Analysis of Si₃N₄ Ultra Fine Powder Using High-pressure Acid Digestion and Slurry Injection in Inductively Coupled Plasma Atomic Emission Spectrometry

K. H. Kim, H. Y. Kim, and H. B. Lim*

College of Natural Science, Dankook University, Youngsan-Ku, Hannam-Dong Mt. #8, Seoul 140-714, Korea
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Si₃N₄ powder has been analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The sample was dissolved by high-pressure acid digestion with HF, H₂SO₄ (1+1), and HNO₃ mixture. This technique is well suited for the impurity analysis of Si₃N₄ because the matrix interference is eliminated. A round-robin samples trace elements, such as Ca, W, Co, Al, Fe, Mg, and Na, were determined. For the direct analysis, slurry nebulization of 0.96 mm Si₃N₄ powder also has been studied by ICP-AES. Emission intensities of Fe were measured as ICP operational conditions were changed. Significant signal difference between slurry particles and aqueous solution was observed in the present experiment. Analytical results of slurry injection and high-pressure acid digestion were compared. For the use of aqueous standard solution for calibration, k-factor was determined to be 1.71 for further application.

Keywords : Si₃N₄, Slurry nebulization, Inductively coupled plasma spectrometry, Atomic emission spectrometry, Acid digestion.

Introduction

Silicon nitride materials have great potential for high temperature, load-bearing application, such as in heat engines, because of their high strength, high thermal-shock resistance, and good oxidation resistance.[1-3] Physical properties of silicon nitride can be determined by controlling not only major constituents but also trace impurities, additives and microstructure.[4,5] Inductively coupled plasma atomic emission spectrometry (ICP-AES) is commonly used for the impurity analysis of ceramic materials.[6-11] However, the conventional dissolution process for ceramics can encounter analytical problems, such as loss of volatile elements and contamination. Significant advances have been made in sample pretreatment and introduction techniques. High-pressure acid digestion is one of the methods used for the dissolution because of relatively small analyte loss and less contamination. But the toilsome and time-consuming dissolution process still remains a problem.

Slurry injection in ICP-AES has been of increasing interest in recent years.[6,12-21] It is a versatile technique for sample introduction, offering many advantages over conventional sample preparation, such as reduced pretreatment time and a lower rate of contamination. However, there are still problems to be solved in slurry injection of ICP-AES, for instance, homogeneity and stability of the slurry sample. In addition, the lack of standard materials makes it difficult to determine impurities in ultra fine ceramic powders. Therefore, the behavior of aqueous droplets and slurry particles should be fully understood for quantitative analysis.

For calibrations using aqueous solutions, both the analyte transport efficiency and the subsequent atomization efficiency of the slurry particle must be identical to those of a simple aqueous solution.[14] Unlike in an aqueous aerosol, the efficiencies in slurries are dependent on the thermal decom-

position of the individual constituents and their particle dimensions. The factors influencing these efficiencies, such as slurry stabilization mechanism, particle size, and slurry preparation, are discussed in a review article.[22] The stable dispersion is related to the homogeneity of slurry and reproducibility of analytical results. Mechanical stirring, ultrasonification, addition of dispersant, and adjustment of pH are the methods commonly used to prevent aggregation and flocculation of the particles.

One way to minimize the signal difference between slurries and aqueous solutions in ICP-AES is the optimization of aerosol gas-flow rate. Reports show that the aerosol gas-flow rate for maximum intensities of slurries increases as particle size decreases and maximizes for aqueous solution.[12,13] The signal intensities of slurries and the solution were equal at low aerosol flow rate. Also noticed was that the application of k-factors compensated for incomplete recoveries when major, minor and trace elements were determined by ICP-AES using aqueous standards.[18]

In the present work, Si₃N₄ ceramic powders were analyzed by ICP-AES with two different sample treatment techniques. One of the methods was high-pressure acid digestion for dissolution and the other was direct slurry injection. For the former, reference materials and round-robin test samples were analyzed by the standard addition method. For the latter, it is intended to develop a convenient slurry preparation technique to provide fast and contamination-free analysis and minimize the use of dispersion additives.

