Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 34 (2008) 1791–1795

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# Synthesis of prismatic β-sialon from the precursor of SBA-15 incorporated with $Al(NO_3)_3$ via carbothermal reduction nitridation

Jinhong Li [*], Hongwen Ma, Qinfang Fang

*National Laboratory of Mineral Materials, School of Materials Sciences and Technology, China University of Geosciences, Beijing 100083, China*

Received 16 December 2005; received in revised form 3 March 2006; accepted 20 April 2006
Available online 29 September 2007

**Abstract**

Prismatic β-sialon was obtained via carbothermal reduction nitridation of the precursor of SBA-15 incorporated with $Al(NO_3)_3$ under $N_2$ atmosphere at 1450 °C. The effects of calcined temperature on the phase and structures of the samples obtained at 550, 1150, 1250, 1350, and 1450 °C were investigated by means of X-ray diffraction. Calcined at 550 °C, the resulting material was amorphous, which was $SiO_2/Al_2O_3$ composites with the similar structure SBA-15, while β-cristobalite, mullite and β-$Si_3N_4$ was formed in the tested temperature range of 1150–1350 °C. Finally, β-sialon with high purity and yield were obtained at 1450 °C. The microstructural evolution of β-sialon at different sintered temperature was examined using scanning electron microscopy and transmission electron microscopy. It was demonstrated that well-shaped prismatic β-sialon, with a high yield of 98% was successfully prepared via carbothermal reduction nitridation from the precursor of SBA-15 with $Al(NO_3)_3$ under $N_2$ atmosphere at 1450 °C.

*Keywords:* β-Sialon; Precursor of SBA-15; Carbothermal reduction nitridation

## 1. Introduction

Sialons are ceramic materials derived from silicon nitride in which silicon and nitrogen are partially replaced simultaneously by aluminium and oxygen atoms, respectively. Such materials are chemically and thermally stable, and possess excellent mechanical properties such as high strength and high fracture toughness. Sialons, therefore, have been found wide range of applications in many fields [1]. β-Sialon is one of the most important forms of sialons, which has a general formula as: $Si_{6-z}Al_zO_zN_{8-z}$ ($0 < z < 4.2$), and is formed when $z$ silicon atoms in $Si_6N_8$ ($2Si_3N_4$) are substituted by $z$ aluminium atoms and $z$ nitrogen atoms by $z$ oxygen atoms [2–4]. Thus, β-sialon has engineering properties and applications similar to those of β-$Si_3N_4$, furthermore, it has such advantages that it can be tailored to particular applications by manipulation of its aluminium content. β-Sialon is a material that has high strength, good thermal-shock resistance, resistance against corrosion and erosion, particularly, superiority to silicon nitride in sinterability and oxidation resistance [5]. β-Sialon is generally prepared by sintering mixtures of $Si_3N_4$, $Al_2O_3$, AlN and $SiO_2$ at temperature higher than 1500 °C [6,7] via carbothermal reduction and nitridation of synthetic $Al_2O_3/SiO_2$ mixtures. Natural aluminosilicate minerals were used as starting materials for the synthesis of sialon ceramics [8]. However, new methods are still required for the synthesis of high purity β-sialon in many cases [9].

In this work, we adopted SBA-15, a kind of hexagonal mesoporous $SiO_2$ directed by triblock copolymer pluronic ($PEO_{20}PPO_{70}PEO_{20}$, P123) [10], and $Al(NO_3)_3$ incorporated in SBA-15 as starting materials to synthesize β-sialon under $N_2$ atmosphere. The starting materials were calcined at 550, 1150, 1250, 1350, and 1450 °C, and the phases and structures of the resulting materials calcined at different temperatures were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

## 2. Experimental

In a typical experiment, 4.0 g of triblock copolymer Pluronic P123 (BASF) template was dissolved in 170 ml of 2M HCl

---

[*] Corresponding author. Tel.: +86 10 82322039; fax: +86 10 82322974.
*E-mail address:* jinhong@cugb.edu.cn (J. Li).

