



Letter

Synthesis of Cu_3N from CuO and NaNH_2 

ARTICLE INFO

Keywords:

Nitride
Oxide
Low-temperature reaction
Copper nitride

ABSTRACT

We report on the low-temperature synthesis of submicron-sized Cu_3N powder produced from CuO and NaNH_2 powder mixture by heating at 150–190 °C in a Teflon-sealed autoclave. The structure was the anti- RuO_3 type with a lattice parameter of 0.3814(1) nm, and strong optical absorption was observed below ~1.9 eV. This synthesis method has the potential of facile control of the reaction with less use of ammonia sources.

© 2014 The Ceramic Society of Japan and the Korean Ceramic Society. Production and hosting by Elsevier B.V. All rights reserved.

Cu_3N has attracted attention for its potential uses in solar energy conversion, catalytic applications and electronic devices. It is a semiconductive nitride with a band gap of ~1.4 eV, which is suitable for solar energy conversion [1]. Incorporation of hydrogen and oxygen and its nonstoichiometry change its transport and optical properties [2–5]. Moreover, some recent studies focus on its catalytic properties, such as Huisgen cycloaddition [6] and electrochemical oxygen reduction [7]. Another interesting feature of Cu_3N is its thermodynamic instability, which allows the formation of Cu metal at low temperature. This can afford the potential applications as recording media [8,9] and conductive ink [10].

The synthesis of Cu_3N powder has been reported by nitridation of Cu nitrate, chloride, fluoride, or complex using an ammonia flow [6,7,10–13]. These methods of synthesis partially rely on the purging of byproducts [14] such as H_2O or HF; thus, kinetic control is important using excess ammonia gas. The other method is sputtering of a Cu target in a nitrogen atmosphere [8–10,15–18], but large volume synthesis is difficult. In order to utilize the potential of Cu_3N , a synthesis technique with less-toxic materials and facile control is highly desirable. Recently, we reported on the synthesis of InN , Mn_6N_5 , and Fe_3N by the nitridation of oxides using liquid NaNH_2 at 240 °C in an autoclave [19–21]. These syntheses needed no ammonia flow, and facile control of the nitridation of oxides in a closed system was achieved. Herein, we report a new approach for the synthesis of Cu_3N powder by the reaction between CuO and NaNH_2 in an autoclave at 150–190 °C. These synthesis temperatures are lower than those of the nitridation of other oxides using NaNH_2 [14–16] and below the melting point of NaNH_2 .

The method for synthesizing Cu_3N was a slight modification to that in previous reports about the synthesis of other nitrides using NaNH_2 [19–21]. First, 0.15 g of CuO (Kanto Kagaku) and 1.0 g of NaNH_2 (Aldrich) were mixed using a mortar and pestle in a nitrogen-filled glovebox and put in a steel crucible. This steel crucible was set in a Teflon-lined autoclave, and then the autoclave was tightly closed. The autoclave was heated to 120, 150,

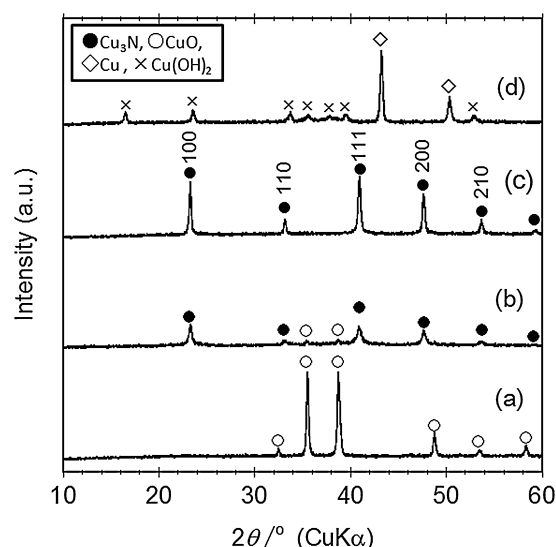


Fig. 1. XRD patterns of the products after the reaction of CuO with NaNH_2 at (a) 120 °C, (b) 150 °C, (c) 170 °C, and (d) 190 °C for 60 h.

