Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 30 (2010) 1537–1541
www.elsevier.com/locate/jeurceramsoc

# Synthesis of single phase Ca-α-SiAlON using Y-type zeolite

Hitoshi Sasaki [a,b], Yasunori Oumi [a], Masahiro Sadakane [a], Tsuneji Sano [a,*]

[a] *Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiya 1-4-1, Higashi-Hiroshima 739-8527, Japan*
[b] *Advanced Ceramics Division, Ceramics Business Group, Covalent Materials Corporation, Shinagawa, Tokyo 141-0032, Japan*

Received 27 July 2009; received in revised form 31 October 2009; accepted 26 November 2009
Available online 23 December 2009

---

**Abstract**

Single phase Ca-α-SiAlON was synthesized for the first time by the carbothermal reduction-nitridation of a physical mixture of Y-type zeolite and CaO. Under well-optimized conditions, which included both a Si/Al ratio of 2.8 for the starting Y-type zeolite and a Ca/Al ratio of 0.63–0.75, highly crystalline, pure Ca-α-SiAlON was obtained. The formation of pure Ca-α-SiAlON was also confirmed by $^{27}$Al and $^{29}$Si MAS NMR measurements.

*Keywords:* Y-type zeolite; SiAlON; Alkaline earth oxide; Powders-solid state reaction; Spectroscopy

---

## 1. Introduction

Silicon aluminum oxynitride SiAlONs, especially α-SiAlON and β-SiAlON, are useful for engineering applications because of their excellent mechanical, thermal, and chemical properties. α-SiAlON has the same crystal structure as α-$Si_3N_4$, in which $Si^{4+}$ and $N^{3-}$ are partially replaced by $Al^{3+}$ and $O^{2-}$, respectively. This substitution leads to a charge imbalance, which is compensated for by the incorporation of interstitial metal cations such as Li, Mg, Ca, and rare-earth. The general formula is expressed as follows: $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, where M is a metal cation with a valance of $+v$, $(m+n)$ Si–N bonds are replaced by $m$ Al–N and $n$ Al–O bonds, and $x$ is the cation solubility ($x = m/v$).[1–5]

SiAlONs can be synthesized by several methods. Typically, SiAlONs are prepared by firing powder compacts of $Si_3N_4$, AlN, $Al_2O_3$, and some oxide sintering additives at high temperatures via the liquid phase mechanism, which requires expensive high-purity starting materials. On the other hand, the carbothermal reduction-nitridation (CRN) method is also known to be useful for the direct synthesis of SiAlONs from a wide range of inexpensive materials. A mixture of $SiO_2$, $Al_2O_3$, and a metal cation source is heated in the presence of carbon under $N_2$ flow.[6–14]

Crystalline aluminosilicate zeolites have become attractive as raw materials for the fabrication of SiAlON powders. Si and Al atoms are uniformly distributed within their framework structures and the Si/Al ratio can be varied easily. It is also possible to introduce metal cations into the zeolitic pores by an ion-exchange method. Sugahara et al. reported the synthesis of β-SiAlON using a zeolite-inclusion polyacrylonitrile compound. However, the purity of the resulting product was not very high. Recently, Tatami et al. succeeded in synthesizing pure β-SiAlON from Y-type zeolite, which is one of the high aluminum content zeolites, having a high ion-exchange capacity. They also tried to synthesize Ca-α-SiAlON from $Ca^{2+}$ ion-exchanged Y-type zeolite, which has recently received considerable attention because of its high thermal stability. However, the synthesis of pure Ca-α-SiAlON from the zeolite has not yet been achieved.[15–19]

From this viewpoint, we also investigated the synthesis of single phase Ca-α-SiAlON by the CRN method using a zeolite as a raw material, and succeeded in synthesizing single phase Ca-α-SiAlON from a physical mixture of CaO and Y-type zeolite with a Si/Al ratio of 2.8 by optimizing the CRN conditions.

