Journal of Alloys and Compounds 508 (2010) 172–176

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis and characterization of magnesium nitride powder formed by Mg direct reaction with N_2

Fujian Zong*, Chunzhan Meng, Zhiming Guo, Feng Ji, Hongdi Xiao, Xijian Zhang, Jin Ma, Honglei Ma

School of Physics, Shandong University, No. 27, Shanda South Road, Jinan 250100, Shandong, China

ARTICLE INFO

Article history:
Received 14 August 2009
Received in revised form 21 July 2010
Accepted 22 July 2010
Available online 19 August 2010

PACS:
61.66.Fn
81.05.Je
68.60.Dv
81.70.Pg
68.37.Hk

Keywords:
Semiconductors
Chemical synthesis
Scanning electron microscopy
Thermal analysis
X-ray diffraction

ABSTRACT

Mg_3N_2 powder of high quality has been synthesized by the direct nitridation reaction of Mg powder with N_2 gas in 1.0 l/min for 60 min at a temperature between 650 °C and 800 °C. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were employed to investigate the thermal nitridation behavior of Mg powder. X-ray diffraction (XRD) indicates that Mg_3N_2 powder has a cubic structure with a lattice constant $a = 0.997$ nm. The scanning electron microscopy (SEM) images of Mg_3N_2 powder show that Mg_3N_2 powder is of a rod-like structure. The Fourier transformed infrared (FTIR) spectra indicate a high quality of the Mg_3N_2 powder fabricated in this way.

1. Introduction

Nowadays the chemistry of metal-nitrides is an active research area in material science. Magnesium nitride (Mg_3N_2) powder is a well-known solid catalyst and is used as an additive in a range of applications, including fabricating special alloys and ceramics, catalyzing polymer cross-linking reactions and hydrogen storage materials [1–4]. Recently, magnesium nitride has also been used as a catalyst in the preparation of some nitrides, such as AlN nanocrystals [5], cubic boron nitride [6], nanocrystalline boron nitride [7], as nitriding agents in the preparation of Group IIIa nitrides MCl_3 (M = Sc, Y, La) [8] and as a convenient source of ammonia in the preparation of primary amides and dihydropyridines [9,10]. MgO nanobelts with a pure morphology and high yield were generated by the direct evaporation of Mg metals under the conditions of initial N_2 gas and subsequent N_2/O_2 atmosphere [11]. The methods for the fabrication of magnesium nitride include Mg direct reaction with N_2 by the addition of MgO as a catalyzer [12], Mg direct reaction with NH_3 [13], the explosion of Mg winding in the ambience of N_2 [14,15], low pressure chemical vapor deposition method [16], reactive pulsed laser deposition method [17], a novel electrochemical process [18], and carbon nanotubes as nanoreactors for fabrication of single-crystalline Mg_3N_2 nanowires [19]. Some of the methods require expensive equipments, and some of them only get a lower production ratio. The direct reaction between Mg powder and N_2 is a valuable method used in large-scale industry.

Magnesium nitride has an anti-bixbyite structure with the body-centered cubic cell with space group Ia-3 (#206), $a = 0.99528(1)$ nm [20]. Its physical properties have been hardly characterized experimentally. Reckeweg et al. reported in 2003 that the band gap of Mg_3N_2 was 2.8 eV (direct) through reflectance measurements [21]. The band gap values of Mg_3N_2 calculated by different methods were reported to be from 1.10 eV to 2.25 eV [22–24]. Jiao Hao et al. took the experimental and theoretical studies on structural phase transformations of Mg_3N_2 at high pressure in 2009, and got that a reversible, first-order structural phase transition from the ambient cubic phase (Ia-3) to a high-pressure monoclinic phase (C2/m) is found to start at about 20.6 GPa and complete at about 32.5 GPa, and further predicted a second phase transition from the monoclinic phase to a hexagonal phase (P-3m1) around 67 GPa [25].

This paper reports that Mg_3N_2 powder of high quality has been synthesized by direct nitridation reaction of Mg powder with N_2 gas

---

* Corresponding author. Tel.: +86 531 88565947; fax: +86 531 88564886.
E-mail address: fjzong@sdu.edu.cn (F. Zong).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.07.224

in 1.0 l/min for 60 min at a temperature between 650 °C and 800 °C. X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) techniques were used to examine the structure and chemical bonding states of Mg_3N_2 powder. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were employed to investigate the thermal nitridation behavior of Mg powder.

