 2 h.
3.1.3. The CRN Mechanism of Quartz

Based on the results described above and literatures reported previously [20,21], it is generally accepted that the CRN reaction of quartz would happen through several steps. The reduction of quartz into SiO, via the pathways as shown by Equation (1) (\( \Delta G \) is the Gibbs free energy of reaction, and \( T \) is the temperature), is the first but a critical step, which enables the further reduction process.

\[
\text{SiO}_2(s) + \text{C}(s) \rightarrow \text{SiO}(g) + \text{CO}(g), \Delta G = 665.578-0.33T \text{ kJ/mol} \tag{1}
\]

The as-reduced SiO \((g)\) is then nitrided into silicon nitride phases by carbon through the Equation (2) [22,23].

\[
3\text{SiO}(g) + 3\text{C}(s) + 2\text{N}_2(g) \rightarrow \text{Si}_3\text{N}_4(s) + 3\text{CO}(g), \Delta G = -830.44 + 0.35T \text{ kJ/mol} \tag{2}
\]

At a temperature of 1550 °C or lower, intermediate phases \( \text{Si}_2\text{N}_2\text{O} \) and \( \text{SiC} \) were preferably formed through Equations (3) and (4), respectively [22,24]. It suggests that under the subcritical temperatures (1470 to 1550 °C), the reaction process was dominated by the reductive atmosphere/conditions while the nitridation processes were less thermodynamically preferred.

\[
2\text{SiO}_2(s) + 3\text{C}(s) + \text{N}_2(g) \rightarrow \text{Si}_2\text{N}_2\text{O}(s) + 3\text{CO}(g), \Delta G = 572.54-0.32T \text{ kJ/mol} \tag{3}
\]

\[
\text{SiO}(g) + 2\text{C}(s) \rightarrow \text{SiC}(s) + \text{CO}(g), \Delta G = -78.60 + 0.01T \text{ kJ/mol} \tag{4}
\]

Figure 5 is a schematic diagram demonstrating the synthesis of \( \beta\)-\( \text{Si}_3\text{N}_4 \) by CRN of quartz in two major steps. As the first step, illustrated by Figure 5a–c, SiO \((g)\) forms via Equation (1) beyond certain temperature. Equation (1) requires direct contact of carbon and SiO\(_2\). Then in the next step, as shown in Figure 5d, \( \text{Si}_3\text{N}_4 \) nucleates from Equation (2), and grows up on the surface of carbon and SiO\(_2\), which is associated with the diffusion rate of SiO. The reaction process is progressive from exterior to interior of the sample pellets as shown in Figure 5f.

**Figure 5.** Reaction schematic diagram for the formation of \( \beta\)-\( \text{Si}_3\text{N}_4 \) by carbothermal reduction-nitridation (CRN) of quartz: (a) the green body of specimen, (b–e) nitridation processes of raw materials, (f) specimens obtained under different holding times.

3.2. Influences of Starting Composition and Additive on Phase Composition and Morphology of Products

In order to elucidate the key factors for the synthesis of \( \beta\)-phase \( \text{Si}_3\text{N}_4 \) from quartz CRN synthesis, we investigated the effects of \( \text{C}/\text{SiO}_2 \) molar ratio, \( \text{Fe}_2\text{O}_3 \) additive content, and the introduction of \( \beta\)-\( \text{Si}_3\text{N}_4 \) seeds on the products.
3.2.1. Influence of C/SiO₂ Molar Ratio on Phase Composition

According to Equation (5), the theoretical C/SiO₂ molar ratio of Si₃N₄ is 2 [25]. Thus, samples S₁–S₄ with different C/SiO₂ molar ratios (2, 2.2, 3, and 4) were designed and subjected to CRN synthesis at 1600 °C for 3 h.

\[
3\text{SiO}_2(s) + 6\text{C}(s) + 2\text{N}_2(g) \rightarrow \text{Si}_3\text{N}_4(s) + 6\text{CO}(g), \Delta G = 1166.30-0.64T \text{kJ/mol} \quad (5)
\]