## 2. Experimental

Y-type zeolite (Tosoh Co., Japan), carbon black (650B, Mitsubishi Chemical Co. Ltd., Japan), and CaO (99.9% pure, Wako Pure Chemical Ind., Ltd. Japan) were used as the starting materials. All of the zeolites were changed to proton-type zeolites

---

[*] Corresponding author. Tel.: +81 82 424 7607; fax: +81 82 424 5494.
*E-mail address:* tsano@hiroshima-u.ac.jp (T. Sano).

0955-2219/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2009.11.017

Table 1
CRN conditions and products obtained.

| Sample no. | Starting mixture | | | | Product | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Si and Al source | Si/Al ratio | M source | M/Al ratio | Phase (by-product) | Bulk chemical composition | | | |
| | | | | | | Si/Al ratio | Ca/Al ratio | Ca/(Si + Al) ratio | N/(Si + Al) ratio |
| 1 | Y-type zeolite | 2.8 | | | β-SiAlON | 2.7 | | | 0.50 |
| 2 | Y-type zeolite | 2.8 | CaO | 0.16 | Ca-α-SiAlON (β-SiAlON) | | | | |
| 3 | Y-type zeolite | 2.8 | CaO | 0.25 | Ca-α-SiAlON (β-SiAlON) | | | | |
| 4 | Y-type zeolite | 2.8 | CaO | 0.50 | Ca-α-SiAlON (β-SiAlON) | | | | |
| 5 | Y-type zeolite | 2.8 | CaO | 0.63 | Ca-α-SiAlON | 3.0 | 0.52 | 0.13 | 0.54 |
| 6 | Y-type zeolite | 2.8 | CaO | 0.75 | Ca-α-SiAlON | 3.0 | 0.54 | 0.13 | 0.54 |
| 7 | Y-type zeolite | 2.8 | CaO | 0.88 | Ca-α-SiAlON | | | | |
| 8 | Y-type zeolite | 2.8 | CaO | 1.00 | Ca-α-SiAlON (unknown) | | | | |
| 9 | Y-type zeolite | 2.8 | CaO | 1.25 | Ca-α-SiAlON (unknown) | | | | |
| 10 | Y-type zeolite | 2.8 | MgO | 0.75 | β-SiAlON (unknown) | | | | |
| 11 | Y-type zeolite | 2.8 | $Y_2O_3$ | 0.75 | β-SiAlON (unknown) | | | | |
| 12 | Y-type zeolite | 3.7 | CaO | 0.75 | Ca-α-SiAlON (β-SiAlON) | | | | |
| 13 | Y-type zeolite | 13.5 | CaO | 0.75 | β-SiAlON | | | | |
| 14 | $SiO_2/Al_2O_3$ | 2.8 | CaO | 0.75 | Unknown (Ca-α-SiAlON) | | | | |

*CRN conditions*: carbon/zeolite = 1.2, temp. = 1450 °C, time = 2 h, $N_2$ flow rate = 1.0 L/min.

by the calcination of $NH_4^+$-type zeolites at 500 °C for 2 h to remove $NH_3$. First, the protonated zeolite was mixed with carbon powder so that the carbon content in all of the samples was 1.2 times the required stoichiometric value. CaO powder was added to the mixture. The mixture thus obtained was dry-mixed for 36 h using a $Si_3N_4$ ball[20,21], and then passed through a 50-mesh sieve. The powder mixture was placed in carbon boats and fired at 1450 °C for 2 h. The firing rate was ca. 10 °C/min and the cooling rate was ca. 20 °C/min. Nitrogen gas flow was fixed at 1.0 L/min during the entire firing cycle. The residual carbon in the resultant powder after the CRN treatment was removed by calcination at 700 °C for 2 h in air. For comparison, $SiO_2$ (Nipsil, Nippon Silica Ind. Co., Japan) and $Al_2O_3$ (AKP-20C, Sumitomo Chemical Co., Ltd) were used as the raw materials. The CRN conditions are listed in Table 1.

