

# Preparation of nanometer AlN powders by combining spray pyrolysis with carbothermal reduction and nitridation

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## Abstract

Nanometer AlN powders were prepared by combining spray pyrolysis with carbothermal reduction and nitridation (CRN). The aluminum oxide/carbon composite powders prepared by spray pyrolysis from a sucrose spray solution were several microns in size, with hollow and porous structures. Precursor powder with 67 wt% carbon content was transformed into phase-pure AlN powder by CRN at temperatures above 1,400 °C. The hollow-structured AlN powder was ground to 20 nm mean size by simple milling.

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## 1. Introduction

Nano-sized nitride powders have attracted recent research attention due their superior physical properties when compared with conventional micron-sized powders. They require only low-temperature sintering, and have good mechanical-properties and high-temperature superplasticity [1–8].

Aluminum nitride ceramics are attractive materials to the electronics industry due to their high thermal and very low electrical conductivities and thermal expansion coefficients similar to silicon's [9,10]. The high melting point, good thermal stability and corrosion resistance of molten aluminum and cryolyte ensure the growing application of AlN in other fields. Rare earth-doped AlN has been investigated because of its potential applications in blue-UV optoelectronic and micro-electronic devices [11–19].

Syntheses of nano-sized AlN powders by gas and solution phase reactions have been extensively studied for a long time [1,20–28]. In gas phase methods, nano-sized AlN powders are formed by direct nitridation of vaporized Al metal, using various heat sources, such as rf plasma, transferred-arc plasma,

laser beams and electron beams [1,20–23]. Carbothermal reduction and other low-temperature chemical approaches have also been attempted to prepare nano-sized AlN powders [24–28]. Qin *et al.* prepared fine AlN powders by the carbothermal reduction of a combustion-synthesized precursor [29].

Spray pyrolysis has advantages in that it can control the morphology and mean size of multicomponent oxide powders. Therefore, spray pyrolysis has been used in the preparation of the precursor powders for oxide materials [30–34]. It has recently been applied in the preparation of nano-sized oxide powders using spray solutions with organic additives. Metal oxide/carbon composite powders with hollow and thin walled structures have been transformed into nano-sized metal oxide powders after treatment at high temperatures under atmospheric conditions [35–37]. Metal oxide/carbon composite powders prepared by spray pyrolysis have also been used as precursors for the preparation of oxynitride phosphor powders by carbothermal reduction and nitridation (CRN) [38].

In this study, nano-sized AlN powders were prepared by combining spray pyrolysis and CRN. Aluminum oxide/carbon composite powders prepared by spray pyrolysis were transformed into nano-sized AlN powders by CRN.

## 2. Experimental

The spray pyrolysis system used in this work is described in detail elsewhere [34]. It consisted of a droplet generator, quartz

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reactor, and particle collector. A 1.7 MHz ultrasonic spray generator with six vibrators was used to generate large amounts of droplets, which were carried into the high-temperature tubular reactor by a carrier gas. The droplets and particles evaporated, decomposed and/or crystallized in the quartz reactor (length 1,200 mm and diameter 50 mm). The aluminum precursor was aluminum nitrate nonahydrate; it was used in this work at 0.1 M. The concentration of the sucrose carbon source was also fixed at 0.1 M. The flow rate of the air carrier gas was 40 Lmin<sup>-1</sup>. The reactor was maintained at 900 °C. The nitridation of the powders was performed in a tube furnace at temperatures between 1,200 and 1,550 °C under a nitrogen atmosphere. Residual carbon in the nitridation product was removed by firing in air at 700 °C for 1 h.

The crystal structures of the as-prepared and post-treated AlN powders were investigated by X-ray diffractometry (XRD, RIGAKU, DMAX-33). Particles' morphologies were investigated by scanning electron microscopy (SEM, JEOL, JSM 6060) and high-resolution transmission electron microscopy (TEM, FEI, Technai, 300 K). The precursor's thermal properties were measured on a thermo-analyzer (TG-DSC, Netzsch, STA409C, Germany) between 40 and 900 °C (10 °C/min).