2. Experimental

About 5 g of pure Mg powder (purity 99.5%, average diameter $\leq 4\,\mu m$, maximum diameter $\leq 13\,\mu m$), put in a quartz boat, were placed in a quartz reaction tube equipped in the resistance heated horizontal tube furnace. The Mg powder was nitrided in a flow of super pure N_2 gas (purity 99.999%) of 1.0 l/min under atmospheric pressure and at a given temperature for 60 min. After nitridation, the quartz boat was cooled down to room temperature in the flow of super pure N_2 gas.

The nitridation behavior of Mg powder was analyzed by using the thermal gravimetric analysis (TGA) and the differential thermal analysis (DTA), in which several milligrams of Mg powder within an open Pt crucible were heated in the furnace of a thermal analysis system (Beijing optical apparatus company, WCT-2A) in the environment of Ar and/or N_2 gas at a heating rate of 10 °C/min from room temperature to 1000 °C, with Al_2O_3 as the reference material.

The structural properties of Mg_3N_2 powder were analyzed by using X-ray diffraction (XRD, Rigaku D/Max-γA with Cu Kα radiation). The morphology of Mg_3N_2 powder was examined using scanning electron microscopy (SEM, JEOL Hitachi-800). Fourier transform infrared (FTIR) measurements were performed only in the middle infrared range of instrument (400–4000 cm^{-1}). The room-temperature infrared transmission spectra were investigated using an FTIR spectrometer (Nicolet, 5DX).

3. Results and discussion

3.1. Thermal gravimetric analysis and differential thermal analysis

The TGA and DTA are employed to investigate the thermal behaviors of Mg and Mg_3N_2 powders. Fig. 1(a) reveals the TGA and DTA curves of Mg powder with a heating rate of 10 °C/min from room temperature to 1000 °C in Ar atmosphere. From Fig. 1(a), it can be seen that there is a sharp endothermal peak in DTA curve but no weight changing in TGA curve as a result of the meltage of Mg powder at about 650 °C, and also there is an evident endothermal peak in DTA curve that goes with an evident weight loss in TGA curve as a result of the vaporization of Mg powder at approximately 689–892 °C. A slight weight loss of about 2% below 600 °C is attributed to the release of H_2O, CO_2, N_2 and O_2 from the surface. When the temperature is about 650 °C (the melting point of metal Mg), the solid state Mg powder is melted into the liquid state Mg. When the temperature is about 689 °C, some of the liquid state Mg will be vaporized into the gas state Mg. The higher the temperature is, the faster the vaporization rate is. Above 892 °C, all of the liquid state Mg will be vaporized.

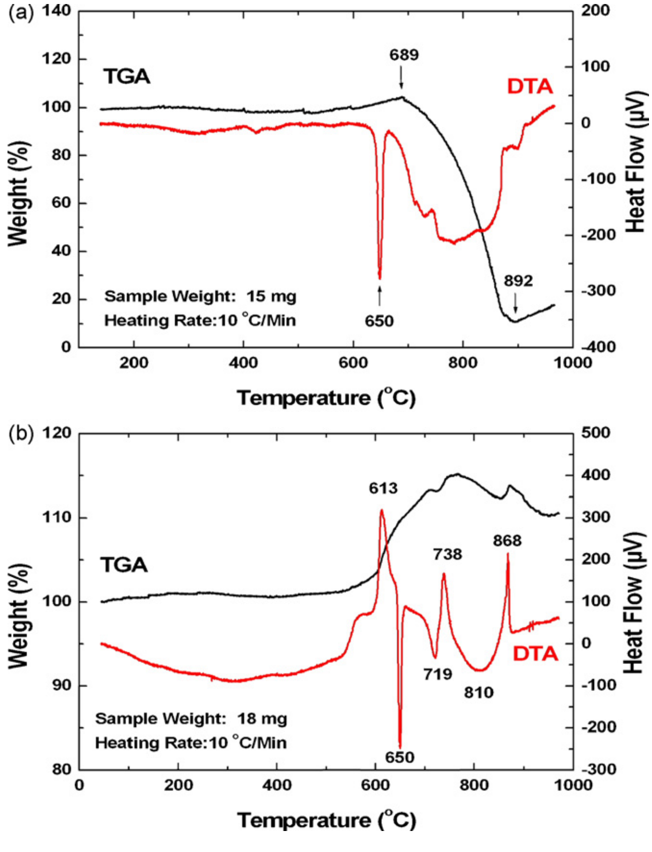


Fig. 1. DTA and TGA curves of Mg powder in different atmospheres. (a) Ar atmosphere; (b) N_2 atmosphere.

