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Low-Temperature Synthesis of Nanocrystalline α-Si_3N_4 Powders by the Reaction of Mg_2Si with NH_4Cl

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Nanocrystalline α-Si_3N_4 powders have been prepared with a yield of 93% by the reaction of Mg_2Si with NH_4Cl in the temperature range of 450° to 600°C in an autoclave. X-ray diffraction patterns of the products can be indexed as the α-Si_3N_4 with the lattice constants $a = 7.770$ and $c = 5.627$ Å. X-ray photoelectron spectroscopy analysis indicates that the composition of the α-Si_3N_4 samples has a Si:N ratio of 0.756. Transmission electron microscopy images show that the α-Si_3N_4 crystallites prepared at 450°, 500°, and 550°C are particles of about 20, 40, and 70 nm in average, respectively.

I. Introduction

SILICON nitride (Si_3N_4) is a very important material for high-temperature applications due to its attractive properties. Such properties include thermal and chemical stability, high strength, stiffness, and good wear, creep and corrosion resistance.[1]

Traditionally, Si_3N_4 powders were prepared by carbothermal reduction of silica in the temperature range of 1500° to 1550°C,[2] or by nitridation of silicon powders in nitrogen in temperatures ranging from 1200° to 1400°C.[3] Some other reactions also developed to prepare Si_3N_4 include: the reaction of $SiCl_4$ with NH_3 to form ultrafine Si_3N_4 powders;[4] the gas-phase ammonolysis of SiH_4 in 500°–1100°C to produce amorphous silicon nitride powders of 50–200 nm;[5] and the pyrolysis of an organic precursor, which was prepared by hydrolyzing a mixture of phenyltrimethoxysilane and tetraethoxysilane in 500°–600°C under nitrogen followed by annealing in 1450°–1550°C to form crystalline Si_3N_4 powders.[6] F. Hofer *et al.* prepared mixtures of oxynitride and nitride of silicon by the reaction of $CaSi_2$ with NH_4Cl.[7] α-Si_3N_4 fibers were prepared by ammonolysis of FeSi at 1370°C,[8] and Si_3N_4 mixtures of both α and β phases were produced by the nitridation of high-silicon ferrosilicon in nitrogen at temperatures ranging from 1300°–1500°C.[9] In earlier research, we prepared nanocrystalline Si_3N_4 through a novel reaction of excessive $SiCl_4$ with NaN_3 heated at 670°C for 30 min in an autoclave.[10] As the reaction is strongly exothermic (calculated $\Delta H^o = -920$ kcal·mol^{-1}), the product, a mixture of α- and β-Si_3N_4, may actually be formed due to instantaneously high local temperature.

In this paper, we report a reaction of Mg_2Si with NH_4Cl in the temperature range of 450°–600°C in an autoclave under a pressure

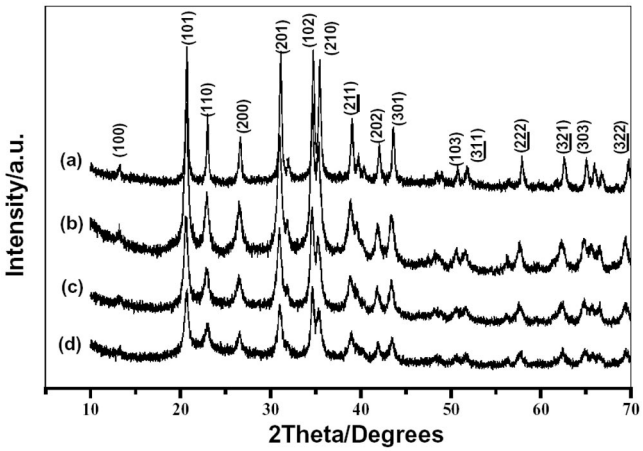

Fig. 1. XRD patterns of the products prepared by reacting Mg_2Si with NH_4Cl for 10 h in an autoclave at (a) 450°, (b) 500°, (c) 550°, and (d) 600°C.