Figure 6 shows the XRD patterns of samples S₁–S₄ nitrided at 1600 °C for 3 h. As seen in the figure, β-Si₃N₄ was the main phase when C/SiO₂ was 2 (sample S₁) and 2.2 (Sample S₂), with trace amount of β-SiC. Peaks of β-Si₃N₄ decreased significantly when a higher C/SiO₂ molar ratio of 3 was adopted in sample S₃, and almost disappeared when the C/SiO₂ ratio further increased to 4 (sample S₄). At the meantime, β-cristobalite was detected which was derived from the phase transformation of residual quartz at high temperature. The results indicate that the theoretical/stoichiometric carbon content as per Equation (5) was optimal for preparing single-phase β-Si₃N₄ from quartz by CRN. Increased amount of β-SiC and other by-products formed in the product of samples with a higher C/SiO₂ molar ratio.

![Figure 6. XRD patterns of samples S₁–S₄ nitrided at 1600 °C for 3 h: (a) S₁, C/SiO₂ = 2; (b) S₂, C/SiO₂ = 2.2; (c) S₃, C/SiO₂ = 3; (d) S₄, C/SiO₂ = 4.](image-url)

3.2.2. Influence of Fe₂O₃ Additive on Phase Composition and Morphology of Products

In order to see the effect of additive, we designed a composition (sample S₅) which added extra 4 wt.% Fe₂O₃ into the starting mixture. The XRD patterns of sample S₁ (Fe₂O₃-free) and S₅ (with extra 4 wt.% Fe₂O₃) are plotted in Figure 7, where the phase assemblages in the samples at different temperatures are compared. At 1470 °C, β-cristobalite, quartz and β-SiC were the main phases in sample S₁. In contrast, much weaker peaks of cristobalite showed in sample S₅ whereas Si₂N₂O and β-Si₃N₄ formed with a considerable amount. At 1570 °C, β-Si₃N₄, β-SiC and Si₂N₂O were present in both sample S₁ and sample S₅, while there was significantly more β-Si₃N₄ and much less β-SiC formed in sample S₅ (comparing to S₁). At 1600 °C, both samples had β-Si₃N₄ as dominant phase and trace amount of β-SiC, and the trace amount of Si₂N₂O were found in S₅. Additionally, peaks appeared at 45.5° in sample S₅ at all temperatures can be assigned to Fe₅Si. The parameters and cell volumes of β-Si₃N₄ synthesized in S₁ and S₅ at 1600 °C (Figure 7e,f) are listed in Table 2. Table 3 is the weight fraction of each phase in S₁ and S₅ at 1570 and 1600 °C. These results illustrate that Fe₂O₃ could enhance the carbothermal reduction process of quartz and nitridation transformation to β-Si₃N₄.
Figure 6. XRD patterns of sample S1(a,c,e), and sample S5(b,d,f) at 1470, 1570, and 1600 °C, respectively.

Figure 7. XRD patterns of sample S1(a,c,e), and sample S5(b,d,f) at 1470, 1570, and 1600 °C, respectively.

Figure 8 shows the SEM images and EDS results of sample S5 nitrided at 1600 °C. As seen in Figure 8a–d, the columnar grains had gear-like morphologies and dominate in the products, which could be assigned to β-Si$_3$N$_4$ upon XRD and EDS results. A trace amount of Fe element was detected (Figure 8f), which was originated from the additive added in this sample. Furthermore, a white-colored product layer was covered on the surface of sample S5 nitrided at 1600 °C for 3 h. SEM observation shows that it was composed of fibers with widths of about 0.3–0.5 µm (Figure 9a,b). EDS result reveals that the fibers were SiC phase (Figure 9d). At the tip of each fiber, there was a spherical particle containing Si-Fe-O elements (Figure 9a,c). It is therefore suggested that the SiC fibers formed through a Vapor - Liquid - Solid (VLS) mechanism [26].