Fig. 1(b) displays the DTA and TGA curves of Mg powder with a heating rate of 10 °C/min from room temperature to 1000 °C in N_2 atmosphere. The relation between DAT curve and temperatures, as well as that between TGA curve and temperatures is very complex. From the room temperature to 550 °C, a slight weight gain of about 1% is attributed to the adsorption of N_2. An evident weight gain with an evident exothermal peak indicates that the initial thermal nitridation takes place at about 550 °C. The higher the temperature is, the faster the nitridation rate is. The nitridation of Mg powder in N_2 atmosphere is associated with the following chemical reaction:

$$3Mg + N_2 \rightarrow Mg_3N_2$$

Due to the competition between the exothermic nitridation process and the endothermic melting process, and that between the nitridation process (exothermic reaction, gaining weight) and the vaporization process (endothermic reaction, losing weight), the complicated relation between DAT curve and temperatures, and that between TGA curve and temperatures can be made clear. When the temperature is below 550 °C, solid state Mg powder is stabilized. When the temperature is between 550 °C and 650 °C, the exothermic nitridation process of solid state Mg powder has the priority, and there is an evident weight gain with an evident exothermal peak. At 650 °C, the endothermic melting process of solid state Mg powder has the priority, and there is an evident endothermal peak with no weight changing. Between 650 °C and 700 °C, the exothermic nitridation process of liquid state Mg has the priority, and there is an evident weight gain with an evident exothermal peak. There is a solid state Mg_3N_2 shell covering the surface of liquid state Mg, which slows down the vaporization process. At about 719 °C, the vaporization process has the priority, and there is an evident endothermal peak with a slight weight loss. At about 738 °C, the nitridation process has the priority again, and there is an evident exothermal peak with an evident weight gain. At about 750 °C, the nitridation process and the vaporization process get a temporary equilibrium, and there is no heat flow and no weight changing. At about 810 °C, the vaporization process has the priority again, and there is an evident endothermal peak with an evident weight loss. At about 868 °C, the nitridation process has the priority, and there is an evident exothermal peak with an evident weight gain. Above 900 °C, all of the liquid state Mg will be nitrided into Mg_3N_2, and/or be vaporized into gas state, and the nitridation reaction of Mg with N_2 will be completed.

Compared with the oxidation reaction between metal Mg and O_2, the nitridation reaction between metal Mg and N_2 is very slow. Due to the competition between the nitridation process (gaining weight) and the vaporization process (losing weight), the maximum of weight increases of 15% is much lower than the theoretical weight increase value (38.4%).

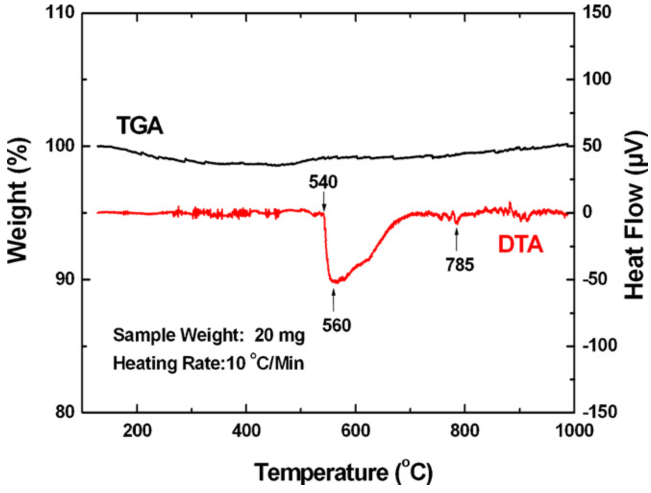


Fig. 2. DTA and TGA curves of Mg_3N_2 powder in N_2 atmosphere.