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2006.04.026

solution via stirring at room temperature, and 8.5 g of tetraethyl orthosilicate followed by 0.8 M $Al(NO_3)_3$ (Beijing Chemical Reagent Center) solution (50 ml) was added via dripping under stirring. The resulting mixture was stirred at 40 °C for 24 h, and then aged at 100 °C for 48 h under static condition. After vaporized the solvent, the as-prepared solid was vacuum-dried at 100 °C overnight. The obtained powder was divided into five portions, each of which was pressed into cylindrical pellets of 15 mm in diameter and 15 mm in height under 100 MPa. Each pellet was put into a graphite crucible placed in a molybdenum-wire furnace under $N_2$ atmosphere of 120 ml/min flow rate, and was heated with a heating rate of 280 °C/h until temperature reached at 550, 1150, 1250, 1350, and 1450 °C, respectively, and was kept at the corresponding temperature for 6.0 h under nitrogen atmosphere at ~0.1 MPa, then all the samples were cooled naturally to room temperature in $N_2$ atmosphere prior to be characterized.

The XRD patterns of the samples obtained at different calcined temperatures were collected on an X-ray diffractometer (X'PERT SW) operated at 40 kV and 10 mA with nickel filtered Cu Kα radiation ($\lambda = 1.54060$ Å). The morphologies and microstructures of the samples were observed by means of scanning electron microscopy (SEM, JEOL, JSM-6700F) and transmission electron microscopy (TEM, JEOL, JEM-2010) equipped with an energy dispersive X-ray spectrometer (EDS) at an accelerating voltage of 200 kV, respectively.

## 3. Results and discussion

In this work, five pellets obtained from TEOS hydrolysis and incorporated with $Al(NO_3)_3$ were calcined at 550, 1150, 1250, 1350, and 1450 °C, respectively. Fig. 1 shows the XRD patterns of the as-prepared samples at different temperatures.

For the sample obtained at 550 °C, there is no peak on its XRD pattern (curve a) in the wide angle, suggesting the amorphous features of this product, which also means sialon was not obtained at this temperature. SEM and TEM observations provide more information for this sample. As displayed in Fig. 2a, this sample is particles with size of about 1 μm, and it possesses ordered hexagonal structure similar to SBA-15 with pore size of 7 nm, as shown in Fig. 3a and b. EDS analysis indicates the sample contains elements Si, Al, O and C during the TEM observation (not shown here). Based on the procedures to prepare SBA-15 reported in literature [10] and the results described above, the mesoporous material in the product is probably $SiO_2$ present in the form of SBA-15, and the adhered material on the SBA-15 surface is $Al_2O_3$ from the decomposition of $Al(NO_3)_3$ at 550 °C. Because of the mesoporous structures of SBA-15, $Al_2O_3$ maybe stays in the inner channels of SBA-15 and/or decorated on the inner and outer surfaces, which facilitates the adequate mixing of $SiO_2$ and $Al_2O_3$.

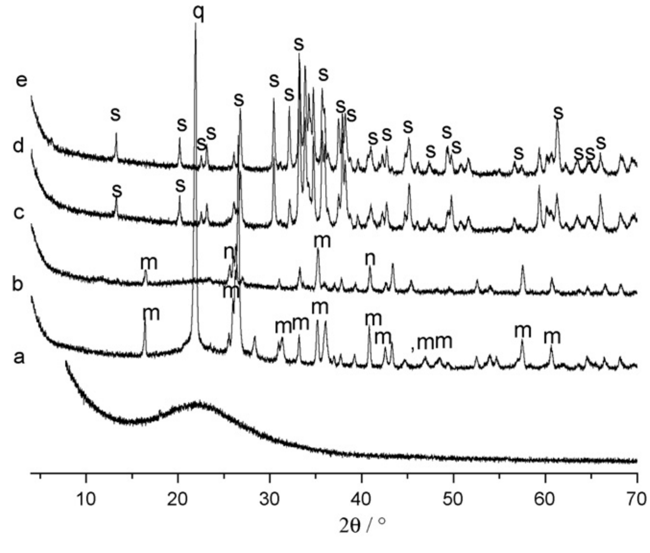

Fig. 1. XRD patterns of the samples obtained at different temperatures: (a) 550 °C; (b) 1150 °C; (c) 1250 °C; (d) 1350 °C; (e) 1450 °C. The phases are denoted as: s, β-sialon; m, mullite; n, $Si_3N_4$; q, β-cristobalite.