Experimental Section

Apparatus and operating condition. Details of the Jobin-Yvon 138 (JY 138) high-resolution nitrogen purge monochromator are given in Table 1. This instrument is equipped with a 40.68 MHz RF generator with a demount-

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Table 1. Instrument Operating Conditions in ICP-AES

ICP	Operating conditions
Model	JY 138 (Jovin–Yvon)
Generator	Frequency : 40.68 MHz
	Forward power : 1.0 kW
Torch	Demountable type
	With sheath gas flow
	Coolant gas flow : 12 L/min
	Auxiliary gas flow : 0.1 L/min
	Aerosol gas flow : 0.9 L/min for slurry
	1.0 L/min for acid digestion
	Observation height : 15 mm
Nebulizer	Concentric (Meinhard)
	Spray chamber : Scott type double pass
	Sample uptake rate : 2.0 mL/min for acid digestion
	3.0 mL/min for slurry
Optics	Czerny-Turner mount
	1.0 m focal length
	2400 grooves mm^{-1}
	second order grating
	nitrogen purge type

able standard torch and a 1 m focal length monochromator. The instrument was operated at 1.0 kW forward power for the dissolved solution and 1.2 kW for the slurry with a coolant flow of 12 L/min. The sheath gas flow was not used in this work. The sample was delivered to a pneumatic nebulizer (Meinhard, concentric type) for the solution and a maximum dissolved solid nebulizer (MDSN, ARL) for the slurrys using a peristaltic pump. Sample uptake rates were 2 and 3 mL/min, respectively. To obtain particle size distribution, an Accusizer TH770 optical particle sizer was used. The suspended slurry with sodium phosphate dibasic (0.01%) was pumped into the circuit through the cuvette in which a laser beam was scattered by the particles.

Dissolution of Si₃N₄ powder. Si₃N₄ ceramic powders were obtained from Sigma-Aldrich (99%, submicron, USA) and BAM (Federal Institute for Material Research and Testing, Germany for round-robin test). Standard materials, JCRM (Japan Ceramic Reference Material, R004 and R005), were purchased from the Ceramic Society of Japan. About 0.6-0.7 g of Si₃N₄ powder sample was transferred into a Pt crucible (No. 20) followed by the addition of 5 ml of (1+1) H_2SO_4, 7 mL of HF, and 2 mL of HNO_3. The mixture in the Pt crucible was allowed to react for 16 h at 220 °C in a high-pressure closed poly(tetrafluoroethylene) (PTFE) vessel (model HU-50, Mitsuoshi Corp., Nagoya, Japan). The resulting solution in the Pt crucible was heated to evaporate gaseous silicon fluoride and unreacted hydrogen fluoride.

Unless stated otherwise. all the chemicals used in this experiment were the products of Dong Woo Pure Chemical Co., Ltd. (Korea). Standard solutions for Mg, Ca, Fe, and Al were prepared from 1000 mg/mL spectroscopic standards (NIST CRM).

Slurry sample preparation. About 1 g of Si₃N₄ powder was transferred quantitatively into 100-mL volumetric polyethylene flasks and diluted with deionized (DI) water to the mark. Slurries were ultrasonically treated for 30 min before being introduced into the ICP. During the sample delivery, slurry homogeneity was maintained by continuous mechanical stirring. The desired pH for stable and homogeneous slurries was attained by adding HCl and/or NH_4OH. The pH measurements were taken with a Mettler Toledo 320 pH meter.

Results and Discussion

Analysis of Si₃N₄ powder using high-pressure acid digestion. After the Si₃N₄ powder was dissolved and formed into fluorosilicic acid by high-pressure acid digestion. the Si matrix in solution was eliminated by evaporation of gaseous silicon fluoride.[23]

$$H_2SiF_6 \rightarrow SiF_4 + 2HF$$
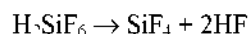
This principle has been used not only for dissolution of elemental silicon in the presence of oxidants, but also for the determination and preparation of standard solutions of silicon dioxides. The procedure accords the advantages of reducing spectral interference of Si matrix in ICP-AES and eliminating HF from the solution. It should be pointed out that the uncontrolled presence of fluorides may often complicate the entire subsequent procedure.