### 3. Results and discussion

The morphology of the aluminum oxide/carbon composite powder prepared by spray pyrolysis is shown in Fig. 1. The particles were hollow and spherical. The high flow rate of the carrier gas and the high rate of gas evolution by the decomposition of the aluminum precursor and sucrose was responsible for their hollow structures. The precursor's TG curve (Fig. 2) clearly shows two weight losses below 600 °C. The first pronounced weight loss at below 200 °C was related to the evaporation of adsorbed water. The second weight loss at below 600 °C was related to the decomposition of carbon. The exothermic peaks at 379 and 475 °C in the DSC curve (Fig. 2)

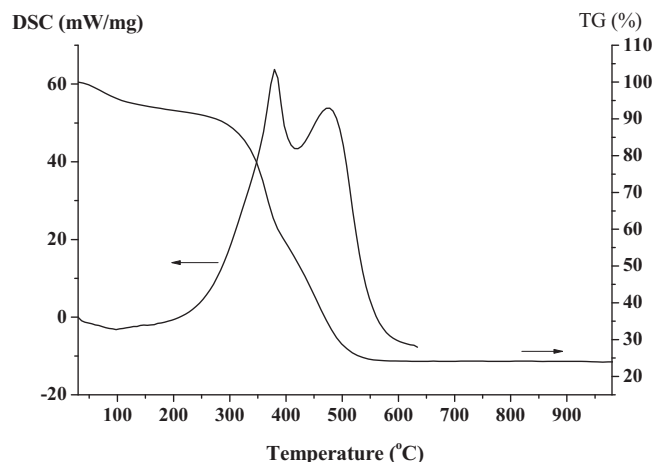


Fig. 2. TG/DSC curves of the precursor powders prepared by spray pyrolysis.

indicate the decomposition of residual carbon. The weight losses by the evaporation of water and by the decomposition of carbon were 9 and 67 wt%, respectively. This work employed spray pyrolysis at a high flow rate of carrier gas, 40 Lmin<sup>-1</sup>, which resulted residence times of the particles inside the hot wall reactor as short as 0.5 s. Therefore, incomplete decomposition of the carbon components was observed even in an air atmosphere.

Fig. 3 shows XRD patterns of the post-treated powder at various temperatures under nitrogen gas. Nitridation of the aluminum oxide powders occurred even at the relatively low temperature of 1,200 °C. However, complete nitridation of the aluminum oxide powder was not observed when the temperature reached 1,300 °C. Phase pure AlN powder was only obtained at post-treatment temperatures above 1,400 °C. The carbon component of the precursor improved the nitridation reaction of aluminum oxide. Phase pure AlN powder was therefore prepared by a combined carbothermal reduction-nitridation method.

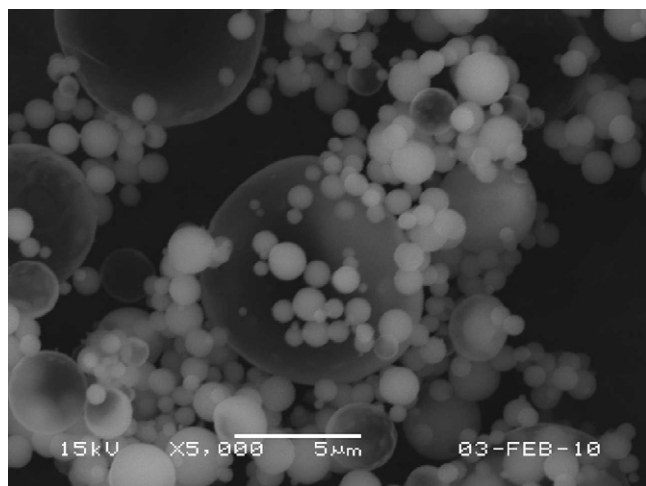


Fig. 1. SEM image of the precursor powders prepared by spray pyrolysis.