In general, the carbothermal reduction nitridation reaction occurs at temperature higher than 1350 °C [11]. In this work, four pellets were sinterated at 1150, 1250, 1350 and 1450 °C, respectively. From their XRD patterns shown in Fig. 1, it can be seen that the peaks assigning to β-cristobalite (JCPDS number: 83-2469) and mullite (JCPDS number: 74-2419) appeared on the XRD patterns of the products obtained at 1150 and 1250 °C. However, there is no peak belonging to β-sialon, suggesting the sinterating temperature of 1250 °C is too low to produce β-sialon. By comparison curve b with curve c, the peaks of mullite in curve c become weak, and β-cristobalite peaks disappear completely, which indicates mullite gradually diminished as increasing the temperature. In addition, we can find $Si_3N_4$ (JCPDS number: 76-1408) formed in the product, which implies the incorporation of N in the $N_2$ atmosphere. When the pellet was sintered at 1350 °C, the peaks corresponding to β-sialon (JCPDS number: 79-0483) are present on the XRD patterns of the as-prepared sample, suggesting the formation of β-sialon at this temperature. When the pellet was sintered at 1450 °C for 6 h, the main phase in the product was β-sialon with only a trace of mullite and β-$Si_3N_4$, as shown in curve e of Fig. 1. Based on the relationship between the value of *Z* and the lattice parameter of β-sialon, the *Z* value of β-sialon was 2.99 for the product obtained at 1450 °C in this work. From normalizing the XRD data, performed by a FORTRAN$^{77}$ program CELLSR [12], lattice constants of the product are deduced, which are consistent with those listed in the JCPDS cards. The yield of β-sialon is approximately 98% (97.96% $Si_{3.01}Al_{2.99}O_{2.99}N_{5.01}$, 2.04% other phases) calculated from the contents of Si, Al in the starting materials with the *Z* value and the content of nitrogen in β-sialon [4].

The morphologies and structures of the products sintered at different temperatures were examined by means of SEM and TEM, and the results are demonstrated in Figs. 2 and 3. Fig. 2 shows the SEM images of the as-prepared samples at different sintered temperatures, which can roughly illustrate the evolution of β-sialon from the pellets to the final β-sialon crystals. Fig. 2a shows the morphology of the products obtained at 550 °C, which are spherical particles with size of about 1 μm. Based on the XRD analysis and the synthesis procedures,