Figure 8. SEM images and EDS patterns of β-Si$_3$N$_4$ in sample S5 nitrided at 1600 °C: (a–d) SEM images with different magnification, (e,f) EDS results of the selected area in (d).
Very interestingly, some spherical particles were observed in sample S5 (arrowed in Figure 8a,b), which were further characterized by SEM and EDS (Figure 10). It is wonderful to see that they were Archimedean solids with sizes of several microns. EDS results illustrate that they contained only Fe and Si elements with the molar ratio of Fe/Si ~2.79. This result clearly reveals that the faceted crystal was Fe₃Si as detected in XRD data. To the best of our knowledge, such a novel morphology of Fe₃Si was never reported in the literature.

Based on the above results, it can be concluded that Fe₂O₃ had a remarkable catalytic effect on the CRN of quartz at a lower temperature than 1600 °C. Under the reductive environment at high temperatures, carbon or CO can reduce Fe₂O₃ to Fe by Equations (6) or (7). It is known that the melting point of pure iron is 1538 °C. Therefore, Fe generally attaches to a support material in the reaction system by forming a liquid phase. In the present study, we speculate that Fe-Si-O liquid formed first (Equation (8), Figure 9). The Fe-containing liquid could dissolve SiO₂ and C, then enhance their reaction to form SiO(g) [27] (Equation (9)), consequently promoting the formation of Si₃N₄O, SiC and even β-Si₃N₄ at lower temperature (Equations (3) and (4), Figure 7). Fe-containing liquid could significantly enhance the nitridation reaction, and the precipitation of β-Si₃N₄ has been known...
to be favored by the presence of Fe-containing liquid [28] (Equation (10)). Fe-Si-O liquids were further reduced to be Fe-Si containing liquid (Equation (11)). The Fe-rich liquid then crystallized as Fe₃Si crystals while cooling (Equation (12)). The Fe-containing liquid phases, as a catalytic phase, promoted the formation of Si₃N₄, which is clearly illustrated by the phase assemblages in the samples at the low temperatures (Figure 5). Nevertheless, it is yet unclear how the unique Archimedean solids formed, which is beyond the objectives of this work and needs further investigation in near future.

$$\text{Fe}_2\text{O}_3(s) + 3\text{C}(s) \rightarrow 2\text{Fe(l)} + 3\text{CO}(g), \Delta G = 474.35 - 0.51T \text{ kJ/mol}$$ (6)

$$\text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightarrow 2\text{Fe(l)} + 3\text{CO}_2(g), \Delta G = -6.32 - 0.01T \text{ kJ/mol}$$ (7)

$$\text{Fe(l)} + \text{SiO}_2(s) + \text{C}(s) \rightarrow \text{Fe-Si-O(l)} + \text{CO}(g)$$ (8)

$$\text{SiO}_2(s) + \text{C}(s) \xrightarrow{\text{Fe-Si-O(l)}} \text{SiO(g)} + \text{CO(g)}, \Delta G = 665.59 - 0.33T \text{ kJ/mol}$$ (9)

$$3\text{SiO}_2(s) + 6\text{C}(s) + 2\text{N}_2(g) \xrightarrow{\text{Fe-Si-O(l)}} \text{Si}_3\text{N}_4(s) + 6\text{CO(g)}, \Delta G = 1166.30 - 0.64T \text{ kJ/mol}$$ (10)

$$\text{Fe-Si-O(l)} + \text{C(s/CO(g)} \rightarrow \text{Fe-Si(l)} + \text{CO}_2(g)$$ (11)

$$\text{Fe-Si(l)} \rightarrow \text{Fe}_3\text{Si(s)}$$ (12)

3.2.3. Influence of β-Si₃N₄ Seeds on Morphology of Products

The microstructure of sample S1 (no seeds) and S6 (with extra 2 wt.% Si₃N₄ seeds) synthesized at 1600 °C for 3 h were shown in Figure 11. In sample S1, the morphology of β-Si₃N₄ grains are short columnar, having grain sizes of around 3 μm. While in sample S6, grains were elongated and the gear-like morphology was rarely observed. From Figure 11c, the widths of the elongated grains are much smaller (0.2–0.5 μm) than those of short columnar grains in S1 (2–3 μm). HRTEM lattice image of the Si₃N₄ elongated grain indicates that the lattice fringe had no obvious distortion (Figure 11f,g). The measured lattice fringe spacing of 0.38 nm matched well with the (110) plane of β-Si₃N₄ (Figure 11f).