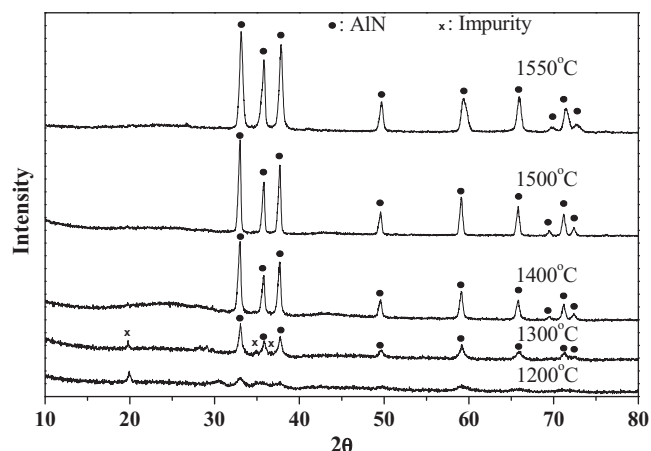
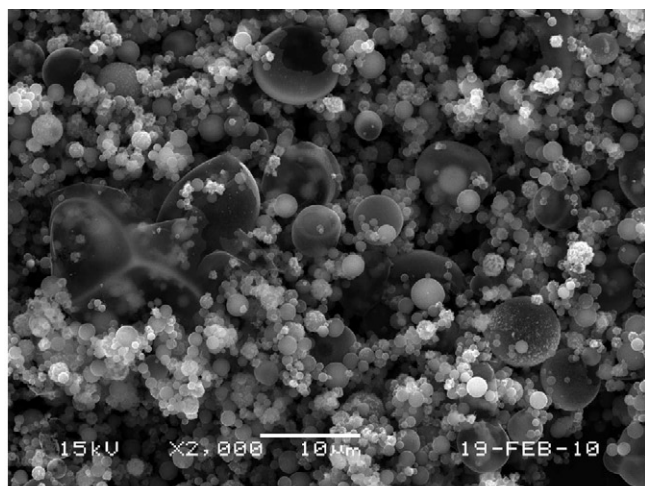
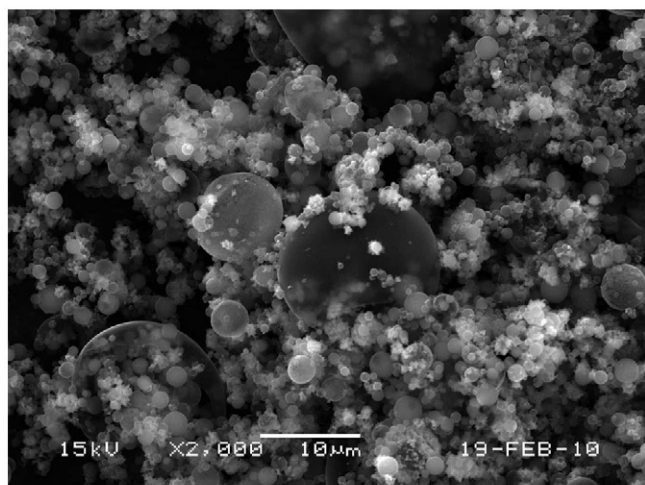


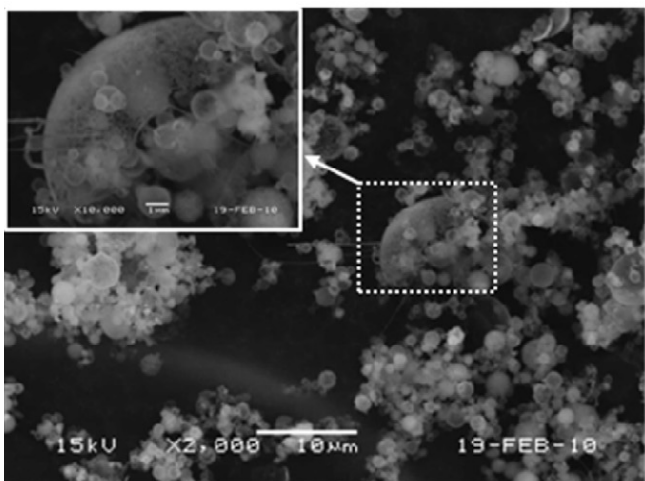
Fig. 3. XRD patterns of the AlN powders post-treated at various temperatures.