170, and 190 °C for 12–60 h. After it cooled down, the autoclave was opened under a normal atmosphere. The crucible was put in ethanol, and the product was obtained by filtration and further washing with ethanol and water. The crystal phase was examined by XRD (Rigaku; RINT-2000), and the morphology was observed using scanning electron microscopy (JEOL; JSM-6500). The specific surface area was measured by BELSORP-mini at 77 K. Surface analysis was performed by X-ray photoelectron spectroscopy (XPS; JEOL; JPS-9200) and the binding energies were corrected by reference to free carbon (284.6 eV). Thermal stability was investigated using a TG-DTA (Rigaku; Thermo plus EVOII) and optical reflectance was measured by a UV–vis spectrophotometer (Jasco; MSV-5200).

Fig. 1 shows the XRD patterns after the reactions of CuO and NaNH_2 at different temperatures for 60 h. At 120 °C, the peaks from unreacted CuO were found. The reactions at 150–170 °C produced

Peer review under responsibility of The Ceramic Society of Japan and the Korean Ceramic Society.

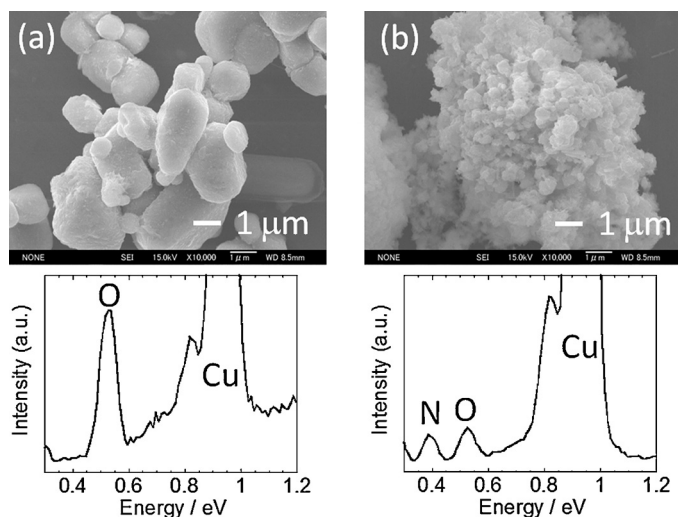


Fig. 2. SEM images of (a) CuO and (b) Cu₃N synthesized at 170 °C for 60 h. Typical EDX spectra are shown.

the peaks of Cu₃N with an anti-RuO₃ structure. The lattice parameter of the synthesized powder at 170 °C was 0.3814(1) nm. This parameter is close to the reported value of stoichiometric Cu₃N determined by neutron diffraction [11]. Nonetheless, four kinds of stoichiometric Cu₃N show slightly different lattice parameters [11], which might be related to inclusion of hydrogen [3]. Incorporation of oxygen does not significantly change the lattice parameter [2]. Thus, we cannot deny the possibility of hydrogen and oxygen incorporation. The nitridation at 170 °C for less reaction time between 12 and 36 h still showed noticeable peaks of CuO phase, indicating that relatively long nitridation of 60 h was necessary. At 190 °C, the nitridation for 60 h gave Cu metal and Cu(OH)₂ phases while that for 12 h produced CuO and Cu₃N with slight Cu metal.

Fig. 2 shows the SEM images of CuO powder before and after the nitridation at 170 °C. Round particles of a few microns in size changed into submicron-sized particles due to the nitridation. This nitridation increased its surface area from 2.2 m² g⁻¹ to 48 m² g⁻¹. The CuO showed signals for O and Cu, and the nitride showed peaks for N and Cu as well as a relatively weak peak for O when compared with that observed in CuO. This oxygen signal implies low-crystalline oxides/hydroxides phases though EDX is not very sensitive to the amounts of nitrogen and oxygen. No Na peak around 1.1 eV was detected.