There are three solid phases of Mg_3N_2 (α, β and γ) at atmospheric pressure [26,27]. At 550 °C the low-temperature α-phase transforms to β-phase, and at 788 °C the β-phase to γ-phase. Fig. 2 reveals the DTA and TGA curves of Mg_3N_2 powder (synthesized at 750 °C for 60 min) with a heating rate of 10 °C/min from room temperature to 1000 °C in N_2 atmosphere. At about 550 °C, the endothermic phase transformation of α-phase to β-phase has the priority, and there is an evident endothermal peak with no weight changing. At about 785 °C, a small endothermal peak indicates the phase transformation of β-phase to γ-phase. At about 650 °C, the endothermic melting process of solid state Mg powder cannot be found and there is no solid state Mg in the Mg_3N_2 powder.

A slight weight loss of about 1.5% below 500 °C is attributed to the release of H_2O, CO_2, N_2 and O_2 from the surface of Mg_3N_2 powder. From 500 °C to 900 °C, a slight weight gain of about 1.5% is attributed to the nitridation reaction between metal Mg at atomic level and N_2. So, the Mg_3N_2 powder is doped with Mg at the atomic level (or Mg-doped Mg_3N_2). The purity of Mg_3N_2 powder is about 96%. The production ratio of Mg_3N_2 powder is about 80%.

3.2. X-ray diffraction

Fig. 3 shows the XRD patterns of Mg_3N_2 powder synthesized by the nitridation reaction of Mg powder with N_2 gas in 1.0 l/min for 60 min at the temperatures of (a) 650 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C. The numbers above the peaks correspond to the values of crystal face indices (*h k l*). In Fig. 3, only the peaks of Mg_3N_2 can be found, which suggests that almost all Mg atoms have turned into Mg_3N_2 and there is no solid state Mg in the Mg_3N_2 powder. It is also clear in the figure that all peaks fairly corresponds to the data of Mg_3N_2 powder recorded in the JCPDS document (Powder Diffraction File Compiled by the Joint Committee on Powder Diffraction, 1985, Card No. #01-1289). Therefore, it can be concluded that Mg_3N_2 is cubic in structure with a lattice constant $a = 0.997$ nm, which is in good agreement with the published value (0.995 nm) recorded in the JCPDS document [20].

3.3. Fourier transform infrared

Fig. 4 displays the Fourier transformed infrared spectra of Mg_3N_2 powder synthesized at 750 °C for 60 min. The absorption peaks located at 408.8 cm^{-1}, 443.6 cm^{-1}, 469.6 cm^{-1}, and 578.5 cm^{-1} fairly correspond to the strong absorption peaks of Mg_3N_2 [28], which indicates the Mg_3N_2 powder of high quality has been fabricated in this way.

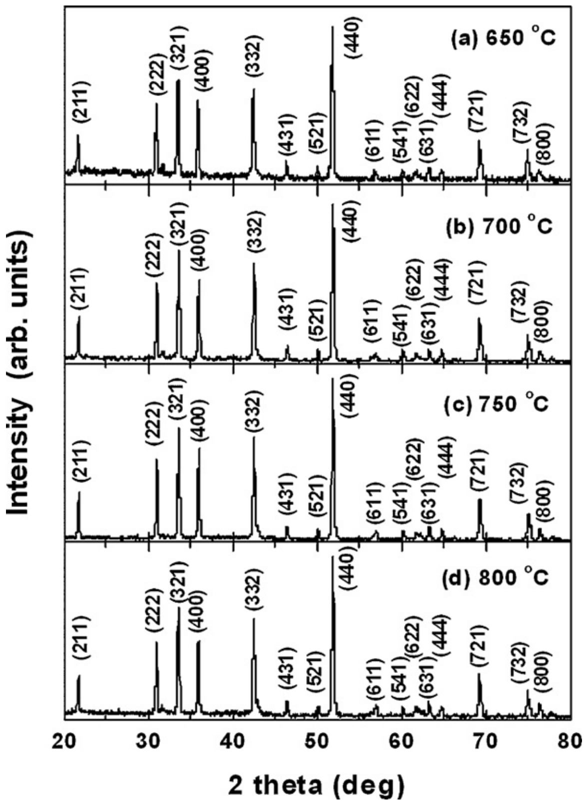


Fig. 3. XRD patterns of the Mg_3N_2 powder synthesized at different temperatures. (a) 650 °C, (b) 700 °C, (c) 750 °C, (d) 800 °C.

