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# Phase Formation of Ca- $\alpha$ -sialon by Reaction Sintering

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## Abstract

*In this study the reaction sintering route for the formation of Ca- $\alpha$ -sialon with a composition on the line  $\text{Si}_3\text{N}_4/\text{CaO}\cdot 3\text{AlN}$  ( $\text{Ca}_{0.8}\text{Si}_{9.6}\text{Al}_{2.4}\text{O}_{0.8}\text{N}_{15.2}$ ,  $m = 1.6$ ,  $n = 0.8$ ) has been investigated. This is compared with the hot-pressing of Ca- $\alpha$ -sialon and the reaction sintering of Y- or lanthanide- $\alpha$ -sialons. The reaction follows the same sequence: first, the formation of a Ca-rich  $\alpha$ -sialon phase ( $m = 1.9$ ) which is gradually transformed to a Ca- $\alpha$ -sialon with a lower Ca concentration ( $m = 1.2$ ). The gehlenite phase ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ , melilite group) is observed as an intermediate product. A potential advantage of Ca- $\alpha$ -sialon over Ln- $\alpha$ -sialon ( $\text{Si}_3\text{N}_4^{1/3}\text{Ln}_2\text{O}_3\cdot 3\text{AlN}$ , where Ln = Y, lanthanide) is liquid phase formation at a lower temperature, which has a positive influence on the processing temperature. Moreover, Ca is cheaper than the lanthanides. The solubility of Ca in the  $\alpha$ -sialon is in agreement with values found in the literature. © 1996 Elsevier Science Limited.*

## 1 Introduction

Sialon ceramic materials have many potential applications because of their good mechanical and chemical properties such as strength, hardness, thermal shock resistance and wear resistance. The sialon ceramics can be divided into two categories:  $\beta$ -sialon with the general formula  $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$  where  $0 < z < 4.2$ ,<sup>1,2</sup> and  $\alpha$ -sialon with the general formula  $\text{Me}_{m/\text{val}}\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$  (where Me = metal like Y, lanthanides, Ca, Mg, Li; val = valency of the metal).<sup>3</sup> The  $\alpha$ - and  $\beta$ -sialon materials have similar structures to  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$ . The  $z$ ,  $m$  and  $n$  parameters are substitution numbers for Al and O. Among the  $\alpha$ -sialon materials Y- $\alpha$ -sialon has been studied most extensively,<sup>3-6</sup> with Ln- $\alpha$ -sialon (Ln

= lanthanide) materials being less well studied. However, most lanthanides are quite expensive and therefore this work is focused on a less expensive alternative, i.e. Ca- $\alpha$ -sialon.

In a previous paper, the preparation of Ca- $\alpha$ -sialon by a carbothermal reduction and nitridation process was reported.<sup>7</sup> In this paper the reaction route for the formation of Ca- $\alpha$ -sialon by reaction sintering is described. The results are compared with results found in the literature concerning the hot-pressing of Ca- $\alpha$ -sialon and reaction sintering of Ln- $\alpha$ -sialon (Ln = Y, lanthanide) to see what are the similarities and differences in reaction paths.

## 2 Experimental Methods

To determine the reaction sequence during reaction sintering, several experiments were carried out. The aim was to prepare Ca- $\alpha$ -sialon with composition  $\text{Ca}_{0.8}\text{Si}_{9.6}\text{Al}_{2.4}\text{O}_{0.8}\text{N}_{15.2}$  ( $m = 1.6$ ,  $n = 0.8$ ). As starting materials,  $\text{Si}_3\text{N}_4$  (LC-12N, Starck;  $\alpha/(\alpha + \beta) > 95\%$ , oxygen content 2 wt%), AlN (Starck, grade C; oxygen content 2 wt%) and CaO [freshly decomposed  $\text{CaCO}_3$  (Merck p.a.)] were used. No correction was made for the oxygen content of the nitride starting materials. All firing experiments were performed with the same batch of mixed starting materials. The mixing of these powders was performed in isopropanol in polyethylene bottles on a roller bench (for 48 h) with  $\text{Si}_3\text{N}_4$  milling balls. Subsequently the powder was dried and pressed into tablets; first uniaxially at 51.7 MPa followed by isostatic pressing at 250 MPa. The firing of the samples was performed in a graphite resistance nitriding furnace at a pressure of 1.3 bar (maximum) of nitrogen. The temperature was increased from room temperature to 800°C at 10°C min<sup>-1</sup> in vacuum, and kept constant for 15 min to decompose the  $\text{CaCO}_3$ . Then the temperature was raised (10°C min<sup>-1</sup>) to the maximum temperature which was varied in the range 1300–1700°C. At 900°C