The product phases were characterized using an X-ray diffractometer (XRD-6000, Shimadzu, Japan) with monochromatized CuKα radiation at 40 kV and 40 mA. The chemical compositions such as the Si/Al, Ca/Al, and Ca/(Si + Al) ratios of the obtained Ca-α-SiAlON were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Vista-Pro, SII Co., Japan). The nitrogen contents were measured by a nitrogen analyzer (TC-136, Leco Co., USA) using an infrared absorbance technique. The crystal morphology was observed using scanning electron microscopy (SEM, JEOL JSM-6320FS) with an energy-dispersive X-ray analysis system (EDX, JED-2110). $^{27}Al$ and $^{29}Si$ MAS NMR spectra were recorded using a 7-mm-diameter zirconia rotor on a Bruker Advance DRX-400 at 104.3 and 79.5 MHz, respectively. $Al(NO_3)_3\cdot 9H_2O$ and $Si(CH_3)_4$ were used as chemical references.

## 3. Result and discussion

First, the influence of the Ca/Al ratio in the starting mixture was investigated. It is difficult to introduce more $Ca^{2+}$ ions into the starting mixture than the ion-exchange capacity when $Ca^{2+}$ ion-exchanged zeolite is the only Ca source used. Therefore, in this study, CaO was employed as a Ca source. Namely, CaO powder was physically mixed with the protonated Y-type zeolite. Fig. 1 shows the XRD patterns of products obtained from the starting physical mixtures with various Ca/Al ratios. In the case where no CaO was added, high crystalline β-SiAlON was obtained (Sample no. 1 in Table 1), as already reported in the previous literature[16]. However, when CaO was added into the starting mixture, the α-SiAlON phase began to appear. The intensities of the peaks corresponding to α-SiAlON increased with an increase in the Ca/Al ratio of the starting mixture, while those assigned to β-SiAlON gradually decreased. It was clear that when the Ca/Al ratio was varied between 0.63 and 0.88, only the α-SiAlON phase was obtained (Sample nos. 5–7), indicating the formation of Ca-α-SiAlON. Although the synthetic region of Ca-α-SiAlON was very narrow, this was the first synthesis of single phase Ca-α-SiAlON from a zeolite. However, when the addition of CaO was continued, an unknown phase was observed along with the Ca-α-SiAlON (Sample nos. 8 and 9). These results indicate that the phase of the product was strongly dependent on the Ca/Al ratio of the starting mixture. When $CaF_2$ and $CaCO_3$ were used as Ca sources instead of CaO, single phase Ca-α-SiAlON was also obtained (not shown). However, when $SiO_2$ and $Al_2O_3$ powders were used as Si and Al sources, an unknown phase was observed along with a small amount of Ca-α-SiAlON (Sample no. 14). Tatami et al. had already indicated the high potential for the synthesis of Ca-α-SiAlON from $Ca^{2+}$ ion-exchanged Y-type zeolite.[16] However, a small amount of β-SiAlON was present in the products. The formation of β-SiAlON was probably due to a lower amount of $Ca^{2+}$ ions, because the maximum Ca/Al ratio in the $Ca^{2+}$ ion-exchanged Y-type zeolite was 0.5.

Fig. 2 shows SEM images of the Ca-α-SiAlONs obtained. In the case of the Ca-α-SiAlON synthesized from a starting mixture with a Ca/Al ratio of 0.63–0.75 (Sample nos. 5 and 6), the shape was angular and similar to the one described in previous reports.[22] However, with a Ca/Al ratio of 0.88 (Sample