Under the experimental conditions. the concentrations of Al, Fe, Ca, and Mg of JCRM R004 and R005 were determined by standard addition and are listed in Table 2. As shown in Table 2. all experimental results are well agreed with the reference values, and standard deviations are listed. For application. the round-robin test sample supplied from BAM was analyzed by ICP-AES and the results are listed in Table 3. From Table 3, DKU represents the analytical results of our experiment and RRT represents the averages of the analytical results obtained by laboratories participating in the round-robin test. The results of RRT were presented and discussed at the autumn session of the working group "Special materials" of the GDMB in Oct. 1999, in Hanau, Germany.[24] Reproducibility for W was not good due to its poor sensitivity in ICP-AES. The low concentration of Mg in the ceramic powder produced a relatively high standard devia-

**Table 2.** Analytical Results of Standard Si₃N₄ Powder (JCRM) Using ICP-AES with High-pressure Acid Digestion   Unit : wt./wt. %

	sample	Al	Fe	Ca	Mg
JCRM R004	Reference value	0.035 ± 0.002	0.028 ± 0.001	0.0036 ± 0.0002	0.0026 ± 0.0001
	The measured value	0.035 ± 0.001	0.028 ± 0.002	0.0035 ± 0.0002	0.0027 ± 0.0001
JCRM R005	Reference value	0.184 ± 0.004	0.130 ± 0.002	0.222 ± 0.009	
	The measured value	0.182 ± 0.004	0.128 ± 0.001	0.238 ± 0.004	

Table 3. Analytical Results of Round Robin Test Si$_3$N$_4$ Powder Using ICP-AES with High-pressure Acid Digestion　　　　　Unit: μg/mL

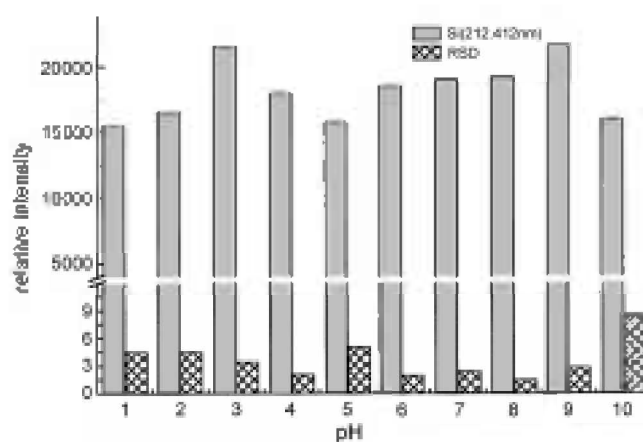| Elements		W	Ca	Al	Co	Fe	Mg	Na
DKU[a]	Mean	43.40	13.89	468.7	43.84	80.07	3.95	7.86
	Std. D.[c]	1.95	0.30	6.4	1.68	1.37	0.36	0.46
RRT[b]	Mean	42.31(20)[d]	14.06(16)	468.7(19)	43.46(20)	79.09(19)	4.24(19)	7.98(18)
	Std. D.	5.31	0.84	10.3	1.67	5.33	0.63	1.75

[a]Analytical result of this work. [b]Average value of the results obtained by the participants for the round robin test. [c]Standard deviation. [d]Numbers of laboratories for averaging.
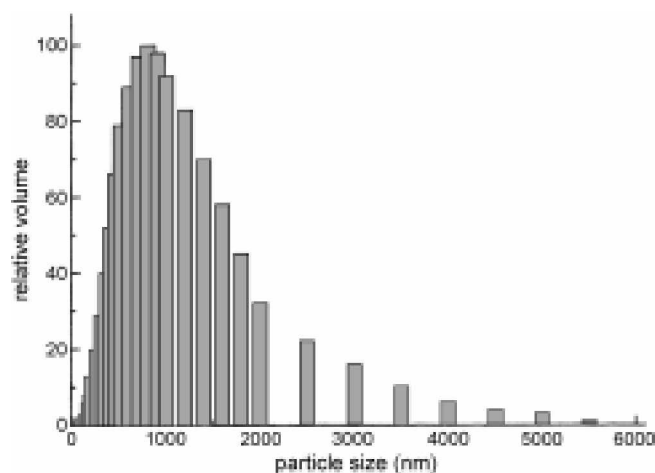
Figure 1. Particle size distribution of commercial Si$_3$N$_4$ powder.

tion in our laboratory, but for the average of the round-robin test it showed good reproducibility. Generally speaking, all results obtained in the present experiment are consistent with all the other corresponding results of the round-robin test and are accepted.