Table I. The X-ray Diffraction Spectrum of the As-prepared α-Si_3N_4 Compared with that of JCPDS# 83-0700

	Experimental		JCPDS# 83-0700	
No.	2θ	d (Å)	*hkl*	d (Å)
1	13.200	6.7013	100	6.7246
2	20.611	4.3056	101	4.3157
3	22.920	3.8768	110	3.8825
4	26.472	3.3641	200	3.3626
5	31.005	2.8818	201	2.8863
6	31.840	2.8081	002	2.8137
7	34.572	2.5923	102	2.5956
8	35.32	2.5392	$\bar{2}10$	2.5416
9	38.872	2.3148	$\bar{2}11$	2.3163
10	39.556	2.2763	$\bar{1}12$	2.2783
11	40.194	2.2416	300	2.2415
12	41.881	2.1552	202	2.1578
13	43.428	2.0819	301	2.0824
14	46.914	1.9350	$\bar{2}20$	1.9412
15	48.182	1.8870	$\bar{2}12$	1.8861
16	48.911	1.8606	310	1.8650
17	50.538	1.8044	$\bar{1}03$	1.8068
18	51.586	1.7702	$\bar{3}11$	1.7703
19	56.091	1.6382	$\bar{2}03$	1.6381
20	57.641	1.5978	$\bar{2}22$	1.5978
21	61.539	1.5056	$\bar{2}13$	1.5093
22	62.239	1.4904	$\bar{3}21$	1.4878
23	64.716	1.4392	$\bar{3}03$	1.4385
24	65.642	1.4211	$\bar{4}11$	1.4199
25	66.430	1.4061	$\bar{0}04$	1.4068
26	69.419	1.3527	$\bar{3}22$	1.3527

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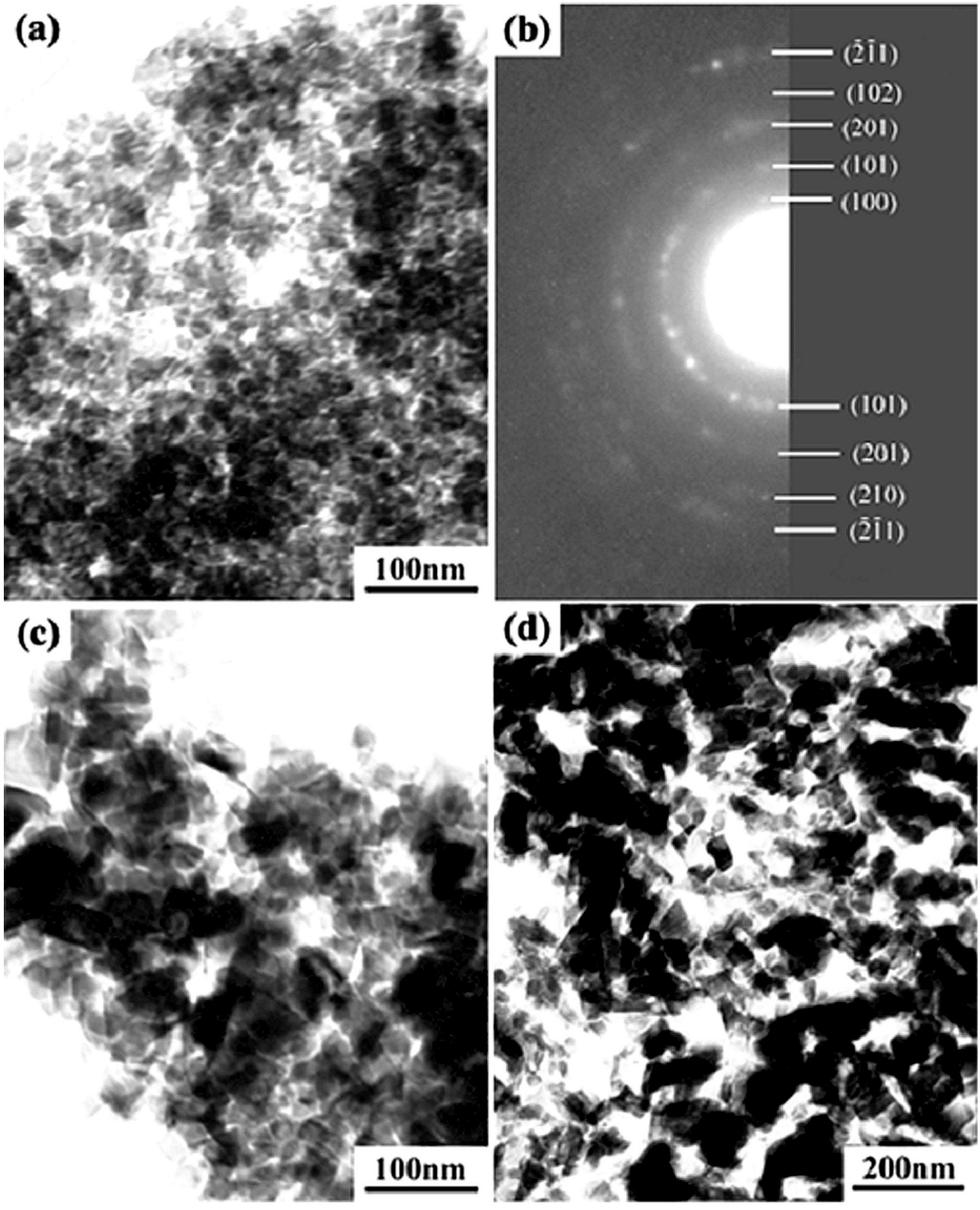