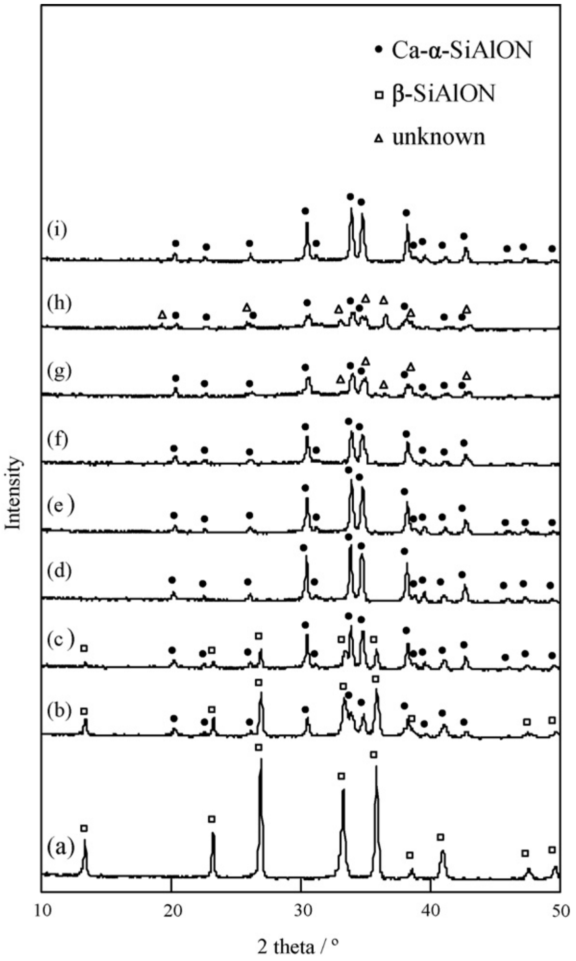

Fig. 1. XRD patterns of the products obtained from physical mixtures of Y-type zeolite and CaO. Sample nos.: (a) 1, (b) 2, (c) 4, (d) 5, (e) 6, (f) 7, (g) 8, (h) 9, (i) 6 after $HNO_3$ treatment.

no. 7), a spherical particle rather than an angular particle was observed. To check whether the spherical particles are Ca-α-SiAlONs or not, the surface Ca/Al ratios of several spherical particles were measured by EDX-SEM at 15 kV and the value was 1.2–1.8, which was considerably higher than that expected from the general formula of Ca-α-SiAlON. This suggests the thermal decomposition of Ca-α-SiAlON by amorphous CaO in the product, which is not detected by XRD. To clarify this, a large amount of CaO (Ca/Al = 2) was mixed with the pure Ca-α-SiAlON obtained (Sample no. 6) and fired at 1450 °C under CRN conditions. The facts that there was a considerable decrease in the XRD peaks assigned to Ca-α-SiAlON and a spherical particle was observed in the SEM image confirmed that the decomposition of part of the Ca-α-SiAlON occurred in the presence of CaO. Therefore, sample no. 7 was not characterized in the following analyses although there were no peaks other than Ca-α-SiAlON in the XRD pattern.

The chemical compositions of the single phase as-synthesized Ca-α-SiAlONs (Sample nos. 5 and 6) were measured by the ICP-AES and the nitrogen analyzer. The Si/Al ratio was approximately consistent with that of the starting Y-type zeolite, indicating that the starting Y-type zeolite was converted into Ca-α-SiAlON. The Ca/(Si + Al) ratio was slightly larger than that expected from the general formula of Ca-α-SiAlON, suggesting the existence of a small amount of amorphous CaO. To remove this, the as-synthesized Ca-α-SiAlON was treated with a 0.5 M $HNO_3$ solution at 60 °C for 6 h. The Si/Al, Ca/Al, Ca/(Si + Al), and N/(Si + Al) ratios of the Ca-α-SiAlON after the $HNO_3$ treatment are listed in Table 1. Although the Si/Al ratio had increased slightly after the $HNO_3$ treatment, the Ca/(Si + Al) ratio decreased to a reasonable value, in relation to what was expected from the general formula of Ca-α-SiAlON. As can be seen in Fig. 2(d) and (e), the morphology was not changed by the $HNO_3$ treatment. Further, there were no differences in the peak intensities of Ca-α-SiAlON in the XRD patterns before and after the $HNO_3$ treatment (Fig. 1(e) and (i)), suggesting that structural degradation of Ca-α-SiAlON did not happen. As it is well recognized that $Mg^{2+}$ and $Y^{3+}$ ions also work as stabilizing elements for α-SiAlON, the synthesis of Mg-α-SiAlON and Y-α-SiAlON was attempted using MgO and $Y_2O_3$ instead of CaO (Sample nos. 10 and 11). However, β-SiAlON was observed as the main phase in the products.