(a) 1400 °C

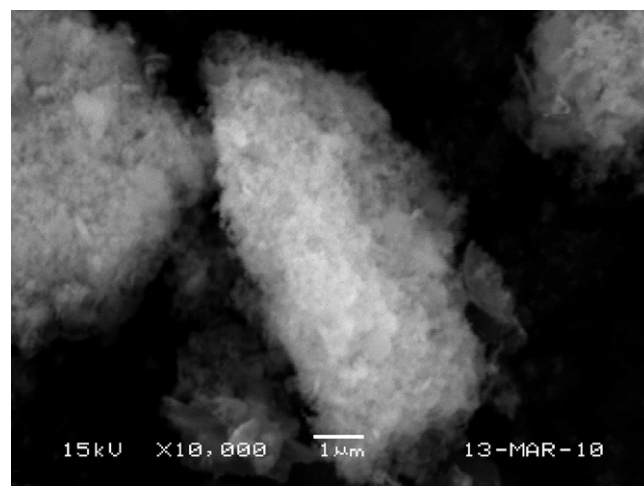


(b) 1500 °C

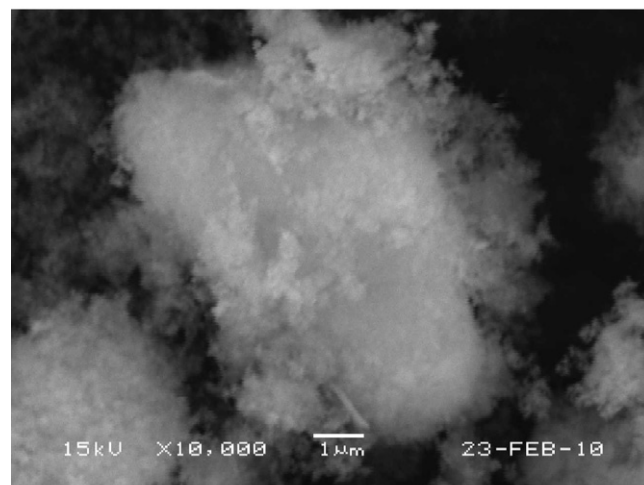


(c) 1550 °C

Fig. 4. SEM images of the AlN powders post-treated at the various temperatures.