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the vacuum was replaced by a nitrogen atmosphere. After reaching the maximum temperature the samples were cooled down immediately ( $10^{\circ}\text{C min}^{-1}$ ), so no soaking time was used. The tablets (five for each temperature) were embedded in a powder mixture of 55 wt%  $\text{Si}_3\text{N}_4$ , 20 wt%  $\text{AlN}$ , 5 wt%  $\text{CaO}$  (decomposed  $\text{CaCO}_3$ ) and 20 wt%  $\text{BN}$  to prevent decomposition of the starting materials at elevated temperatures.  $\text{BN}$  was added to this mixture to prevent sintering of the powder bed mixture.

Densification during heat-up was measured using dilatometry. This was performed in a graphite resistance furnace in a static nitrogen atmosphere (heating rate  $5^{\circ}\text{ min}^{-1}$ , no soaking time at maximum temperature). A 15 min holding time at  $1350^{\circ}\text{C}$  was implemented, thereafter shrinkage rate started to drop. The difference in heating rates in the dilatometry and reaction sintering experiments was used to get a clear separation of the different shrinkage rate maxima. The dilatometer was set up to measure horizontal displacement. The samples were pressed into bars with the aid of polyethylene glycol as a binder material, first uniaxially and then isostatically at 250 MPa. The size of the bars was approximately  $15 \times 5 \times 5\text{ mm}^3$ . To remove the binder and decompose the  $\text{CaCO}_3$  to  $\text{CaO}$  and  $\text{CO}_2$ , the bars were carefully heated up in air to  $900^{\circ}\text{C}$  and soaked for 1 h. The dilatometer samples were not used for further investigation. Only samples with a weight loss  $<5\%$  were used for further analysis.

The samples were analysed by X-ray diffraction (Rigaku, Geigerflex,  $\text{Cu K}\alpha$  radiation,  $0.0125^{\circ}\text{ min}^{-1}$ ,  $2\theta = 10\text{--}97^{\circ}$ , 5 s counting time, 35 kV, 20 mA). For X-ray diffraction the tablets were powdered

as fine as possible by mortar and pestle. The determination of phase composition by X-ray diffraction was performed qualitatively by estimation of the intensities of peaks in the diffractograms belonging to various compounds. To determine the cell parameters, the peaks with the highest intensity were generally chosen. It would have been better to use the peaks at high reflection angles, but the intensity of these peaks was too low. The computer program REFCEL<sup>8</sup> was used to calculate the cell parameters. The  $d$ - or  $2\theta$ -values and the  $hkl$ -values of the 10 strongest peaks ( $hkl = 101, 201, 102, 210, 211, 301, 222, 321, 411, 322$ ) were used as input for this program.

### 3 Results and Discussion

#### 3.1 Shrinkage behaviour

It is generally accepted that the shrinkage during densification of  $\alpha$ -sialon occurs as a consequence of liquid phase sintering, which proceeds in three stages:<sup>3</sup>

- (1) primary particle rearrangement, immediately following the formation of liquid phase, brought about by solid particles sliding over each other under the action of capillary forces;
- (2) a solution/precipitation process which will occur if the solid particles have sufficient solubility in the liquid phase; and
- (3) coalescence and closed pore elimination.

By reaction of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  on the surface of the nitride starting materials with  $\text{CaO}$ , a liquid phase can be formed at the eutectic temperature.