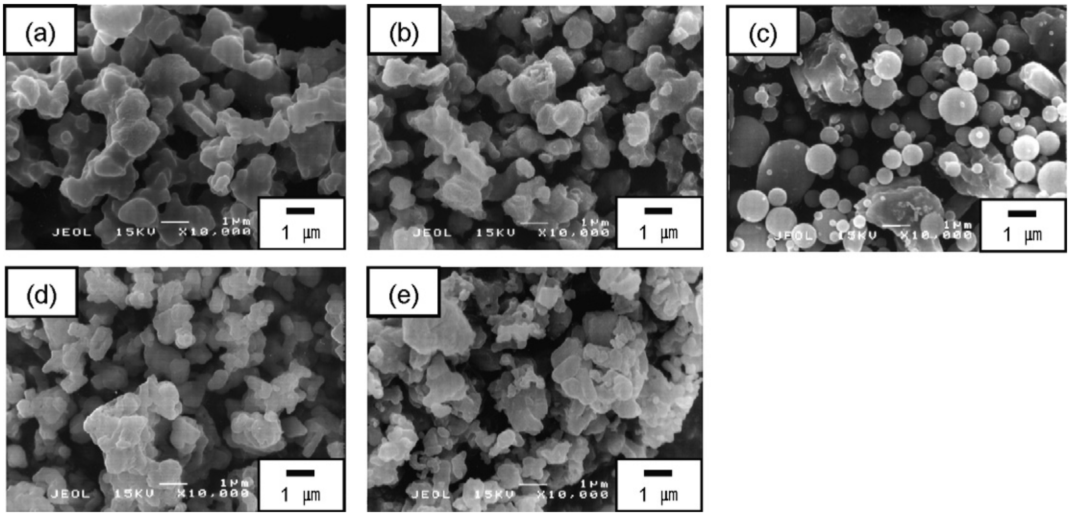

Fig. 2. SEM images of the α-SiAlONs obtained from Y-type zeolite. Sample nos.: (a) 5, (b) 6, (c) 7, (d) 5 after $HNO_3$ treatment, (e) 6 after $HNO_3$ treatment.

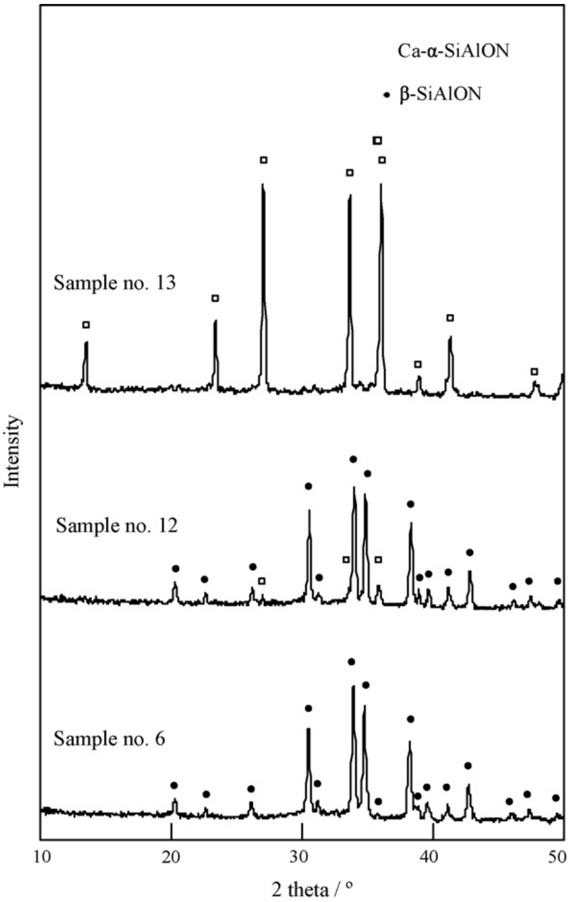

Fig. 3. XRD patterns of the products obtained from Y-type zeolites with various Si/Al ratios.