Fig. 3 shows the XPS analysis of Cu 2p, N 1s and O 1s orbitals. The Cu 2p peak at binding energy of 932.4 eV was found with a shoulder around 934 eV. The former energy is close to the reported value of Cu₃N thin film: 932.8 eV [22]. This energy is slightly different

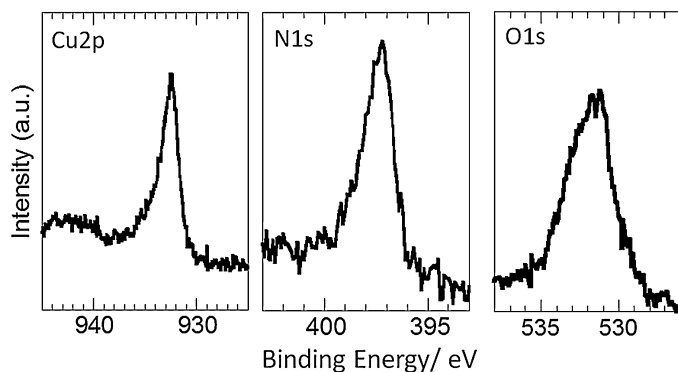


Fig. 3. XPS profiles of Cu₃N powder synthesized at 170 °C for 60 h.

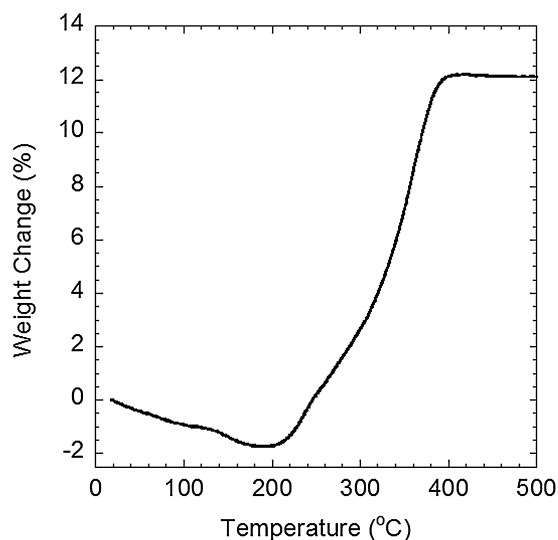


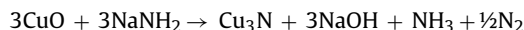
Fig. 4. Weight change upon thermal oxidation of Cu₃N synthesized at 170 °C for 60 h: airflow of 100 mL min⁻¹, heating rate of 10 K min⁻¹.

from the energy of Cu metal (932.1 eV; not shown), and this slight difference between Cu and Cu₃N agrees with close binding energies of Cu⁰ and Cu¹⁺ [22]. The shoulder at 934 eV can be assigned to Cu²⁺, such as CuO and Cu(OH)₂ [23]. The nitrogen profile shows the asymmetric peak at 397.2 eV with a shoulder toward high energy. This peak shape would be attributed to adsorbed N on the surface at 397.7 eV and N in the bulk of Cu₃N at 398.7 eV [22]. The O 1s peak is relatively broad, and could be composed of oxygen in CuO and Cu(OH)₂ at 531 eV and the other oxygen source such as OH, H₂O and CO₂ at 532.2 eV [23].

Thermal oxidation of Cu₃N synthesized at 170 °C by heating under airflow is shown in Fig. 4. Mass loss of 1.1% below 140 °C would be due to adsorbed species. The loss of 0.7% between 140 and 180 °C can be explained by decomposition of Cu(OH)₂ [24] and further heating above 200 °C causes the oxidation of Cu₃N with a gain of 13.9%. Similar oxidation behavior has been reported in the literature [10]. The product after the oxidation was found to be CuO by XRD. Theoretical mass change of Cu(OH)₂ decomposition and Cu₃N oxidation are -18.5% and +16.6%, respectively. This gives the estimate of 3.5 mass% of Cu(OH)₂ and 83.7 mass% of Cu₃N. Residual except adsorbed species could account for 11.7 mass% of CuO. Therefore, Cu(OH)₂ and CuO likely exist as low-crystallinity impurities. Relatively large amount of oxygen was found in many nitride powders with high surface area or small particle size [20,25,26], and thus this may be a feature of such nitride powder after exposure to air and water.