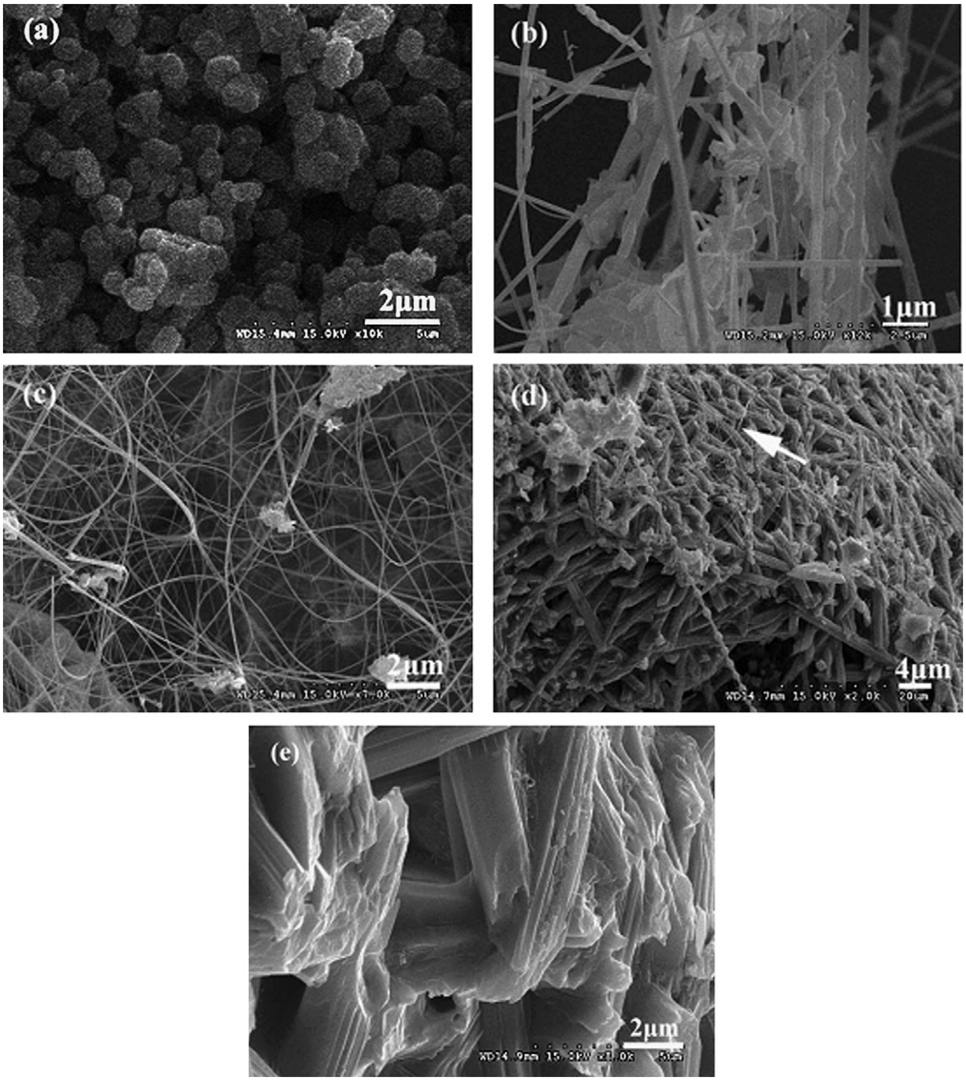

Fig. 2. SEM images of the as-prepared samples at different temperatures: (a) 550 °C; (b) 1150 °C; (c) 1250 °C; (d) 1350 °C; (e) 1450 °C.

this product is an amorphous mixture of $SiO_2$ and $Al_2O_3$ containing some carbon-based materials from pyrolysis of P123. Fig. 2b and c demonstrated the morphologies of the products prepared at 1150 and 1250 °C. There are many wires with diameter of 300 nm and length of about tens of microns in these two samples, which can be also observed using transmission electron microscope, as shown in Fig. 3c. The EDS analysis for this wire during TEM observation shows that it mainly contains element Si and N. Through the XRD and EDS analysis, it can be deduced that the wires in the products obtained at 1150 and 1250 °C are $Si_3N_4$, and the others are mainly mullite. In the product obtained at 1350 °C, vast majority of prismatic materials appear, as displayed in Fig. 2d, which are β-sialon based on the XRD analysis. From this graph, we can also observe some $Si_3N_4$ wires decorated with small β-sialon crystals (as demonstrated by an arrow in Fig. 2d), which indicates the reaction to form β-sialon crystals was probably not finished at this temperature. When the pellet was sintered at 1450 °C for 6 h, the $Si_3N_4$ wires disappeared completely, as shown in Fig. 2e, and the well-grown prismatic β-sialon crystals have been formed. The EDS analysis (Fig. 4a) indicates the atom ratio of Si:Al is 1.04, which agrees well with calculated formula $Si_{3.01}Al_{2.99}O_{2.99}N_{5.01}$. Selected diffraction patterns (Fig. 4b) indicate the final sialon is β type.

The exact mechanism to form β-sialon in this work is unclear. However, we propose a possible mechanism based our results as follows. During the calcining process in nitrogen flow, the precursor of $SiO_2$ was first dehydrated to produce amorphous $SiO_2$, and $Al(NO_3)_3$ decomposed into amorphous $Al_2O_3$, while the organic triblock copolymer pluronic P123 was carbonized to form amorphous carbon [10] at relatively low temperatures in nitrogen atmosphere. Then with increasing the heating temperature, β-cristobalite and mullite was formed. Meanwhile, a portion of oxygen in the sample was removed by carbon and substituted by nitrogen to form β-$Si_3N_4$ when temperature increased to certain value, and β-sialon was finally formed when temperature increased to enough high value.

