

Thermochemical Insights into Rapid Solid-State Reaction Synthesis of β -Sialon

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Sialons (Si–Al–O–N) are useful as engineering components because they combine the toughness of silicon nitride with phase stability. Competing reactions occur during conventional processing, making it difficult to form single-phase material without high-temperature/long-time heat treatments. Thermochemical insights into sialon formation are complicated by impure samples, glassy phases, and slow reactions. Here we report the first direct thermochemical measurement of the energetics of a specially synthesized (single-phase, glass-free) β -sialon of composition $\text{Si}_{3.17}\text{Al}_{2.83}\text{O}_{2.83}\text{N}_{5.17}$ by dissolution calorimetry in molten (Li,Na) BO_2 at 770 °C. A remarkable feature of our synthesis by a pulsed electric discharge method is that the unreacted starting powders (aluminum oxide, aluminum nitride, and silicon nitride) were simultaneously reacted and densified to form the single-phase β sialon, all in just 7 min—a hitherto unattained processing record. Thermochemical measurements gave the first direct determination of the standard enthalpy of formation: -67.8 ± 15.5 kJ/mol from the compounds and -2768.3 ± 8.2 kJ/mol from the elements. The thermochemical data suggest new, possibly self-sustaining, reaction paths to refractory nitride materials.

Although solid-state synthesis by cation substitution has produced many ceramic oxides, replacement of anions also forms a rich variety of non-oxide ceramics and glasses (e.g., silicon oxynitrides called sialons^{1,2}). Conventional synthesis of sialons,^{3,4} by sintering of pressed powdered mixtures of Si_3N_4 and Al_2O_3 at high temperatures, usually requires 1 h to several days. Alternately, hot pressing^{5,6} or hot isostatic pressing (HIP)⁷ produces fully dense sialon parts while pressureless sintering⁸ offers the flexibility of producing complex shapes. A number of synthesis methods, including carbothermal reduction of aluminosilicates in nitrogen,⁹ sol–gel processing,¹⁰ and combustion synthesis,¹¹ can also lead to sialon powders that are subsequently consolidated. Notwithstanding their frequent use in modern materials processing, the above methods of sialon production always involve two steps (reaction(s) to form the sialon powder followed by densification) and often lead to microstructures with multiple phases and glassy films at the grain boundaries. Obtaining reliable thermochemical data by direct calorimetric measurements thus suffers from two critical problems: (i) the lack of phase pure samples and (ii) the absence of a well-defined calorimetric reaction, such as dissolution in a suitable solvent, to obtain thermochemical data on these very refractory materials. Here we report thermochemical insights developed from the first calorimetric measurements on a glass-free β -sialon synthesized by a special electric pulse discharge method. This method starts with the constituent powders and reacts them to form the β -sialon, which is simultaneously densified to a bulk solid—the whole process being completed in just 7 min. While earlier work¹² showed that the electric pulse process consolidates nanometer size powders (e.g., AlN, YBCO) without grain growth, the present work demonstrates for the first time that unreacted constituent powders undergo rapid reaction to form the β -sialon phase parallel with densification.

In our synthesis of $\text{Si}_{3.17}\text{Al}_{2.83}\text{O}_{2.83}\text{N}_{5.17}$, a ground mixture of starting powders was placed in a graphite die. The starting powders (particle size of the order of a few micrometers) consisted of silicon nitride and aluminum oxide (from Alfa Aesar) and a low oxygen content aluminum nitride powder

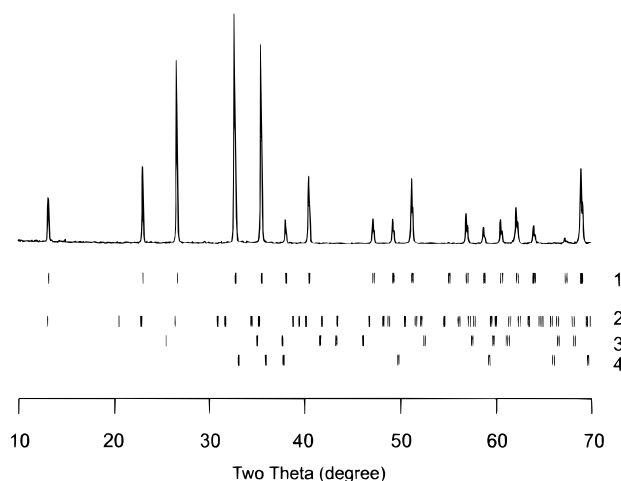


Figure 1. Powder X-ray diffraction pattern of the β -sialon sample after simultaneous rapid solid-state reaction and densification. X-ray diffraction patterns of the unreacted starting materials are also shown to confirm that the synthesis product is phase pure. The patterns are (1) β -sialon, $\text{Si}_{3.17}\text{Al}_{2.83}\text{O}_{2.83}\text{N}_{5.17}$, indexed in space group $P6_3$; (2) silicon nitride (α); (3) aluminum oxide; (4) aluminum nitride.