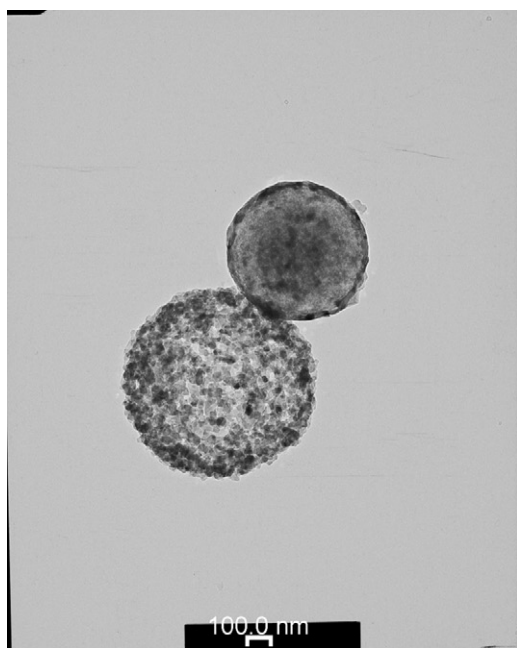
(a) 1500 °C



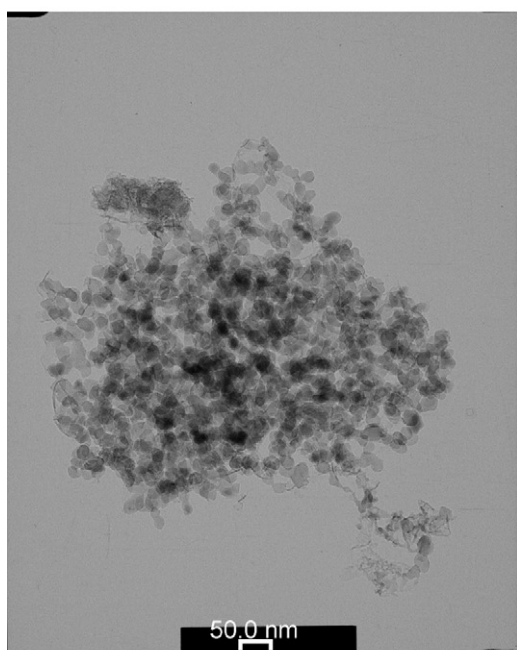
(b) 1550 °C

Fig. 5. SEM images of the AlN powders obtained after milling process.

Fig. 4 shows the AlN powders' morphologies. The powders post-treated at various temperatures under nitrogen were fired in air at 700 °C for 1 h to eliminate any residual carbon. The AlN powders maintained the spherical morphologies of the precursor irrespective of the treatment temperature. Fig. 5 shows the AlN powders' morphologies after milling using a planetary mill. The spherical shape of the AlN powder was lost after milling when the post-treatment temperature reached 1,550 °C. The powders with hollow structures were transformed into nano-sized powders by milling. Fig. 6 shows TEM images of the AlN powder post-treated at 1,500 °C before and after milling. The powders had an aggregated structure of nano-sized primary powders. The mean size of the particles measured from the TEM image Fig. 6 (b) was 20 nm.



(a) before milling



(b) after milling

Fig. 6. TEM images of the AlN powders post-treated at 1500 °C.

#### 4. Conclusions

Aluminum oxide/carbon composite powders were prepared by spray pyrolysis and used as precursors for the production of AlN powders. Sucrose was used as a carbon source. The precursor's spherical shape and hollow structure were maintained after post-treatment at 1,500 °C. The AlN powders

prepared by combining spray pyrolysis with carbothermal reduction and nitridation (CRN) had aggregated structures of nano-sized primary powders. Nano-sized AlN powders were obtained by the milling of the hollow and porous powders.