![Figure 11. SEM, TEM/HRTEM images and EDS patterns of (a,b) sample S1 and (c–g) S6 nitrided at 1600 °C for 3 h.](image-url)

It is reported that introducing seeds into the starting materials could affect the microstructure of synthesized products and improve the physical properties of final ceramics [29,30]. For example, in the synthesis of Sialon powders, the addition of Sialon seeds would increase the growth competition among the grains, leading to an elongated columnar morphology, thus improving flexural strength and fracture toughness [24,31]. Herein, a significantly increased aspect ratio of Si₃N₄ grains was
achieved by adding seeds into the starting mixtures. The addition of seeds could trigger heterogeneous nucleation [32]:

\[
\Delta G^* = \frac{16\pi \sigma^3}{3\Delta G_N} f(\theta) = \Delta G_{N} f(\theta)
\]

where \( \theta \) is contact angle between new \( \text{Si}_3\text{N}_4 \) nucleus and \( \text{Si}_3\text{N}_4 \) seeds, \( f(\theta) \) is the influence function of \( \theta \), and \( \Delta G^* \) is Gibbs free energy of homogeneous nucleation. Therefore, when the contact angle was 0–180°, nucleation power could be reduced. Moreover, while crystal structure of seeds was the same as that of \( \text{Si}_3\text{N}_4 \), \( \theta \) would be very small, which would reduce \( \Delta G \) and make more nuclei formed at the early stage of nitriding process. Thus, the growth competition between those nuclei would make the smaller and long columnization of \( \text{Si}_3\text{N}_4 \) grains.

3.3. The Possible Mechanisms of \( \beta \)-\( \text{Si}_3\text{N}_4 \) Single Polymorph Formation

Usually, \( \alpha \)- and \( \beta \)-\( \text{Si}_3\text{N}_4 \) polymorphs are present in the products from carbothermal reduction nitridation of \( \text{SiO}_2 \), and some related researches reported in the literature are summarized in Table 4. The phase composition ratio of \( \alpha/\beta \)-\( \text{Si}_3\text{N}_4 \) in the CRN products was highly affected by additives (or impurities). For example, Sun et al. [8] reported that the yield of \( \beta \)-\( \text{Si}_3\text{N}_4 \) increased from 42.8% to 81.8% when improving \( \text{CaF}_2 \) additive contents (Table 4 (1 and 2)). Wang et al. [22] revealed that the introduction of \( \text{CaF}_2 \)-\( \text{Y}_2\text{O}_3 \) additives significantly promoted the conversion of \( \alpha \)-\( \text{Si}_3\text{N}_4 \) to \( \beta \)-\( \text{Si}_3\text{N}_4 \) (Table 4 (3 and 4)). Furthermore, the CRN temperature was another key factor. According to the literatures [33–35], the increasing CRN temperature was beneficial for the transformation of \( \alpha \)-\( \text{Si}_3\text{N}_4 \) to \( \beta \)-\( \text{Si}_3\text{N}_4 \) (Table 4 (6 and 7), (8 and 9), (10 and 11)), and when it was higher than 1500 °C, \( \beta \)-\( \text{Si}_3\text{N}_4 \) emerged as the major phase, even single phase at 1700 °C (Table 4 (5)).