Compared with the samples prepared in literature [13], the as-synthesized β-sialon in this work shows a rod shape with much fine crystal edges along the length. This may be explained

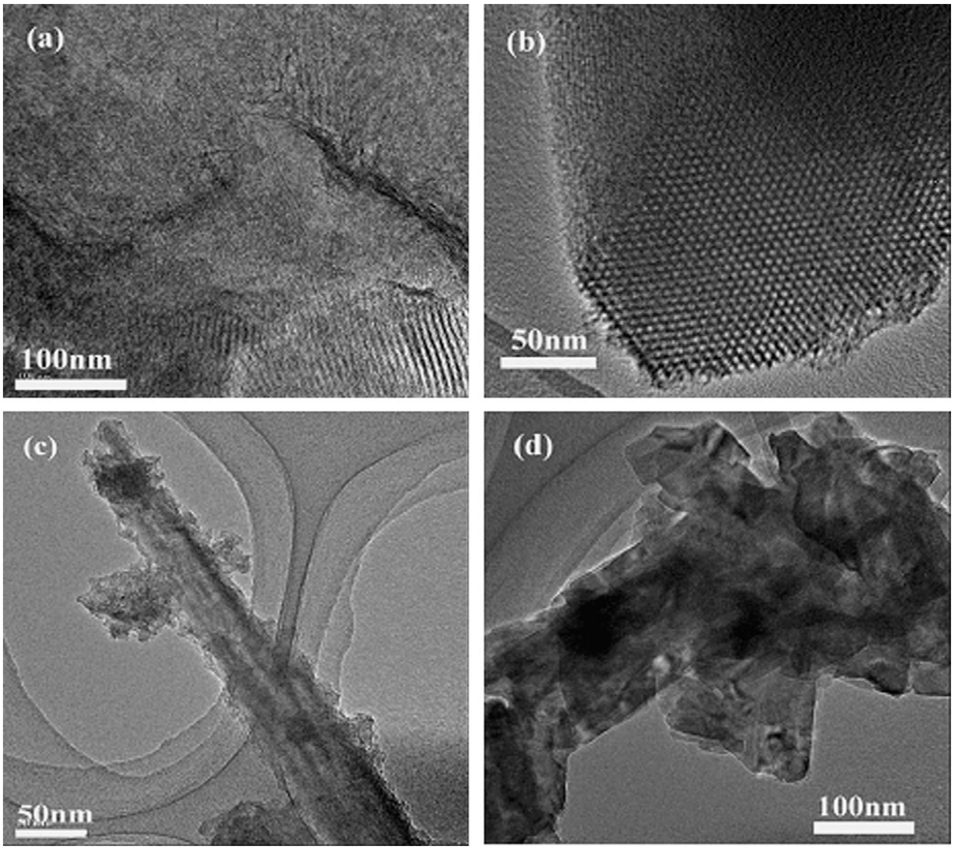

Fig. 3. TEM images of the samples prepared at different sintered temperatures: (a) and (b) 550 °C; (c) 1250 °C; (d) 1450 °C.

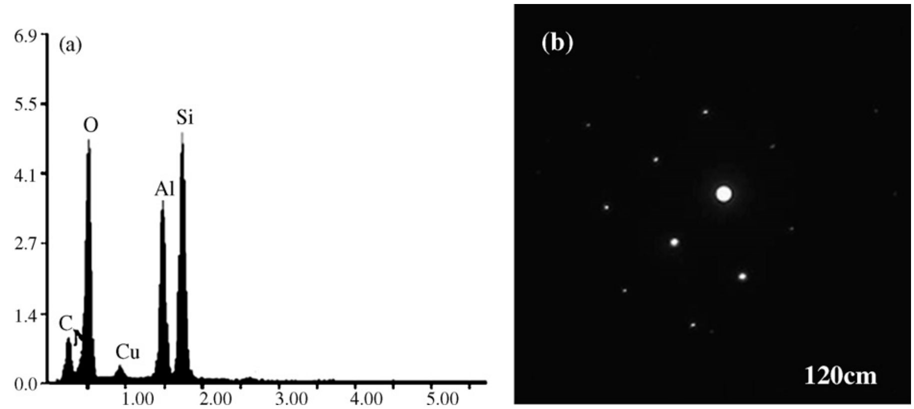

Fig. 4. EDS analysis (a) of the sample shown in Fig. 3d, and selected area diffraction (SAED) pattern (b) of the sample shown in Fig. 3d.