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#### References

- [1] K. Baba, N. Shohata, M. Yonezawa, Synthesis and properties of ultrafine AlN powder by RF plasma, *Appl. Phys. Lett.* 54 (1989) 2309–2311.
- [2] M. Mitomo, Y.W. Kim, H. Hirotsuru, Fabrication of silicon carbide nanoceramics, *J. Mater. Res.* 11 (1996) 1601–1604.
- [3] J.F. Yang, T. Ohji, T. Sekino, C.L. Li, K. Niihara, Phase transformation microstructure and mechanical properties of  $\text{Si}_3\text{N}_4/\text{SiC}$  composite, *J. Eur. Ceram. Soc.* 21 (2001) 2179–2183.
- [4] J.F. Yang, T. Sekino, Y.H. Choa, K. Niihara, T. Ohji, Microstructure and mechanical properties of sinter-post-HIPed  $\text{Si}_3\text{N}_4\text{--SiC}$  composites, *J. Am. Ceram. Soc.* 84 (2001) 406–412.
- [5] F. Wakai, Y. Kodama, S. Sakaguchi, N. Murayama, K. Izaki, K. Niihara, A superplastic covalent crystal composite, *Nature* 344 (1990) 421–423.
- [6] M. Mitomo, H. Hirotsuru, H. Suematsu, T. Nishimura, “Fine-grained silicon nitride ceramics prepared from  $\beta$ -powder, *J. Am. Ceram. Soc.* 78 (1995) 211–214.
- [7] T. Nagano, K. Kaneko, G.D. Zhan, M. Mitomo, Superplasticity of liquid-phase-sintered beta-SiC with  $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3\text{--AlN}$  additions in an  $\text{N}_2$  atmosphere, *J. Am. Ceram. Soc.* 83 (2000) 2497–2502.
- [8] T. Suehiro, N. Hirotsaki, K. Komeya, Synthesis and sintering properties of aluminium nitride nanopowder prepared by the gas-reduction–nitridation method, *Nanotechnology* 14 (2003) 487–491.
- [9] V.A. Virkar, T.B. Jackson, A.T. Cutler, Thermodynamic and kinetic effects of oxygen removal on the thermal conductivity of aluminum nitride, *Am. Ceram. Soc. Bull.* 72 (1989) 2031–2042.
- [10] T. Yamakawa, J. Tatami, K. Komeya, T. Meguro, Synthesis of AlN powder from  $\text{Al}(\text{OH})_3$  by reduction–nitridation in a mixture of  $\text{NH}_3\text{--C}_3\text{H}_8$  gas, *J. Eur. Ceram. Soc.* 26 (2006) 2413–2418.
- [11] W.M. Jadwisieniczak, H.J. Lozykowski, I. Berishev, A. Bensaoula, I.G. Brown, Visible emission from AlN doped with Eu and Tb ions, *J. Appl. Phys.* 89 (2001) 4384–4390.
- [12] F.S. Liu, H.W. Dong, Q.L. Liu, J.K. Liang, J. Luo, Y. Zhang, L.T. Yang, G.H. Rao, Characterization and photoluminescence of AlN:Eu films, *Opt. Mater.* 28 (2006) 1029–1036.
- [13] A. Sato, K. Azumada, T. Atsumori, K. Hara, Characterization of AlN:Mn thin film phosphors prepared by metalorganic chemical vapor deposition, *J. Crystal Growth* 298 (2007) 379–382.
- [14] H.S. Do, S.W. Choi, S.H. Hong, Blue-emitting AlN:Eu<sup>2+</sup> powder phosphor prepared by spark plasma sintering, *J. Am. Ceram. Soc.* 93 (2010) 356–358.
- [15] N. Hirotsaki, R.J. Xie, K. Inoue, T. Sekiguchi, B. Dierre, K. Tamura, Blue-emitting AlN:Eu<sup>2+</sup> nitride phosphor for field emission displays, *Appl. Phys. Lett.* 91 (2007) 061101.
- [16] U. Vetter, J. Zenneck, H. Hofsass, Intense ultra violet cathodoluminescence at 318 nm from  $\text{Gd}^{3+}$ -doped AlN, *Appl. Phys. Lett.* 83 (2003) 2145–2147.
- [17] J. MacKenzie, C. Abernathy, S. Pearton, U. Hommerich, X. Wu, R. Schwartz, R.G. Wilson, J. Zavada, Er doping of AlN during growth by metalorganic molecular beam epitaxy, *Appl. Phys. Lett.* 69 (1996) 2083–2085.
- [18] Y. Taniyasu, M. Kasu, T. Makimoto, Field emission properties of heavily Si-doped AlN in triode-type display structure, *Appl. Phys. Lett.* 84 (2004) 2115–2147.