Fig. 2. TEM images and selected area electron diffraction (SAED) patterns of the α-Si_3N_4 samples prepared at (a and b) 450°, (c) 500° and (d) 550°C.

of about 30–40 MPa. Preparation of nanocrystalline α-Si_3N_4 powders are based on the reaction as follows:

$$3\,Mg_2Si + 12\,NH_4Cl \xrightarrow{450\text{–}600\ ^\circ C} \text{alpha-}Si_3N_4 + 6\,MgCl_2 + 8\,NH_3 + 12\,H_2 \quad (1)$$

II. Experimental Procedure

In a typical process, 26.08 mmol of Mg_2Si (99.5%, stock # 12837 Alfa Aesar, Ward Hill, MA, USA) and 0.1047 to 0.1122 mol of NH_4Cl (99.5%, analytical pure grade, Shanghai Chemical Reagent Corp., Shanghai, P. R. China) were mixed and placed in an autoclave with a glass-tube liner. The autoclave of

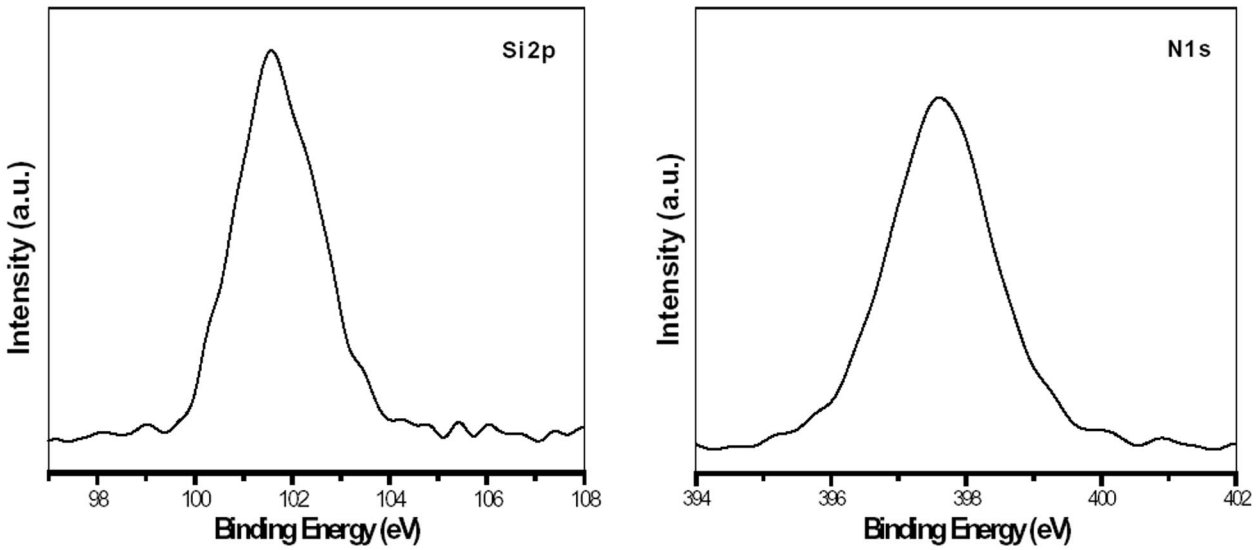

Fig. 3. XPS spectra of the as-prepared α-Si_3N_4 powders.

about 75 mL in capacity was sealed under an argon atmosphere and maintained at 450°, 500°, 550°, and 600°C (± 5°C) for 10 h. The autoclave was cooled to room temperature naturally. The products were collected and washed with distilled water several times to remove $MgCl_2$ and remaining NH_4Cl. The final products were dried in vacuum at 70°C for 12 h and white powder products were obtained.