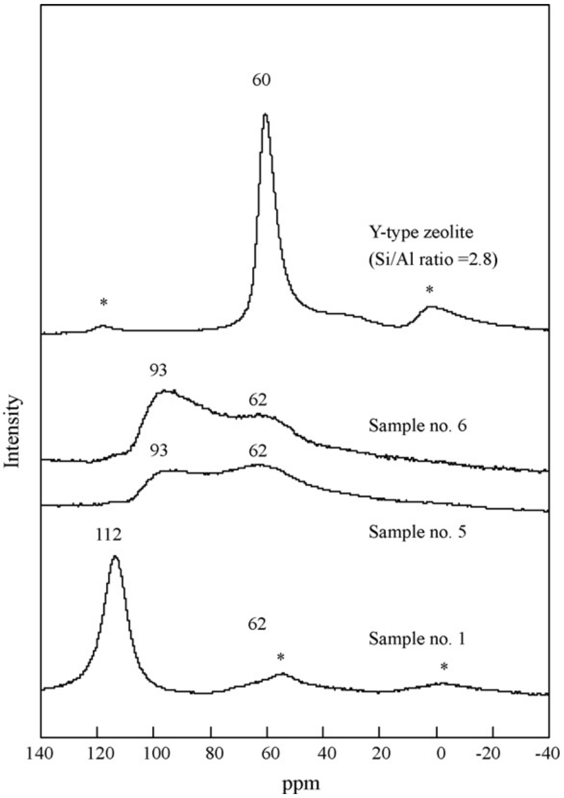

Fig. 4. $^{27}$Al MAS NMR spectra of the products obtained from Y-type zeolite. Asterisks denote spinning side bands.

As Si and Al atoms are distributed uniformly on an atomic level within the zeolite framework and the Si/Al ratio can be varied within a wide range, the effect of the Si/Al ratio of the starting Y-type zeolite on the synthesis of Ca-α-SiAlON was investigated. Fig. 3 shows the XRD patterns of the products obtained from Y-type zeolites with Si/Al ratios of 3.7 and 13.5, which were prepared by a dealumination treatment involving a combination of steaming at 700 °C and $H_2SO_4$ treatment at 75 °C for 4 h. As can be seen in Fig. 3, single phase Ca-α-SiAlON was not obtained, but the β-SiAlON phase was observed (Sample nos. 12 and 13). It may be concluded that the Si/Al ratio of the starting zeolite is a crucial factor for the synthesis of Ca-α-SiAlON. However, the exact reason for the strong Si/Al ratio dependence was not clarified at the present stage.

To get a better understanding of the process of formation of Ca-α-SiAlON, the obtained Ca-α-SiAlON samples were characterized by means of $^{27}$Al and $^{29}$Si MAS NMR techniques. Fig. 4 shows the representative $^{27}$Al MAS NMR spectra. For a reference, the $^{27}$Al MAS NMR spectrum of the starting Y-type zeolite with a Si/Al ratio of 2.8 is also shown, in which a strong peak due to tetrahedrally coordinated Al species (framework Al) was observed at around 60 ppm. In the case of β-SiAlON (Sample no. 1), a sharp peak assigned to Al–N units was observed at ca. 112 ppm, while a broad peak assigned to tetrahedral Al–O units was observed at ca. 62 ppm. This is consistent with