Since FTIR measurements were carried out at room temperature with the samples exposed to the air, the H_2O molecules were absorbed on the surface, and a little of Mg_3N_2 powder was hydrolyzed by the following chemical reaction:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3, \; NH_3 + H_2O \rightarrow NH_4OH.$$

The absorption of H_2O at 1620 cm^{-1} corresponds to the H-OH bending modes [29,30], and the absorption peak at 1400 cm^{-1} corresponds to the γ4-bending mode of NH_4^+ [28].

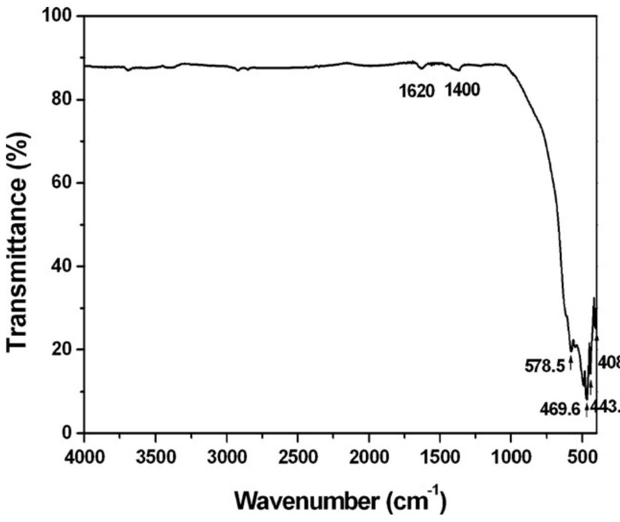
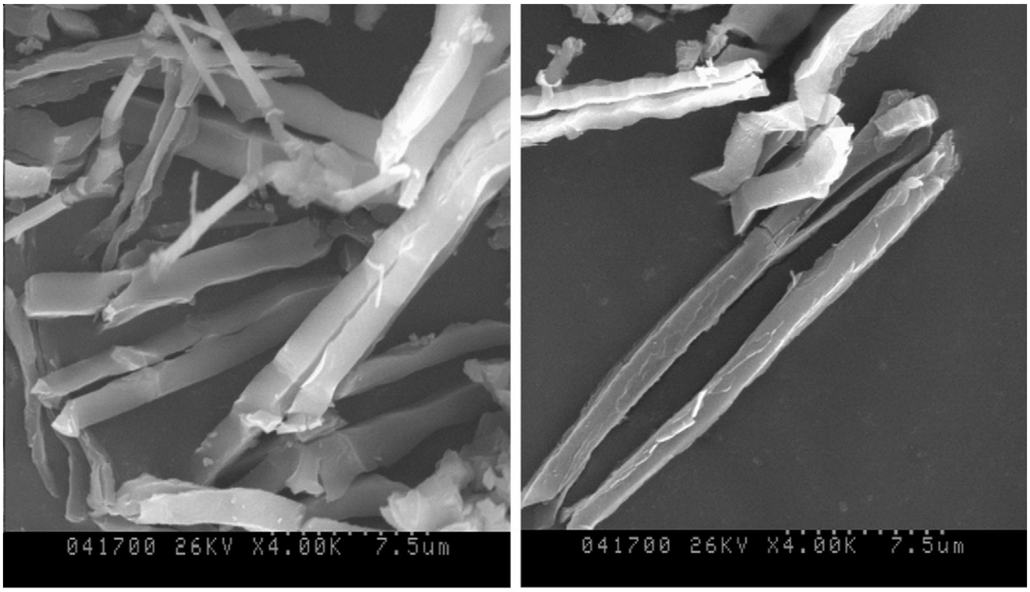
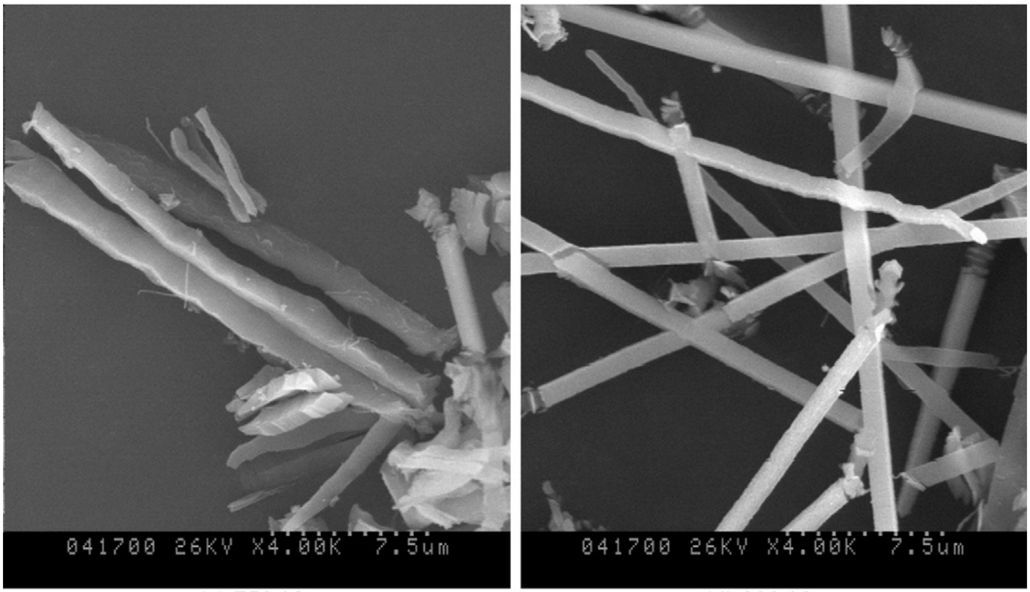