Fig. 5 presents the optical absorption after the nitridation at 170 °C. Strong absorption is found above ~660 nm, which corresponds to ~1.9 eV. The synthesized powder was brown, which was consistent with this absorption. Brown powder and film have been also reported in the literature describing Cu₃N [10,13,16,17]. However, this absorption is different from that in other reports (~1.4 eV) [1,18]. This discrepancy could be related to the surface and/or oxygen incorporation in the product [2].

The synthesis reaction can be formulated as follows:



NaNH₂ does not melt at 170 °C (m.p. ~210 °C). Since the reaction without mixing of CuO with NaNH₂ yielded more unreacted CuO, solid–solid contact was quite important. Unreacted CuO phase after the nitridation at 170 °C with less reaction time suggests relatively low reaction rate of this solid–solid reaction. Further increasing temperature to 190 °C produced Cu metal and Cu(OH)₂.

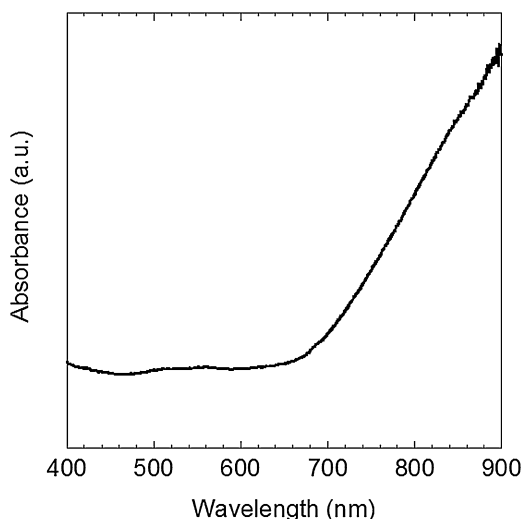


Fig. 5. UV-vis spectrum of Cu_3N powder synthesized at 170°C for 60 h.

This would be attributed to the low decomposition temperature of Cu_3N , suggested by TG analysis. The nitridation mechanism would be different from the previously reported nitridation of Mn_2O_3 and Fe_2O_3 with melted NaNH_2 at 240°C , which complete the reaction in 36 h [20]. Lower reaction temperature with well-mixed starting materials and relatively long reaction time would be necessary for this solid–solid reaction for Cu_3N synthesis. Further investigation of pressure versus the amount of reactants is highly desired for scaling up this synthesis in safety.

The thermodynamic driving force is believed to be the formation of NaOH^{15} by considering the free formation energies of the components (298 K): CuO : -129.7 kJ/mol [27], NaOH : -379.7 kJ/mol [27], NaNH_2 : -64.0 kJ/mol [27], NH_3 : -16.4 kJ/mol [27], and N_2 : 0 kJ/mol [27]. We could use the enthalpy as the estimated free energy of Cu_3N , $+74.5$ kJ/mol [28], assuming that the entropy affects only a few tens kJ/mol on the free energy. The energy of this nitridation is calculated to be -499.9 kJ; thus, this reaction would be thermodynamically favorable.

In summary, this low-temperature method using NaNH_2 produced Cu_3N from CuO in a closed system at 150 – 190°C , which shows the potential of easy control of the nitridation with a low usage of ammonia source.

Acknowledgement

This work was partially supported by JSPS Grant-in-Aid for Young Scientists (No. 25820330).