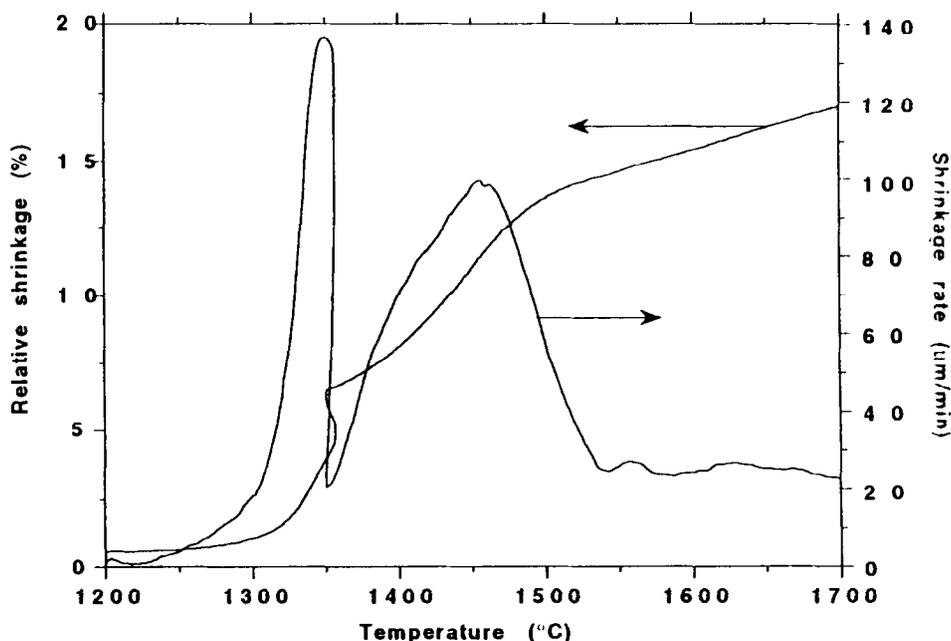


Fig. 1. Dilatometer curve of reaction mixture of  $\text{CaO}$ ,  $\text{Si}_3\text{N}_4$  and  $\text{AlN}$  with a composition  $\text{Ca}_{0.8}\text{Si}_{1.6}\text{Al}_{2.8}\text{O}_{0.8}\text{N}_{1.2}$ . The kink in the shrinkage curve at the holding temperature of  $1350^{\circ}\text{C}$  (15 min) is a result of an overshoot when it is reached. The final density of this sample is 95% of the theoretical density.

According to the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> phase diagram the lowest eutectic temperature is 1170°C.<sup>9</sup> To increase the amount of liquid phase the temperature should be somewhat higher, in agreement with the fact that shrinkage starts at about 1225°C (Fig. 1) due to particle rearrangement. The amount of liquid phase increases further at higher temperatures, more so because dissolution of nitrogen lowers the eutectic temperature.<sup>10</sup> As a result, a maximum shrinkage rate is observed at about 1350°C (Fig. 1), which corresponds with the temperature (1360°C) reported for this stage during reaction hot-pressing of Ca- $\alpha$ -sialon.<sup>11</sup> Reaction sintering of Si<sub>3</sub>N<sub>4</sub>/AlN/Y<sub>2</sub>O<sub>3</sub> compositions on the line Si<sub>3</sub>N<sub>4</sub>/1/3 Y<sub>2</sub>O<sub>3</sub>·3AlN shows the first shrinkage rate maximum at a significantly higher temperature of 1500°C<sup>12</sup> to 1550°C.<sup>13</sup> At about 1450°C the second shrinkage rate maximum can be discerned for Ca- $\alpha$ -sialon (Fig. 1), which is ascribed to the occurrence of the solution/precipitation mechanism (stage 2). The temperature observed for this stage agrees with the value reported for the second shrinkage step during reaction hot-pressing of Ca- $\alpha$ -sialon.<sup>11</sup> Chen and co-workers<sup>11,14,15</sup> pointed out that the position of the second peak is closely related to the temperature at which the major nitride component in the mixture is wetted by the liquid phase. For Si<sub>3</sub>N<sub>4</sub>, which is the major component in our reaction mixture, complete wetting was observed at 1450°C, corresponding with the second peak in Fig. 1. For the Ca system preferential wetting of the nitride starting material present in the largest amount (i.e. Si<sub>3</sub>N<sub>4</sub>) takes place,<sup>14</sup> whereas for the Y system preferential wetting of the AlN starting material occurs.<sup>15</sup> From the present study and our earlier research on Y- $\alpha$ -sialon,<sup>16</sup> we conclude that the densification during reaction sintering is quite similar to that during reaction hot-pressing observed by Chen and co-workers.<sup>11,14,15</sup>