III. Results and Discussion

The X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (XRD)(D/MAX-γA, Rigaku, Japan) with Cu Kα radiation (wavelength λ = 1.54178 E). Figure 1 shows the XRD patterns of the as-prepared products at 350°–600°C. As shown in Table I, all the 26 peaks can be indexed as the hexagonal cell of α-Si_3N_4, with lattice constants of $a = 7.770$ and $c = 5.627$ Å (The rms error is 3.153×10^{-4}, calculated by the least squares fitting method), in good agreement with $a = 7.765$ and $c = 5.627$ Å (JCPDS card# 83–0700). No evidence of β-Si_3N_4, cubic-Si_3N_4, and impurities were observed. As reaction temperatures decrease from 600° to 450°C, the diffraction peaks broaden, indicating the crystalline particles of the products become smaller.

The morphology of the α-Si_3N_4 powders was investigated by transmission electron microscopy (TEM) (H-800, Hitachi, Japan), which was taken with a Hitachi H-800 transmission electron microscope. Figure 3 shows the typical TEM images and selected area electron diffraction (SAED) patterns of the samples prepared at 450°, 500°, and 550°C for 10 h. The products have particle morphology. The α-Si_3N_4 crystallites prepared in 450° (Fig. 3(a) and (b)), 500° (Fig. 3(c)), 550° (Fig. 3(d)), and 600°C (not published) are about 20, 40, 70, and 90 nm in average, respectively. As shown in Fig. 3(b), the diffraction rings from inner to outer, at d-spacings of 6.70, 4.29, 2.90, 2.60, 2.54, and 2.30 Å, match α-Si_3N_4 (100), (101), (201), (102), (210) and (−2–11) planes, in good agreement with the XRD results.

The composition of the as-prepared α-Si_3N_4 powders was studied by X-ray photoelectron spectroscopy (XPS) (ESCALAB MKII, VG Scientific, U.K.), which was recorded on a VGES-CALAB MKII X-ray photoelectron spectrometer with a non-monochromatized Mg Kα X-rays (h_γ = 1253.6 eV) as the excitation source. As shown in Fig. 2, the binding energy of Si*2p* and N*1s* are 101.70 and 397.75 eV, respectively, which are in good agreement with those of Si_3N_4 (101.7–102.34 eV and 397.4–397.9 eV, respectively[11,12,13,14,15]). The quantification of the peaks gives a Si:N ratio of 0.756, which is close to that of Si_3N_4 (0.750). In addition to silicon and nitrogen, no other peaks were observed in the wide-scan XPS spectrum except a small amount of carbon (reference mark) and oxygen, with binding energies of C*1s* and O*1s* at 284.26 and 531.95 eV, respectively, in which oxygen is from surface adsorption.[16]

According to the free energy calculations, the reaction between Mg_2Si and NH_4Cl to form α-Si_3N_4, $MgCl_2$, NH_3, and hydrogen gases is thermodynamically spontaneous (calculated $\Delta G^o = -400$ kcal·mol^{-1}) and mildly exothermic (calculated $\Delta H^o = -227$ kcal·mol^{-1}). A gust of gases with an ammonia smell were noticed when the autoclave was unsealed. An approximately stoichiometric amount of $Mg(OH)_2$ according to the amounts of Mg_2Si was obtained by treating the water used to wash products with NaOH. The maximal pressure is about 30 to 40 MPa in the temperature range of 450° to 600°C, which is estimated according to the amount of NH_3 and hydrogen treated as ideal gases. Varying the reaction temperature in the range of 450°–600°C did not significantly affect the crystallinity or the yields of Si_3N_4 (about 93% according to the amount of Mg_2Si). In comparison, polycrystalline silicon powders were found unreacted and Si_3N_4 was not produced when excessive NH_4Cl and mixed powders of magnesium and silicon were heated at 600°C for 10 h in an autoclave. A mixture of amorphous Si_3N_4 and polycrystalline silicon was produced when $CaSi_2$ (Alfa Aesar, stock #14676) was heated with excessive NH_4Cl at 600°C for 10 h in an autoclave. When FeSi powders (primitive cubic phase, $a = 4.415$ Å, prepared by the reaction of $FeCl_3$ and Mg_2Si at 600°C for 12 h[17]) were used instead of Mg_2Si, Si_3N_4 was not produced and the FeSi remained unreacted, indicating that Mg_2Si is the key factor for preparing nanocrystalline α-Si_3N_4 at the low temperature range of 450° to 600°C.

IV. Conclusions

In summary, about 20- to 90-nm α-Si_3N_4 powders have been prepared by the reaction of Mg_2Si with NH_4Cl in the temperature range of 450° to 600°C in an autoclave. XRD patterns of the products can be indexed as α-Si_3N_4 with the lattice constants of $a = 7.770$ and $c = 5.627$ Å. XPS analysis indicates that the composition of the α-Si_3N_4 samples has a Si:N ratio of 0.756. Such nanocrystalline α-Si_3N_4 powders hold great potential for improving properties of ceramic structural materials. This study demonstrates an important route to nanocrystalline α-Si_3N_4 that can be applied for industrial use in the future.