Fig. 4. FTIR spectrum of Mg_3N_2 powder synthesized at 750 °C.



(a) 650 ºC (b) 700 ºC



(c) 750 ºC (d) 800 ºC

Fig. 5. SEM images of Mg_3N_2 powder synthesized at different temperatures. (a) 650 °C, (b) 700 °C, (c) 750 °C, (d) 800 °C.

3.4. *Scanning electron microscopy*

Fig. 5 shows the SEM images of Mg_3N_2 powder synthesized by the nitridation reaction of Mg powder with N_2 gas in 1.0 l/min for 60 min at temperatures of (a) 650 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C, in which rod-like structure about 1 μm in diameter and about 20 μm in length can be clearly observed. As the temperature increases, the diameter decreases and the length increases. It can be seen that at low temperatures there are clear edges and corners, which become smoother and smoother as the temperature increases.

4. Conclusions

Magnesium nitride (Mg_3N_2) powder of high quality has been synthesized successfully through the direct nitridation reaction of Mg powder with N_2 gas in 1.0 l/min for 60 min at a nitridation temperature between 650 °C and 800 °C. The TGA and DTA curves of Mg powder in Ar atmosphere show that the melting point of metal Mg is 650 °C. When the temperature is about 689 °C, some of the liquid state Mg will be vaporized into the gas state Mg. The higher the temperature is, the faster the vaporization rate is. The DTA and TGA curves of Mg powder in N_2 atmosphere indicate that the initial thermal nitridation takes place at about 550 °C. The higher the temperature is, the faster the nitridation rate is. X-ray diffraction (XRD) indicates that Mg_3N_2 powder has a cubic structure with a lattice constant $a = 0.997$ nm. The SEM images of Mg_3N_2 powder show that Mg_3N_2 powder is of a rod-like structure. The Fourier transformed infrared spectra of Mg_3N_2 powder indicate a high quality of the Mg_3N_2 powder fabricated in this way.

Acknowledgement

This work is supported by the Nature Science Foundation of Shandong Province (No. Y2007G41).