Table 4. Comparison of reaction conditions and products by carbothermal reduction nitridation of \( \text{SiO}_2 \) reported in the literature and the present study.

| No. | Raw Materials | Carbon Source | Additive | T/°C·h | Products | Reference |
|-----|---------------|---------------|----------|--------|----------|-----------|
| 1   | Amorphous \( \text{SiO}_2 \) | carbon black | \( \text{CaF}_2 \)-1% | 1500-2 | \( \beta \) (42.8%) and \( \alpha \) | [8] |
| 2   | Amorphous \( \text{SiO}_2 \) | carbon black | \( \text{CaF}_2 \)-10% | 1500-2 | \( \beta \) (81.8%) and \( \beta \) | [8] |
| 3   | Amorphous \( \text{SiO}_2 \) | carbon black | None | 1500-2 | \( \beta \) (52.4%) and \( \alpha \) | [22] |
| 4   | Amorphous \( \text{SiO}_2 \) | carbon black | \( \text{CaF}_2 \)-\( \text{Y}_2\text{O}_3 \) | 1500-2 | \( \beta \) (90%) and \( \alpha \) | [22] |
| 5   | Amorphous \( \text{SiO}_2 \) | carbon black | \( \text{CaF}_2 \)-\( \text{Y}_2\text{O}_3 \) | 1700-2 | \( \beta \) (100%) | [22] |
| 6   | Quartz powder | carbon black | \( \text{Y}_2\text{O}_3 \), Bentonite | 1450-3 | \( \beta \) (26.9%), \( \alpha \) | [34] |
| 7   | Quartz powder | carbon black | \( \text{Y}_2\text{O}_3 \), Bentonite | 1500-3 | \( \beta \) (85.7%), \( \alpha \) | [34] |
| 8   | Synthetic silica | activated charcoal | \( \text{MgO} \) or \( \text{Y}_2\text{O}_3 \) | 1375-3 | \( \text{Si}_3\text{N}_2\text{O} \), \( \beta \):\( \alpha \) = 1:9 | [35] |
| 9   | Synthetic silica | activated charcoal | \( \text{MgO} \) or \( \text{Y}_2\text{O}_3 \) | 1475-3 | \( \beta \):\( \alpha \) = 1:2 | [35] |
| 10  | Quartz sand | activated charcoal | \( \text{Fe(NO}_3)_3 \) | 1300-3 | quartz, \( \text{Si}_3\text{N}_2\text{O} \), \( \beta \):\( \alpha \) = 3:4 | [36] |
| 11  | Quartz sand | activated charcoal | \( \text{Fe(NO}_3)_3 \) | 1540-3 | \( \beta \):\( \alpha \) = 9:1 | [36] |
| 12  | Quartz | coke powders | None | 1470-3 | cristobalite, SiC and \( \text{Si}_3\text{N}_2\text{O} \) | This article |
| 13  | Quartz | coke powders | \( \text{Fe}_2\text{O}_3 \) | 1470-3 | SiC, \( \text{Si}_3\text{N}_2\text{O} \), \( \beta \), quartz | This article |
| 14  | Quartz | coke powders | None | 1600-3 | \( \beta \) (100%) | This article |

Note: \( \alpha \), \( \beta \)-\( \text{Si}_3\text{N}_4 \)