References

[1]F. Rodriguezreinoso and J. Narciso, "Synthesis of SiC and Si_3N_4–An Overview," *Adv. Mater.*, **7** [2] 209–11 (1995).

[2]S. J. P. Durham, K. Shanker, and R. A. L. Drew, "Carbothermal Synthesis of Silicon Nitride–Effect of Reaction Conditions," *J. Am. Ceram. Soc.*, **74** [1] 31–37 (1991).

[3]V. Pavarajarn and S. Kimura, "Catalytic Effects of Metals on Direct Nitridation of Slicon," *J. Am. Ceram. Soc.*, **84** [8] 1669–74 (2001).

[4]H. R. Orthner, R. Brink, and P. Roth, "Synthesis of Ultrafine Silicon Nitride Powders," *Int. J. Meter. & Product Tech.*, **15** [6] 495–502 (2000).

[5]S. Sahu, S. Kavecky, and J. Szepvolgyi, "Preparation of Fine Amorphous Silicon Nitride Powder in the System SiH_4-Ar-NH_3," *J. Eur. Ceram. Soc.*, **15** [11] 1071–77 (1995).

[6]J. Y. Choi, Y. T. Moon, D. K. Kim, and C. H. Kim, "Pyrolytic Conversion of Spherical Organo-silica Powder to Silicon Nitride Under Nitrogen," *J. Am. Ceram. Soc.*, **81** [9] 2294–2300 (1998).

[7]F. Hofer, W. Veigl, and E. Hengge, "Preparation of Mixtures of Silicon Oxynitride and Silicon Nitride by the Reaction of Calcium Silicide with Ammonium Chloride," *Adv. Mater.*, **4** [7–8] 501–04 (1992).

[8]T. E. Warner and D. J. Fray, "Synthesis of Silicon Nitride Fibers from Ferrosilicon," *J. Mater. Sci. Lett.*, **19** [9] 733–34 (2000).

[9]M. V. Vlasova, V. A. Lavrenko, L. Y. Dyubova, J. G. Gonzalez-Rodriguez, and M. G. Kakasey, "Nitriding of Ferrosilicon Powders," *J. Mater. Synthesis & Processing*, **9** [3] 111–17 (2001).

[10]K. B. Tang, J. Q. Hu, Q. Y. Lu, Y. Xie, J. S. Zhu, and Y. T. Qian, "A Novel Low-Temperature Synthetic Route to Crystalline Si_3N_4," *Adv. Mater.*, **11** [8] 653–55 (1999).

[11]T. Goto and T. Hirai, "ESCA Study of Amorphous CVD Si_3N_4-BN Composites," *J. Mater. Sci. Lett.*, *7*, 548–50 (1988).

[12]G. M. Ingo and N. Zacchetti, "XPS Investigation on the Growth-Mode of *a*-SiN*x* and Silicon and Nitrogeon Chemical Bondings," *High Temperature Sci.*, **28** 137–51 (1990).

[13]G. M. Ingo, N. Zacchetti, D. della Sala, and C. Coluzza, "X-ray Photoelectron Spectroscopy Investigation on the Chemical Structure of Amorphous Silicon Nitride (*a*-SiN_x)," *J. Vac. Sci. Technol.*, **A7**[5] 3048 (1989).

[14]J. A. Taylor, G. M. Lancaster, and J. W. Rabalais, "Chemical Reactions of N_2^+ Ion Beams with Group IV Elements and Their Oxides," *J. Electron Spectrosc. Relat. Phenom.*, **13**[3] 435–44 (1978).

[15]J. A. Taylor, G. M. Lancaster, A. Ignatiev, and J. W. Rabalais, "Interactions of Ion Beams with Surfaces. Reactions of Nitrogen with Silicon and Its Oxides," *J. Chem. Phys.*, **68**[4] 1776–84 (1978).

[16]A. Pashutski, A. Hoffman, and M. Folkman, *Surf. Sci.* **208**, L91–L97, (1989).

[17]J. C. Fitzmaurice, A. L. Hector, I. P. Parkin, and A. T. Rowley, "Synthesis of Metal Silicide Powders by Thermolysis of Metal Chlorides with Magnesium Silicide," *Phosphorus Sulfur & Silicon & Relat. Elements*, **101** [1–4] 47–55 (1995). □