### 3.2 Phase formation

Powder X-ray diffraction was used to analyse the phase composition of the tablets. The amounts of

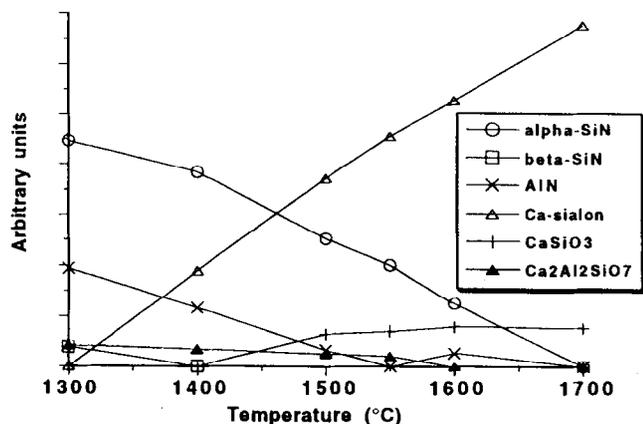


Fig. 2. Phase composition of product after firing at different temperatures.

the crystalline phases are presented in Fig. 2 as a function of the reaction sintering temperature. The figure shows that the formation of Ca- $\alpha$ -sialon starts at a temperature between 1300 and 1400°C. This is related to the formation of a significant amount of liquid phase at 1350°C, as deduced from the first peak in the shrinkage curve. From the dilatometer curve it was concluded that at 1450°C the solution/precipitation mechanism plays a dominant role. This corresponds with the temperature in Fig. 2 where the amounts of the raw materials, Si<sub>3</sub>N<sub>4</sub> as well as AlN, start to decrease significantly.  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, which was near the detection limit, was no longer detectable above 1300°C. AlN disappears in the range 1500–1600°C.  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> can still be determined at 1600°C. The amount of Ca- $\alpha$ -sialon increases with increasing temperature until near-complete conversion at 1700°C. Only one crystalline intermediate product could be determined: this is Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> (gehlenite) or more likely a compound with the general formula Ca<sub>2</sub>Al<sub>2-x</sub>Si<sub>1+x</sub>O<sub>7-x</sub>N<sub>x</sub>, according to the calculated cell parameters which are different from that of pure gehlenite. This product is observed at 1300°C and can be detected until 1600°C, at which temperature it is completely dissolved. The amount, however, is near the detection limit. The presence of this intermediate phase is in agreement with the results Hewett *et al.*<sup>17</sup> reported for the reaction hot-pressing of Ca- $\alpha$ -sialon. Besides this gehlenite intermediate they also found a very small amount of M-phase (2CaO·Si<sub>3</sub>N<sub>4</sub>·AlN) at low temperatures (up to about 1400°C), which was not detected in our samples. In our investigation CaSiO<sub>3</sub> appears between 1400°C and 1500°C and remains in the mixture even at 1700°C. It may be formed during cooling, and its presence in the end product is ascribed to the surface oxygen present on the nitride starting materials. It can be calculated that the oxygen content of the nitride raw materials corresponds with 2–3 wt% CaSiO<sub>3</sub> in the end product. According to this calculation the *m*-value of the resulting Ca- $\alpha$ -sialon shifts a little, from 1.6 to 1.4 at minimum. According to Hintzen *et al.*<sup>18</sup> the *m*- and *n*-values can be calculated from the relations:

$$a (\text{\AA}) = 7.749 + 0.0023 n + 0.0673 m \quad (1)$$

$$c (\text{\AA}) = 5.632 - 0.0054 n + 0.0550 m. \quad (2)$$

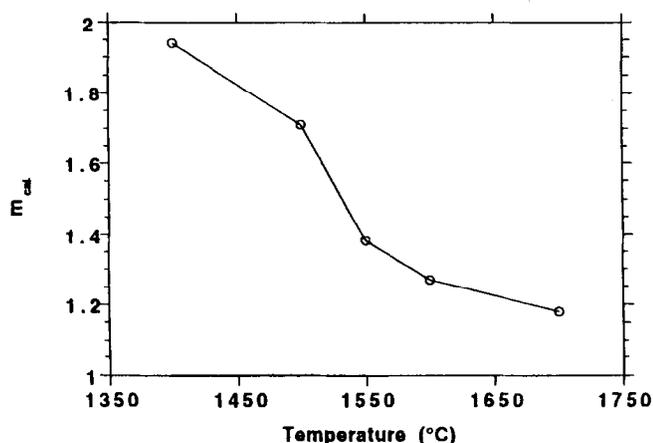
From these relations it can be seen that the *m*-value is the dominant parameter; therefore the *n*-value is not calculated.

At the beginning of the reaction (1400°C) the cell parameters of the Ca- $\alpha$ -sialon material are large ( $a = 7.883 \text{\AA}$ ,  $c = 5.731 \text{\AA}$ , see Table 1) which is ascribed to the formation of a Ca-rich Ca- $\alpha$ -sialon material. From the eqns (1) and (2) the *m*-value can

**Table 1.** Influence of sintering temperature on the lattice parameters of Ca- $\alpha$ -sialon, and the  $m$ -values calculated with equations (1) and (2)

Temperature ( $^{\circ}\text{C}$ )	$a$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )	$m_{\text{cal}}$
1400	7.883	5.731	1.9
1500	7.865	5.725	1.7
1550	7.845	5.700	1.4
1600	7.842	5.685	1.3
1700	7.830	5.694	1.2

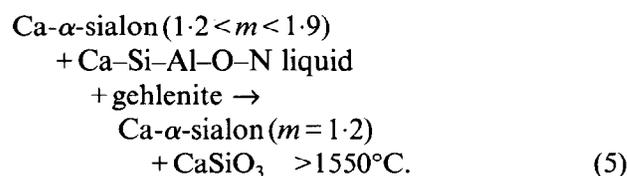
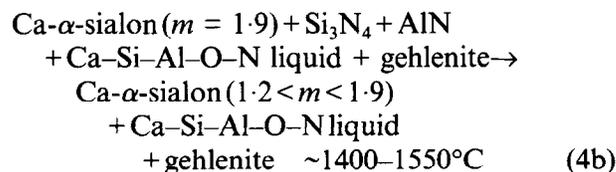
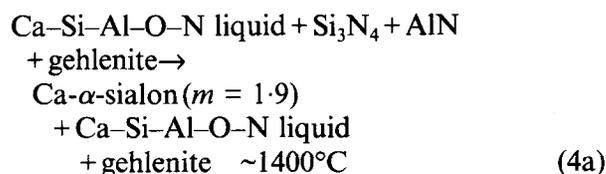
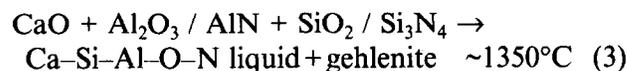
be calculated to be 1.9. This  $m$ -value is smaller than 2.8 which is reported as the upper limit of the solubility of Ca in  $\alpha$ -sialon.<sup>19</sup> The presence of still large amounts of  $\text{Si}_3\text{N}_4$  and AlN at 1400 $^{\circ}\text{C}$  also is in agreement with the presence of Ca- $\alpha$ -sialon with a high Ca concentration. For increasing sintering temperatures the lattice parameters of the Ca- $\alpha$ -sialon become smaller (Table 1). This corresponds to a decreasing  $m$ -value (Fig. 3), and indicates the formation of Ca- $\alpha$ -sialon with lower Ca concentrations at higher temperatures. The final Ca- $\alpha$ -sialon composition (1700 $^{\circ}\text{C}$ ) has small lattice parameters ( $a = 7.830 \text{ \AA}$ ,  $c = 5.694 \text{ \AA}$ ) resulting in  $m = 1.2$ . From the comparison of the experimentally found  $m$ -value (1.2) with the  $m$ -value expected from the weighed-out starting composition (1.4–1.6), it can be concluded that 75–85% of the amount of calcium is incorporated in the Ca- $\alpha$ -sialon lattice. Such percentages are generally found for Ca- $\alpha$ -sialon systems.<sup>18</sup> The reaction is finished according to the cell parameters calculated from the samples fired at 1700 $^{\circ}\text{C}$ , in agreement with the presence of nearly single-phase Ca- $\alpha$ -sialon. The decrease of the cell parameters of Ca- $\alpha$ -sialon during the reaction corresponds with the results that Sun *et al.*<sup>20</sup> reported for reaction sintering of Ca- $\alpha/\beta$ -sialon composite materials. In the latter case, however, the shift of the boundary between the single-phase  $\alpha$ -region and the two-phase  $\alpha/\beta$ -region with temperature may also play an important role.