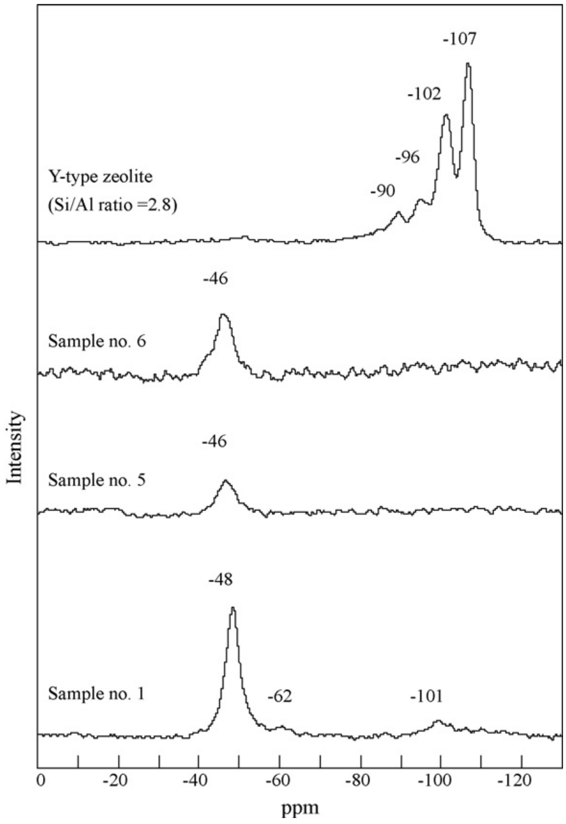

Fig. 5. $^{29}$Si MAS NMR spectra of the products obtained from Y-type zeolite.

those reported in the previous literature.[23] On the other hand, in the case of single phase Ca-α-SiAlONs (Sample nos. 5 and 6), a peak assigned to Al–O–N units and a weak broad peak assigned to tetrahedral Al–O units were observed at ca. 93 and 62 ppm, respectively. Fig. 5 shows the $^{29}$Si MAS NMR spectra of several samples. For the starting Y-type zeolite, four peaks assigned to Si(3Al), Si(2Al), Si(1Al), and Si(0Al) were observed at −90, −96, −102, and −107 ppm, respectively. In the case of β-SiAlON (Sample no. 1), the peaks assigned to Si–N, Si–O–N, and Si–O–Al were observed at −48, −62, and −101 ppm, respectively. On the other hand, only one peak was observed at −46 ppm for single phase Ca-α-SiAlON (Sample nos. 5 and 6), which is consistent with the result reported in the previous literature.[24] These $^{27}$Al and $^{29}$Si MAS NMR results also strongly indicate the formation of Ca-α-SiAlON.

## 4. Conclusions

Highly crystalline pure Ca-α-SiAlON was synthesized for the first time by the carbothermal reduction-nitridation of a physical mixture of Y-type zeolite and CaO under well-optimized conditions. Both the Si/Al ratio of the starting zeolite and the Ca/Al ratio of the starting mixture were crucial factors for the synthesis of Ca-α-SiAlON. Namely, when the Si/Al ratio of the Y-type zeolite was 2.8 and the Ca/Al ratio in the starting mixture was varied between 0.63 and 0.75, pure Ca-α-SiAlON was obtained, indicating a very narrow synthesis region. The formation of Si–N, Al–N, and Al–O bonds in the Ca-α-SiAlON was also confirmed by $^{27}$Al and $^{29}$Si MAS NMR investigations.