Optimizations for slurry. For the study of slurry injection, Si$_3$N$_4$ powder purchased from Sigma-Aldrich was used. Since particle size of the slurry influences nebulization and atomization efficiencies, it should be controlled carefully for precise quantitative analysis. As shown in Figure 1, the measured mean particle size for the slurry was 0.96 μm. It is known that, if the particle size of the slurry was >1.5 μm, the particles do not behave like aqueous solution in the standard torch ICP-AES, and their intensities can be smaller than that of the solution.[13]

As discussed in the previous reports, the stability of the dispersion is related to the homogeneity of the slurry and a stable dispersion leads to reproducible analytical results.[12] The pH of the slurry must also be controlled for stable suspension by an electrostatic stabilizing mechanism. The repulsion between the constituent colloidal particles that have the same charge on their surface can cause them to disperse homogeneously. Since the most stable condition of the slurry can be obtained when the zeta potential value is high, the best reproducibility can be obtained at a pH far away from the isoelectric point. For Si$_3$N$_4$, the function of pH and zeta potential represents the activity of the acidic group (SiOH) and the basic group (SiNH$_2$, Si$_2$NH, Si$_3$N) of the surface.[25,26] If the basic group is dominant, the potential will be positive. The isoelectric point of Si$_3$N$_4$ powder was in the

range of pH 2-9. In the present study, net Si intensity and relative standard deviation of the slurry were examined as a function of pH, as shown in Figure 2. As shown in Figure 3, relatively small intensity and poor reproducibility were observed at pH 5 and 10. The best signal intensity at acidic condition was obtained at pH 3, when the pH of slurries was varied in the range of 1-10. Observation showed that the slurries were remarkably stable for more than 4 hrs at pH 2 to 4. Therefore, the pH of the slurries was adjusted to 3 in the subsequent analyses.

Effect of operating conditions in ICP-AES. The important factors in slurry analysis are not only particle size and
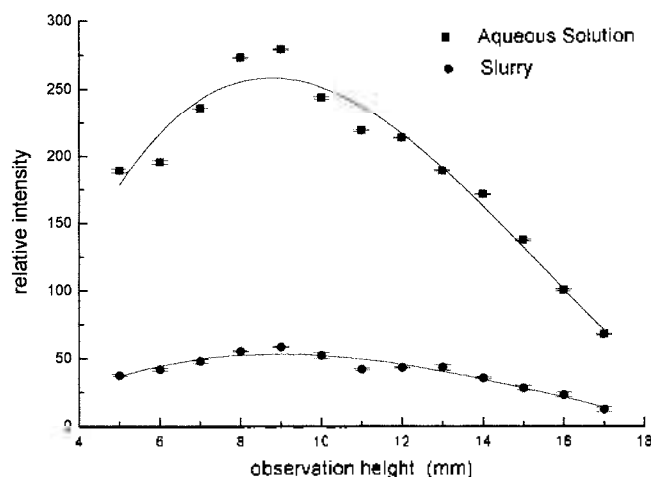

Figure 2. Effect of pH on the emission intensity of Si (212.412 nm) and its relative standard deviation in slurry injection ICP-AES.

Figure 3. Intensity change of Fe (238.204 nm) for Si$_3$N$_4$ slurry as the observation height varied in ICP-AES.