References

- [1] A. Zakutayev, C.M. Caskey, A.N. Fioretti, D.S. Ginley, J. Vidal, V. Stevanovic, E. Tea and S. Lany, *J. Phys. Chem. Lett.*, **5**, 1117–1125 (2014).
- [2] A. Fallberg, M. Ottosson and J.-O. Carlsson, *J. Cryst. Growth*, **312**, 1779–1784 (2010).
- [3] J. Wang, J.T. Chen, B.B. Miao, F. Zhang and P.X. Yan, *J. Appl. Phys.*, **100**, 103509 (2006).
- [4] M.G. Moreno-Armenta, G. Soto and N. Takeuchi, *J. Alloys Compd.*, **509**, 1471–1476 (2011).
- [5] J. Blucher and K. Bang, *Mater. Sci. Eng. A*, **117**, L1–L3 (1989).
- [6] B.S. Lee, M. Yi, S.Y. Chu, J.Y. Lee, H.R. Kwon, K.R. Lee, D. Kang, W.S. Kim, H.B. Lim, J. Lee, H.J. Youn, D.Y. Chi and N.H. Hur, *Chem. Commun.*, **46**, 3935–3937 (2010).
- [7] H. Wu and W. Chen, *J. Am. Chem. Soc.*, **133**, 15236–15239 (2011).
- [8] T. Maruyama and T. Morishita, *Appl. Phys. Lett.*, **69**, 890–891 (1996).
- [9] A. Masaaki, U. Kazuo and T. Akira, *Jpn. J. Appl. Phys.*, **29**, 1985 (1990).
- [10] T. Nakamura, H. Hayashi, T.A. Hanaoka and T. Ebina, *Inorg. Chem.*, **53**, 710–715 (2014).
- [11] G. Paniconi, Z. Stoeva, H. Doberstein, R.I. Smith, B.L. Gallagher and D.H. Gregory, *Solid State Sci.*, **9**, 907–913 (2007).
- [12] D. Wang and Y. Li, *Chem. Commun.*, **47**, 3604–3606 (2011).
- [13] R. Deshmukh and U. Schubert, *J. Mater. Chem.*, **21**, 18534–18536 (2011).
- [14] S.H. Elder, F.J. DiSalvo, L. Topor and A. Navrotsky, *Chem. Mater.*, **5**, 1545–1553 (1993).
- [15] D. Dorrnanian, L. Dejam and G. Mosayebian, *J. Theor. Appl. Phys.*, **6**, 1–9 (2012).
- [16] X. Qian, Z. Huang, Z. Cui and J. Guo, *J. Wuhan Univ. Technol., Mater. Sci. Ed.*, **25**, 935–937 (2010).
- [17] G.H. Yue, P.X. Yan, J.Z. Liu, M.X. Wang, M. Li and X.M. Yuan, *J. Appl. Phys.*, **98**, 103506 (2005).
- [18] K.J. Kim, J.H. Kim and J.H.H. Kang, *J. Cryst. Growth*, **222**, 767–772 (2001).
- [19] A. Miura, T. Takei and N. Kumada, *Cryst. Growth Des.*, **12**, 4545–4547 (2012).
- [20] A. Miura, T. Takei and N. Kumada, *Inorg. Chem.*, **52**, 11787–11791 (2013).
- [21] A. Miura, T. Takei and N. Kumada, *J. Ceram. Soc. Jpn.*, **122**, 86–88 (2014).
- [22] C. Navío, M. Capitán, J. Álvarez, F. Yndurain and R. Miranda, *Phys. Rev. B*, **76**, (2007).
- [23] Z. Ai, L. Zhang, S. Lee and W. Ho, *J. Phys. Chem. C*, **113**, 20896–20902 (2009).
- [24] M. Endoh, A. Doi and M. Kawada, *Proc. Okayama Univ. Sci.*, **8**, 97–107 (1972).
- [25] M. Yang, M.J. MacLeod, F. Tessier and F.J. DiSalvo, *J. Am. Ceram. Soc.*, **95**, 3084–3089 (2012).
- [26] A. Miura, M. Lowe, B.M. Leonard, C.V. Subban, Y. Masubuchi, S. Kikkawa, R. Dronskowski, R.G. Hennig, H.D. Abruña and F.J. DiSalvo, *J. Solid State Chem.*, **184**, 7–11 (2011).
- [27] D.R. Lide, *CRC Handbook of Chemistry and Physics*, vol. 83, 83rd ed., CRC Press, Florida (2002), 5–5–5–50.
- [28] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nutall, *J. Phys. Chem. Ref. Data*, **11**, (Suppl. 2) 2–156 (1982).

Akira Miura*
Takahiro Takei
Nobuhiro Kumada

Center for Crystal Science and Technology, University
of Yamanashi, 7-32 Miyamae, Kofu 400-8511, Japan

*Corresponding author. Tel.: +81 55 220 8614.
E-mail address: amiura@yamanashi.ac.jp (A. Miura)

3 August 2014

Available online 16 September 2014