## References

1. Jack KH. SiAlONs and related nitrogen ceramics. *J Mater Sci* 1976;**11**:1135–58.
2. Hampshire S, Park HK, Thompson DP, Jack KH. α′-SiAlON ceramics. *Nature* 1978;**274**:880–2.
3. Huang ZK, Greil P, Petzow G. Formation of α-$Si_3N_4$ solid solutions in the system $Si_3N_4$-A1N-$Y_2O_3$. *J Am Ceram Soc* 1983;**66**:C96–7.
4. Mitomo M, Tajima Y, Sintering. Properties and applications of silicon nitride and SiAlON ceramics. *J Ceram Soc Jpn* 1991;**99**:1014–25.
5. Mitomo M. Fundamental science of refractories: major components, their crystal structures and properties. *SiAlON Refractories* 1995;**47**:149–53.
6. Mitomo M, Kuramoto N, Tsutsumi M, Suzuki H. The formation of single phase Si–Al–O–N ceramics. *J Ceram Soc Jpn (Yogyo-Kyokai-Shi)* 1978;**86**:526–31.
7. Yoshimatsu H, Mitomo M, Mihashi H, Ohmori S, Yabuki T. The preparation of SiAlON powder from kaolinite. *J Ceram Soc Jpn (Yogyo-kyokai-Shi)* 1983;**91**:442–9.
8. Yoshimatsu H, Yabuki T, Mihashi H. Preparation of SiAlON powder from mixture of $SiO_2$ and $Al_2O_3{\cdot}2H_2O$ by thermal carbon reduction. *J Ceram Soc Jpn (Yogyo-kyokai-Shi)* 1987;**95**:28–32.
9. Wang PL, Li YW, Yan DS. Effect of amount and atomic ratio of dual modifiers Ca and Mg on phase formation and mechanical properties of Ca, Mg-α-SiAlONs. *J Mater Sci* 2000;**35**:1585–8.
10. Wang PL, Li YW, Yan DS. Effect of dual elements (Ca, Mg) and (Ca, La) on cell dimensions of multi-cation α-SiAlONs. *J Eur Ceram Soc* 2000;**20**:1333–7.
11. Chen W, Wang P, Chen D, Zhang B, Jiang J, Cheng Y, Yan D. Synthesis of (Ca, Mg)-SiAlON from slag by self-propagating high-temperature synthesis. *J Mater Chem* 2002;**12**:1199–202.
12. Seeber AJ, Cheng Y-B. Thermal stability of mixed-cation α-SiAlON ceramics. *Mater Sci Eng A* 2003;**339**:115–23.
13. Suehiro T, Hirosaki N, Xie RJ, Mitomo M. Powder synthesis of Ca-α′-SiAlON as a host material for phosphors. *Chem Mater* 2005;**17**:308–14.
14. Liu G, Chen K, Zhou H, Ren K, Pereira C, Ferreira JMF. Fabrication of (Ca + Yb)- and (Ca + Sr)-stabilized α-SiAlON by combustion synthesis. *Mater Res Bull* 2006;**41**:547–52.
15. Sugahara Y, Hiraiwa H, Kuroda K, Kato C. Nitride formation by the carbothermal reduction of a zeolite-polyacrylonitrile inclusion compound. *J Mater Sci* 1988;**23**:3181–6.
16. Wakihara T, Kamiwaki S, Tatami J, Komeya K, Meguro T. Synthesis of Ca-α SiAlON using zeolite as a raw material. *J Ceram Soc Jpn* 2007;**115**:294–6.
17. Li FJ, Wakihara T, Tatami J, Komeya K, Meguro T. Synthesis of β-SiAlON powder by carbothermal reduction-nitridation of zeolites with different compositions. *J Eur Ceram Soc* 2007;**27**:2535–40.
18. Li FJ, Wakihara T, Tatami J, Komeya K, Meguro T, MacKenzie KJT. Elucidation of the formation mechanism of β-SiAlON from a zeolite. *J Am Ceram Soc* 2007;**90**:1541–4.
19. Yamakawa T, Wakihara T, Tatami J, Komeya K, Meguro T. Synthesis of β-SiAlON from a zeolite by reduction nitridation in a mixture of $NH_3$-$C_3H_8$. *J Ceram Soc Jpn* 2008;**116**:325–8.
20. Tani E, Umebayashi S, Okuzono K. Effect of composition on mechanical properties of β-SiAlON. *J Ceram Soc Jpn (Yogyo-kyokai-Shi)* 1985;**93**:370–5.
21. Masaki H, Wada S. Wear of media balls during the ball milling of $Si_3N_4$ powder. *J Ceram Soc Jpn* 1993;**101**:221–3.
22. Xie RJ, Hirosaki N, Mitomo M, Suehiro T, Xu X, Tanaka H. Photoluminescence of rare-earth-doped Ca-α-SiAlON phosphors: Composition and concentration dependence. *J Am Ceram Soc* 2005;**88**:2883–8.
23. Wakihara T, Saito Y, Tatami J, Komeya K, Meguro T, Mackenzie KJD, Takagi S, Yokouchi M. NMR study on the formation mechanism of β-SiAlON from zeolite by nitridation using ammonia gas. *J Ceram Soc Jpn* 2008;**116**:980–3.
24. Hewett CL, Cheng Y-B, Muddle BC. Preparation of fine-grained calcium α-SiAlON. *J Mater Sci Lett* 1994;**13**:1612–5.