(supplied by Dow Chemical Company). The synthesis involved applying a 25 V/750A dc electrical pulse (90 ms on/off cycles for a total time of 60 s) and, immediately thereafter, resistance heating to 1800 °C (360 s) to form a dense disk. Powder X-ray diffraction showed a single-phase material, identified as a β -sialon phase, with sharp peaks indicating good crystallinity and no peaks for other phases (Figure 1).

The unit cell parameters were refined in the $P6_3$ space group using Rietveld methods and the program GSAS. They are $c = 7.6785(1)$ Å and $a = 2.9769(1)$ Å, which gives a cell volume of $152.00(1)$ Å³. The cell dimensions fall close to the regression lines given by Haviar and Jonhannesen¹³ relating cell dimensions to composition. Examination of this sample using a Cameca SX50 electron microprobe (with spectrometers set for Si, Al, O, and N) revealed a very homogeneous sample with no significant variation of count rates across a traverse including 10–15 different points and gave the expected Si:Al stoichiometry. The specimen for transmission electron microscopy (TEM)

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TABLE 1: Enthalpy of Formation of Sialon from Oxides and Nitrides^a

	reaction	ΔH (kJ/mol)
(1)	$\text{Si}_{3.17}\text{Al}_{2.83}\text{O}_{2.83}\text{N}_{5.17}(\text{crystal}, 25^\circ\text{C}) + 3.878\text{O}_2(\text{gas}, 770^\circ\text{C}) \rightarrow 3.17\text{SiO}_2(\text{dissolved}, 770^\circ\text{C}) + 1.415\text{Al}_2\text{O}_3(\text{dissolved}, 770^\circ\text{C}) + 2.585\text{N}_2(\text{gas}, 770^\circ\text{C})$	-2228.8 ± 8.2 (17)
(2)	$\text{Si}_3\text{N}_4(\alpha, \text{crystal}, 25^\circ\text{C}) + 3\text{O}_2(\text{gas}, 770^\circ\text{C}) \rightarrow 3\text{SiO}_2(\text{dissolved}, 770^\circ\text{C}) + 2\text{N}_2(\text{gas}, 770^\circ\text{C})$	-1897.2 ± 12.3 (10)
(3)	$\text{AlN}(\text{crystal}, 25^\circ\text{C}) + \frac{3}{4}\text{O}_2(\text{gas}, 770^\circ\text{C}) \rightarrow \frac{1}{2}\text{Al}_2\text{O}_3(\text{dissolved}, 770^\circ\text{C}) + \frac{1}{2}\text{N}_2(\text{gas}, 770^\circ\text{C})$	-456.0 ± 1.7 (5)
(4)	$\text{Al}_2\text{O}_3(\text{crystal}, 25^\circ\text{C}) \rightarrow \text{Al}_2\text{O}_3(\text{dissolved}, 770^\circ\text{C})$	135.2 ± 1.1 (8)
	$1.057\text{Si}_3\text{N}_4(\alpha) + 0.943\text{AlN} + 0.943\text{Al}_2\text{O}_3 \rightarrow \text{Si}_{3.17}\text{Al}_{2.83}\text{O}_{2.83}\text{N}_{5.17}$ $\Delta H_f = -\Delta H_1 + 3.17\Delta H_2 + 0.943\Delta H_3 + 0.943\Delta H_4$	-67.8 ± 15.5

^a The heat effect for reactions 1–4 was measured by oxidative drop solution calorimetry. Value is mean of the number of experiments indicated in parentheses. Error is 2 standard deviations of the mean.

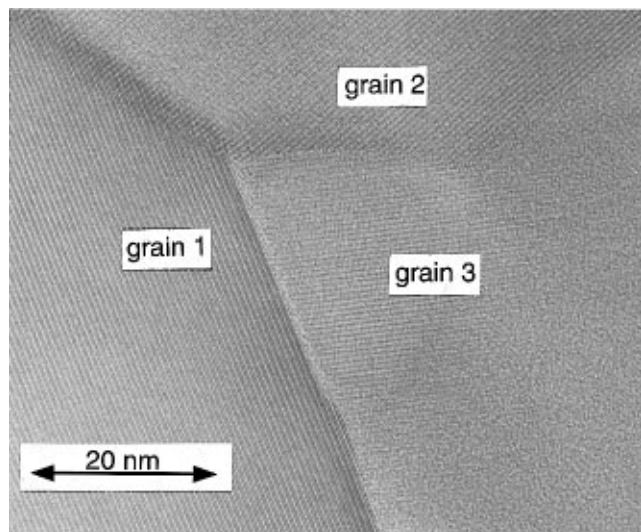


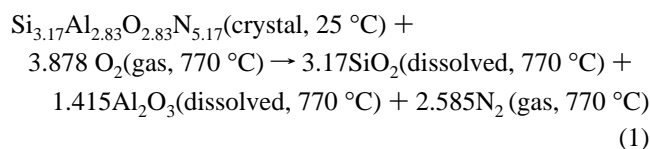
Figure 2. High-resolution transmission electron microscopy (HRTEM) image of the β -sialon sample showing lattice fringes in all three grains with no amorphous films at grain boundaries or the triple-point junction.