that the hexagonal structure of amorphous $SiO_2$ formed at relatively low temperature has a great influence on the morphology of β-sialon. It has been accepted that the morphology of the crystals is determined by two factors: one is the crystalline habit and the other is the driving force or steric hindrance for crystal growth. As to β-$Si_3N_4$ derived from $SiO_2$ with hexagonal structure, the packing density on the layers perpendicular to the *c*-direction base plane is much lower. Therefore, comparing to the prism plane, the base plane has priority for nucleation and has higher growth rate, which renders β-sialon to develop into elongated prism.

## 4. Conclusion

Well-shaped prismatic β-sialon was successfully prepared via carbothermal reduction nitridation of the precursor of SBA-15 incorporated with $Al(NO_3)_3$ under $N_2$ atmosphere at 1450 °C. A high yield of 98% for β-sialon can be reached. At the temperature of 550 °C, the calcined material was amorphous $SiO_2/Al_2O_3$ composites with the similar structure SBA-15, when the temperature climbed to 1150–1350 °C, β-$SiO_2$, mullite and β-$Si_3N_4$ was formed, and the final product of β-sialon were obtained at the temperature of 1450 °C for 6 h.

This work provides a simple method to prepare prismatic β-sialon with high purity and yield.

## Acknowledgements

Financial supports by National Science Foundation of China (No. 40602008), Research Fund of China University of Geosciences (No. 51900961008) and Research fund of National Laboratory of Mineral Materials (No. A05005) are gratefully acknowledged.

## References

[1] K.H. Jack, W.I. Wilson, Ceramics based on the Si–Al–ON and related systems, Nature 28 (1972) 238–239.
[2] J.G. Lee, I.B. Cutler, Sinterable sialon powder by reaction of clay with carbon and nitrogen, Am. Ceram. Soc. Bull. 58 (9) (1979) 869–871.
[3] Y. Oyama, O. Kamigaito, Silicon and nitride-solid solubility of some oxide in $Si_3N_4$, Jpn. J. Appl. Phys. 10 (1971) 16737–21642.
[4] K.H. Jack, Review: sialons and related nitrogen ceramics, J. Mater. Sci. 11 (1976) 1135–1158.
[5] M. Mitomo, N. Kuramoto, Y. Inomata, Fabrication of high-strength sialon by reaction sintering, J. Mater. Sci. 14 (1979) 2309–2316.
[6] K.H. Jack, The crystal chemistry of the sialons and related nitrogen ceramics, in: F.L. Riely (Ed.), Nitrogen Ceramics, Noordhoff International, Leyden, The Netherlands, 1976, pp. 109–126.
[7] M.H. Lewis, B.D. Powell, P. Drew, The formation of single-phase Si–Al–N–O ceramics, in: F.L. Riely (Ed.), Nitrogen Ceramics, vol. 12, Noordhoff International, Leyden, The Netherlands, 1977, pp. 61–74.
[8] A.D. Mazzoni, E.F. Aglietti, Mechanism of carbonitriding reaction of $SiO_2$–$Al_2O_3$ minerals in Si–Al–ON systems, Appl. Clay Sci. 12 (1998) 447–461.
[9] J.D. Kenneth, MacKenzie, D.V. Barneveld, Carbothermal synthesis of β-sialon from mechanochemically activated precursors, J. Eur. Ceram. Soc. 26 (2006) 209–215.
[10] D. Zhao, J. Feng, Q. Hou, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, Science 279 (1998) 548–552.
[11] Z.J. Shen, M. Nygren, Tailoring microstructures of sialon ceramics by manipulating the kinetics, Key Eng. Mater. 237 (2003) 149–156.
[12] H.W. Ma, Software on Thermodynamics in Crystalline Petrology, Geological Publishing House, Beijing, PRC, 1999, pp. 19–26 (in Chinese).
[13] J. Zheng, B. Forslund, Carbothermal preparation of β-sialon powder at elevated nitrogen pressures, J. Eur. Ceram. Soc. 19 (1999) 175–185.