**Fig. 3.** Influence of sintering temperature on the  $m$ -values calculated from the measured lattice parameters using eqns (1) and (2).

### 3.3 Reaction mechanism

From the results discussed so far, the following reaction mechanism can be derived.



Reaction (3) occurs at about 1350 $^{\circ}\text{C}$ , reaction (4) in the range 1400–1550 $^{\circ}\text{C}$  and reaction (5) if the temperature is higher than 1550 $^{\circ}\text{C}$ . The  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in eqn (3) are present on the surface of the starting  $\text{Si}_3\text{N}_4$  and AlN powder.

The reaction scheme proposed in this study is similar to that observed by Watari *et al.*<sup>13</sup> for reaction sintering of Ln- $\alpha$ -sialons (Ln = Y, Er, Yb). They proposed a reaction sequence, starting with lanthanide oxides (Y, Er, Yb), in which first a liquid phase is formed, subsequently  $\alpha$ -sialons with high concentrations of lanthanide ions and finally  $\alpha$ -sialons with low lanthanide concentrations. In this case a melilite-like compound ( $\text{Ln}_2\text{Si}_3\text{O}_3\text{N}_4$ ) is also found as an intermediate, in agreement with results found by Cao and co-workers for reaction sintering of Y-sialon materials.<sup>3,12,16</sup> There are strong similarities between the reaction sequence proposed for Ln- $\alpha$ -sialons and the work described in the present paper for Ca- $\alpha$ -sialon. In both cases a melilite like compound  $\text{M}_2(\text{Al,Si})_3(\text{O,N})_7$  (M = Ca, Y, lanthanide) was observed as an intermediate product, but there is no end product present which can be exchanged by  $\text{CaSiO}_3$  in their reaction sequence.

Potential advantages of Ca- $\alpha$ -sialon are the lower processing temperature (densification) and the much cheaper starting materials.

### 4 Conclusions

Reaction sintering of a mixture of CaO,  $\text{Si}_3\text{N}_4$  and AlN on the line  $\text{Si}_3\text{N}_4/\text{CaO} \cdot 3\text{AlN}$  ( $\text{Ca}_{0.8}\text{Si}_{9.6}\text{Al}_{2.4}\text{O}_{0.8}$

$N_{1.52}$ ,  $m = 1.6$ ,  $n = 0.8$ ) starts at a temperature of about 1350°C due to the formation of a Ca-Si-Al-O-N liquid, as deduced from shrinkage rate measurements. At about 1450°C the solution precipitation mechanism is dominant, promoting the formation of Ca- $\alpha$ -sialon. First, a Ca- $\alpha$ -sialon is formed which contains more Ca than aimed at ( $m = 1.9$ ). Subsequently this Ca-rich  $\alpha$ -sialon reacts with the  $Si_3N_4$  and AlN still present until finally  $m = 1.2$  is reached, indicating that not the total amount of Ca is incorporated in the  $\alpha$ -sialon matrix. As an intermediate product  $Ca_2Al_{2-x}Si_{1+x}O_{7-x}N_x$  (gehlenite, belonging to the melilite group) was found. This is comparable to the intermediate products in the formation of Ln- $\alpha$ -sialon (Ln = Y, lanthanide) where  $Ln_2Si_3O_3N_4$  melilite phases are formed. In the final product, besides Ca- $\alpha$ -sialon,  $CaSiO_3$  was observed due to the presence of oxygen in the nitride starting materials, which was not corrected for. Potential advantages of Ca- $\alpha$ -sialon over Ln- $\alpha$ -sialon are the lower processing temperature and the much cheaper starting materials.

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