References

[1] H. Woolf, I. Brown, M. Bowden, Curr. Appl. Phys. 8 (2008) 459–462.
[2] I.P. Jain, P. Jain, A. Jain, J. Alloys Compd. 503 (2010) 303–339.
[3] O. Reckeweg, J.C. Molstad, F.J. DiSalvo, J. Alloys Compd. 315 (2001) 134–142.
[4] W. Paszkowicz, M. Knapp, J.Z. Domagala, G. Kamler, S. Podsiadlo, J. Alloys Compd. 328 (2001) 272–275.
[5] G. Yan, G. Chen, H. Lu, Int. J. Refract. Met. Hard Mater. 26 (2008) 5–8.
[6] H. Lorenz, I. Orgzall, E. Hinze, Diamond Relat. Mater. 4 (1995) 1046–1049.
[7] L. Chen, M. Huang, T. Luo, Y. Gu, L. Shi, Z. Yang, Y. Qian, Mater. Lett. 58 (2004) 3634–3636.
[8] I.P. Parkin, A.M. Nartowski, Polyhedron 17 (1998) 2617–2622.
[9] G.E. Veitch, K.L. Bridgwood, S.V. Ley, Org. Lett. 10 (2008) 3623–3625.
[10] K.L. Bridgwood, G.E. Veitch, S.V. Ley, Org. Lett. 10 (2008) 3627–3629.
[11] R. Ma, Y. Bando, Chem. Phys. Lett. 370 (2003) 770–773.
[12] Z.G. Szabo, S. Perezel, M. Gabor, G. Zsoltb, A.K. Galwey, Thermochim. Acta 64 (1983) 167–178.
[13] C. Xue, Y. Ai, L. Sun, C. Sun, H. Zhuang, F. Wang, Z. Yang, L. Qin, J. Chen, H. Li, Rare Met. Mater. Eng. 36 (2007) 2020–2022.
[14] M.J. Joncich, J.W. Vaughn, B.F. Knutsen, Can. J. Chem. 44 (1966) 137–142.
[15] L. Mei, J.-T. Li, Scripta Mater. 60 (2009) 141–143.
[16] T. Murata, K. Itatani, F.S. Howell, J. Am. Ceram. Soc. 76 (1993) 2909–2911.
[17] G. Soto, J.A. Diaz, W. de la Cruz, A. Reyes, E.C. Samano, J. Non-Cryst. Solids 342 (2004) 65–69.
[18] K. Toyoura, T. Goto, K. Hachiya, R. Hagiwara, Electrochim. Acta 51 (2005) 56–60.
[19] J. Hu, Y. Bando, J. Zhan, C. Zhi, D. Golberg, Nano Lett. 6 (2006) 1136–1140.
[20] D.E. Partin, D.J. Williams, M. O'Keeffe, J. Solid State Chem. 132 (1997) 56–59.
[21] O. Reckeweg, C. Lind, A. Simon, F.J. DiSalvoa, Z. Naturforsch. B 58 (2003) 159–162.
[22] C.M. Fang, R.A. de Groot, R.J. Bruls, H.T. Hintzen, G. de With, J. Phys. Condens. Matter 11 (1999) 4833–4842.
[23] Ma.G.M. Armenta, A. Reyes-Serrato, M.A. Borja, Phys. Rev. B 62 (2000) 4890–4898.
[24] E. Orhan, S. Jobec, R. Brec, R. Marchand, J.-Y. Saillard, J. Mater. Chem. 12 (2002) 2475–2479.
[25] J. Hao, Y. Li, Q. Zhou, D. liu, M. Li, F. Li, W. Lei, X. Chen, Y. Ma, Q. Cui, G. Zou, J. Liu, X. Li, Inorg. Chem. 48 (2009) 9737–9741.
[26] I.S. Gladkaya, G.N. Kremkova, N.A. Bendeliani, J. Mater. Sci. Lett. 12 (1993) 1547–1548.
[27] G. Vissokov, J. Univ. Chem. Technol. Metall. 40 (2005) 193–198.
[28] A.M. Heyns1, L.C. Prinsloo, K.-J. Range, M. Stassen, J. Solid State Chem. 137 (1998) 33–41.
[29] M. Manzoli, A. Chiorino, F. Boccuzzi, Appl. Catal. B 52 (2004) 259–266.
[30] Y.-G. Yang, H.-L. Ma, C.-S. Xue, H.-Z. Zhuang, X.-T. Hao, J. Ma, S.-Y. Teng, Appl. Surf. Sci. 193 (2002) 254–260.