- [19] K. Inoue, N. Hirosaki, R.J. Xie, T. Takeda, Highly efficient and thermally stable blue-emitting AlN: Eu<sup>2+</sup> phosphor for ultraviolet white light-emitting diodes, *J. Phys. Chem. C* 113 (2009) 9392–9397.
- [20] S. Iwama, K. Hayakawa, T. Arizumi, Ultrafine powders of TiN and AlN produced by a reactive gas evaporation technique with electron beam heating, *J. Cryst. Growth* 56 (1982) 265–269.
- [21] G.P. Johnston, R.E. Muenchausen, D.M. Smith, S.R. Fortyn, Reactive laser ablation synthesis of nanosize aluminum nitride, *J. Am. Ceram. Soc.* 75 (1992) 3465–3468.
- [22] S.E. Pratsinis, G. Wang, S. Panda, T. Guillon, A.W. Weimer, Aerosol synthesis of AlN by nitridation of aluminum vapor and clusters, *J. Mater. Res.* 10 (1995) 512–520.
- [23] F.J. Moura, R.J. Munz, Vapor-Phase synthesis of nanosize aluminum nitride particles using a two-stage transferred arc reactor, *J. Am. Ceram. Soc.* 80 (1997) 2425–2428.
- [24] W.S. Jung, S.K. Ahn, Preparation of aluminum nitride powder from a (hydroxo)(succinato)aluminum(III) complex, *J. Mater. Chem.* 4 (1994) 949–953.
- [25] L.C. Pathak, A.K. Ray, S. Das, C.S. Sivaramakrishnan, P. Ramachandrarao, Carbothermal synthesis of nanocrystalline aluminum nitride powders, *J. Am. Ceram. Soc.* 82 (1999) 257–260.
- [26] T. Wade, J. Park, E.G. Garza, C.B. Ross, D.M. Smith, R.M. Crooks, Electrochemical synthesis of ceramic materials. 2. Synthesis of aluminum nitride (AlN) and an AlN polymer precursor: chemistry and materials characterization, *J. Am. Chem. Soc.* 114 (1992) 9457–9464.
- [27] H. Yamane, M. Shimada, F.J. Disalvo, Synthesis of aluminum nitride powder using a Na flux, *J. Mater. Sci. Lett.* 17 (1998) 399–401.
- [28] Q. Lu, J. Hu, K. Tang, Y. Qian, G. Zhou, X. Liu, J. Xing, A low temperature nitridation route for nanocrystalline AlN, *Chem. Lett.* 28 (1999) 1239–1240.
- [29] M. Qin, X. Du, Z. Li, I.S. Humail, X. Qu, Synthesis of aluminum nitride powder by carbothermal reduction of a combustion synthesis precursor, *Mater. Res. Bull.* 43 (2008) 2954–2960.
- [30] Y.C. Kang, H.S. Roh, S.B. Park, Preparation of Y<sub>2</sub>O<sub>3</sub>:Eu phosphor particles of filled morphology at high precursor concentrations by spray pyrolysis, *Adv. Mater.* 12 (2000) 451–453.
- [31] Y. Shimomura, N. Kijima, High-luminance Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> phosphor synthesis by high temperature and alkali metal ion-added spray pyrolysis, *J. Electrochem. Soc.* 151 (2004) H86–H92.
- [32] Y.H. Zhou, J. Lin, Morphology control and luminescence properties of YVO<sub>4</sub>:Eu phosphors prepared by spray pyrolysis, *Opt. Mater.* 27 (2005) 1426–1432.
- [33] N. Joffin, J. Dexpert-Ghys, M. Verelst, G. Baret, A. Garcia, The influence of microstructure on luminescent properties of Y<sub>2</sub>O<sub>3</sub>:Eu prepared by spray pyrolysis, *J. Lumin.* 113 (2005) 249–257.
- [34] J.R. Sohn, Y.C. Kang, H.D. Park, Morphological control of Y<sub>2</sub>O<sub>3</sub>:Eu phosphor particles by adding polymeric precursors in spray pyrolysis, *Jpn. J. Appl. Phys.* 41 (2002) 3006–3009.
- [35] S.H. Ju, H.C. Jang, Y.C. Kang, LiCo<sub>1-x</sub>Al<sub>x</sub>O<sub>2</sub> (0 ≤ x ≤ 0.05) cathode powders prepared from the nanosized Co<sub>1-x</sub>Al<sub>x</sub>O<sub>y</sub> precursor powders, *Mater. Chem. Phys.* 112 (2008) 536–541.
- [36] D.S. Jung, H.Y. Koo, H.C. Jang, Y.C. Kang, Effects of La content on the properties of Ba<sub>1-x</sub>La<sub>x</sub>TiO<sub>3</sub> powders prepared by spray pyrolysis, *Met. Mater. Int.* 15 (2009) 809–814.
- [37] H.C. Jang, D.S. Jung, J.H. Kim, Y.C. Kang, Y.H. Cho, J.H. Lee, Characteristics of samaria-doped ceria nanoparticles prepared by spray pyrolysis, *Ceram. Inter.* 36 (2010) 465–471.
- [38] S.H. Lee, H.Y. Koo, S.M. Lee, Y.C. Kang, Characteristics of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce phosphor powders prepared by spray pyrolysis from ethylenediaminetetraacetic acid solution, *Ceram. Inter.* 36 (2010) 611–615.