Table 4. Analytical Results of Commercial Si$_3$N$_4$ Powder (0.96 μm) Using ICP-AES   Unit: μg/mL

Element (Wavelength)	High-pressure Acid digestion (Relative Standard Deviation, %)	Slurry Nebulization (Relative Standard Deviation, %)
Fe 238.204 nm	30.0 (3.09)	17.5 (3.86)

stability, but also operating conditions in ICP-AES. such as forward power. observation height, and aerosol flow rate. Those conditions influence analyte transport efficiency and subsequent atomization efficiency in ICP-AES. Height-dependent intensity variations in 0.2-2 μm clay slurries were observed by Laird *et al.*[27] Figures 3 and 4 show the effect of observation height and aerosol flow rate on an emission intensity of ~30 μg/mL Fe (238.204 nm), respectively. As shown in the figures, the best signal intensities for slurries and solutions are obtained at 9 mm above the load coil in observation height and 0.9 mL/min in aerosol gas-flow rate. Another thing that should be noted from the figure is the intensity difference between the slurries and the solution. The direct use of pure solutions for calibration in slurry analysis is limited because the signal-generation process for the solution is different for the slurries. As reported. the aerosol gas-flow rate for maximum intensities of slurries increased as the particle size decreased and maximized for the aqueous solution. and this result corresponds with the relationship between residence time and particle size.[12] From Figure 4. the intensity difference increased with increased aerosol flow rate and maximized at a flow rate of 0.9 mL/min. As expected. the signal intensities of the slurries and solution approached each other and became equal at very low aerosol flow rate because of long residence time and relatively higher temperature. In this work. a significant signal difference for the slurry of 0.96 μm was observed. as shown in the figures. The signal intensities for the slurry were significantly smaller than those for the aqueous solution.

Analysis of Si$_3$N$_4$ powder using slurry injection. Since standard materials are not readily available due to the various chemical compositions of fine ceramics. quantitative analysis is difficult. The use of aqueous standard solution can lead to the reduction of analysis time and labor, which is very important in the manufacturing process. If there were no signal difference between the particles and an aqueous solution. the aqueous calibration could be used. However. as discussed previously, the signal difference was relatively large for the slurries used in this experiment. so true calibration was impossible and large deviation was expected. Table 4 shows the comparison of analytical results of commercially available Si$_3$N$_4$ powder, using slurry injection and high-pressure acid digestion. All analytical results were obtained by the standard addition method. using aqueous standard solution. As shown in Table 4, the concentration of Fe for the acid digestion is higher than that for the slurry.

An alternative method for the compensation is the use of the empirical correction factor. It has been shown that, when analyte concentrations are determined using aqueous standards. the application of *k*-factors can compensate for incomplete recoveries.[18] These factors were defined by the
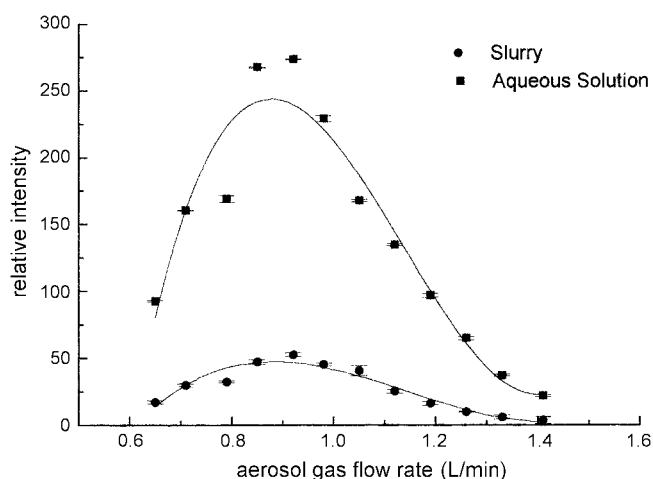
Figure 4. Influence of aerosol gas flow rate on Fe (230.204 nm) intensity for Si$_3$N$_4$ slurry in ICP-AES.

slopes of the correlation functions between the measured and certified values and were reproducible within analytical precision. Since the *k* factors can be influenced by ICP operating conditions. optimized conditions should be constantly maintained for the application. In the present work. the k factor for Fe (238.204 nm) in Si$_3$N$_4$ slurry was determined to be 1.71 by ten replicate experiments at optimized conditions.

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