Herein, we successfully produced \( \beta \)-\( \text{Si}_3\text{N}_4 \) as the single polymorph (no \( \alpha \) phase co-exists), either with or without \( \text{Fe}_2\text{O}_3 \) as an additive. It is widely known that the \( \alpha \)-\( \text{Si}_3\text{N}_4 \) derives from \( \text{SiO}_3 \) vapor while \( \beta \)-\( \text{Si}_3\text{N}_4 \) from liquid phase during CNR process, and also there exist phase transformation between \( \alpha \)-\( \text{Si}_3\text{N}_4 \) and \( \beta \)-\( \text{Si}_3\text{N}_4 \) [34,35]. As \( \text{SiO}_3 \) vapor always forms during the reduction process, \( \alpha \)-\( \text{Si}_3\text{N}_4 \) can form (temporarily at least) during the CRN process. In our study, the \( \beta \)-\( \text{Si}_3\text{N}_4 \) as the single polymorph formed regardless of adding \( \text{Fe}_2\text{O}_3 \) or not. Thus, we speculate the following three possible reasons that lead to the formation of single \( \beta \)-\( \text{Si}_3\text{N}_4 \) polymorph. Firstly, the silicon source used in this work was quartz mineral rather than commercial/pure amorphous or crystalline \( \text{SiO}_2 \) powders in other literatures reported. The high temperature stability of quartz made nitriding formation process of \( \text{Si}_3\text{N}_4 \) took
place at 1570 °C in catalyst-free sample. Secondly, according to the results and discussion above, α-Si₃N₄ was metastable at high temperature. α-phase might be generated in this work, but it was converted to β-phase at such high temperature. Last, the impurities in quartz raw material including 0.13 wt.% Fe₂O₃, or the formed eutectic liquid phases, contributed to the formation of pure β-phase in products, by either promoting the α-to-β phase transformation or direct formation of β-phase. The gear-like morphology of β-Si₃N₄ should be formed via coalescence in the iron-containing liquid phase.

3.4. PL Spectrum of Synthesized β-Si₃N₄ Samples

The functional applications of Si₃N₄ had attracted increasing interest, for instance, the optical properties of Si₃N₄ films or nanostructures have been studied [36,37]. However, Si₃N₄ microcrystals had not attracted much attention in terms of their optical properties. In this context, PL emission properties (excitation at 330 nm) of β-Si₃N₄ microcrystals with different morphologies were tested by using samples S5 and S6 nitrided at 1600 °C. The PL spectra are showed in Figure 12. The spectrum of these two samples showed a broad purple emission band with the maximum at 393 nm and it could be further fitted into two Gaussian peaks 390 nm (3.17 eV) of purple spectral region and 441 nm (2.81 eV) of blue spectral region. It has been reported that as an indirect gap semiconductor, the luminescence of Si₃N₄ is attributed to a defect luminescence mechanism. The PL process of Si₃N₄ could be caused by the existing defect of it which including ≡Si-Si≡, =N−, ≡Si⁰ and ≡Si−, and those were corresponding to four types of defects of Si–Si bond, N–N bond, and Si–N dangling bonds [38,39]. The experimental data may shed light on potential application of Si₃N₄ microcrystals in optical devices.

![Figure 12. PL spectrum of (a) S5 and (b) S6 nitrided at 1600 °C.](image)

4. Conclusions

A carbothermal reduction-nitridation (CRN) method was used for the preparation of β-Si₃N₄ powders from natural quartz and coke powders. β-Si₃N₄ powders with relatively high purity were obtained at 1600 °C for 3 h, with trace amount of β-SiC formed as a by-product. The results indicated that β-Si₃N₄ powders were obtained in the products, accompanied by the appearance of β-SiC and Si₂N₂O during the CRN process. The temperature, holding time, C/SiO₂ molar ratio, Fe₂O₃ addition, and β-Si₃N₄ seeds played important roles for the synthesis β-Si₃N₄ powders. The optimal nitriding temperature was 1600 °C and holding time was 3 h. A stoichiometric molar ratio of C/SiO₂ of 2 was preferred for preparing β-Si₃N₄ with better phase purity. Fe₂O₃ under the reducing environment formed Fe-containing liquid phases, which promoted the reaction thermodynamics of the CRN process. The products were mainly gear-like β-Si₃N₄ grains and Fe₂Si Archimedean solids. On the other hand, adding β-Si₃N₄ seeds into the starting mixture led to elongated β-Si₃N₄ grains with much finer widths and big specific ratio. The as-synthesized Si₃N₄ microcrystals exhibited an intense violet-blue spectral range with two maximum peaks at 441 nm (3.17 eV) and 390 nm (2.81 eV), which may shed light on potential application of Si₃N₄ microcrystals in optical devices.
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