was prepared by mechanical thinning to about 100 μm , followed by dimple grinding to a thickness of about 10 μm and final thinning to electron transparency by Ar ion-beam milling using a liquid nitrogen cooled stage. High-resolution transmission electron microscopy (HRTEM) data were collected with a JEOL ARM-1000 with 1.6 D point to point resolution (at 1000 kV) operated at 800 kV. Low-magnification TEM images showed an approximate grain size of 2 μm . The electron diffraction pattern showed no halos indicative of an amorphous phase. Excellent grain–grain contact in several regions examined by HRTEM and the lattice fringes (Figure 2) are evidence of crystallinity and the absence of glassy phase at the grain boundaries.

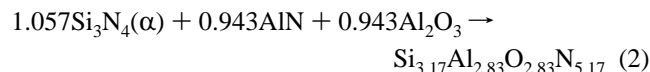
Thermochemical measurements were made on the above sialon sample on the basis of our recent progress in applying high-temperature solution calorimetric techniques to nitrides. The new experimental method we have developed involves oxidative dissolution to convert the nitride or oxynitride into a dissolved mixture of oxides plus evolved nitrogen gas at high temperature in a Calvet-type microcalorimeter.^{14–18} The lead borate solvent commonly used for oxides^{14,17} is not suitable because of reduction of lead by the nitride. However, good results for some molybdenum and tungsten nitrides were obtained using a sodium molybdate solvent, $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$.¹⁵ McHale et al.,¹⁶ in a calorimetric study of the Ca–Zn–N system, showed that the molten molybdate acts as an oxidation catalyst. Transient reduction of Mo^{6+} to lower oxidation states speeds the dissolution by transporting reduced species away from the surface of the dissolving nitride into the bulk of the melt, where they are rapidly reoxidized by O_2 gas bubbled through the solvent. This gas bubbling also stirs the melt effectively.

Sialons present a special experimental problem in that their oxidation products, SiO_2 and Al_2O_3 , dissolve very slowly or not at all in molten sodium molybdate. We have therefore developed a new technique that combines the advantages of molybdate-catalyzed oxidation and an alkali borate solvent (52 wt % $\text{LiBO}_2 \cdot 48$ wt % NaBO_2), which contains no reducible cations and readily dissolves alumina and silica.¹⁸ The enthalpies of oxidative solution of Si_3N_4 , AlN, and the sialon sample were measured at 770 $^\circ\text{C}$. Drop solution techniques^{14,17} were used, in which the samples were dropped from room temperature into the alkali borate solvent at 770 $^\circ\text{C}$. Oxygen gas was both bubbled through the solvent and flushed over it. In addition to providing a strong oxidizing environment on the top surface of the melt, the flushing also helps to accelerate reaction by removing the nitrogen gas evolved. To provide catalysis by molybdate species, which proved to be essential for rapid reaction, the sialon was mixed with sodium molybdate, $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$, in a weight ratio of sialon:molybdate = 1:3. The heat effect associated with the molybdate was measured by separate drops of pellets made of $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ and was subtracted from the total heat effect measured.

The heat effect associated with the nitride or sialon sample includes the heat content involved in raising its temperature to that of the calorimeter and the heat of oxidative dissolution of the sample. The calorimetric reaction is:



The measured enthalpies of drop solution are given in Table 1, which also gives the thermochemical cycles needed to calculate the enthalpy of formation. For the reaction



the enthalpy of formation (from oxide and nitrides at 25 $^\circ\text{C}$) is substantially exothermic, -67.8 ± 15.5 kJ mol⁻¹. This corresponds to a standard enthalpy of formation from the elements of -2768.3 ± 8.2 kJ mol⁻¹ (see Table 2).

This calorimetric determination represents the first direct thermochemical data ever obtained for a well-characterized sialon phase. Moon et al.²⁰ reported an indirect measurement of the enthalpy by mass spectrometry for two more aluminum-rich sialons. Though their data show large uncertainties (25–50 kJ/mol), they appear generally compatible with our new data, with the heat of formation from the elements becoming more exothermic with increasing Al/(Al + Si) ratio. Our data also show that the sialon is significantly more stable in enthalpy (and also, free energy, since the $T\Delta S$ is likely to be small) than the nitrides/oxide mixture. Using these new thermochemical data,

