Journal of Alloys and Compounds 509 (2011) 7874–7876

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Hydrothermal synthesis of $MgCO_3$ and its optical properties

Shibing Ni, Tao Li, Xuelin Yang*

College of Mechanical and Material Engineering, Three Gorges University, 8 Daxue Road, Yichang 443002, PR China

ARTICLE INFO

Article history:
Received 2 December 2010
Received in revised form 8 April 2011
Accepted 11 April 2011
Available online 20 April 2011

Keywords:
Ceramics
Composite materials
Magnesium carbonate
Crystal growth
Photoluminescence

ABSTRACT

Well-crystallized magnesium carbonate micro-particles were successfully synthesized by a simple hydrothermal method. The structure of the as-synthesized products was characterized by X-ray diffraction (XRD), which is in good agreement with hexagonal rhomb-centered $MgCO_3$. Field emission scanning electron microscopy (FE-SEM) characterization indicates that the as-synthesized $MgCO_3$ micro-particles are of mean size about 30 μm. The photoluminescence properties of the as-synthesized $MgCO_3$ were measured at room temperature, which shows wide emissions with three emission centers ranging from violet to red. The violet emission center locates at 425 nm, the green emission center locates at 550 nm, and the red emission center locates at 698 nm.

1. Introduction

Magnesium carbonate ($MgCO_3$) has attracted much attention for many years due to its wide applications in diverse areas such as rubber industry, medicine, thermal insulating fillers, active starting materials of magnesia or carbon nanotubes, minerals, and seawater treatment [1–10]. Stimulated by those applications, different methods such as solid reaction, precipitation, and water bath were developed to synthesize $MgCO_3$ [11–13]. However, those researches have mainly focused on morphology controlled fabrication and growth process investigation. To the best of our knowledge, no research about the photoluminescence properties of $MgCO_3$ was reported by now. The main object of this paper is to develop a simple method to synthesize $MgCO_3$ and to research its photoluminescence properties.

2. Experimental

All the chemicals were analytical grade and purchased from Tianjing Chemical Reagents. In a typical process, 2.5 mmol hexamethylenetetramine, 2.5 mmol magnesium acetate, and 0.5 g sodium sulfate were dissolved in 30 ml distilled water. After stirring for 20 min, the obtained homogeneous solution was transferred into a 50 ml-teflonlined autoclave, distilled water was subsequently added to 80% of its capacity. The autoclave was at last sealed and placed in an oven, heated at 160 °C for 24 h. The precipitate was washed with distilled water and ethanol for 4 times at 6000 rpm for 5 min. Finally the resulting products were dried in an oven at 60 °C for 24 h. The structure and morphology of the products were characterized by X-ray powder diffraction (Rigaku RINT2400 with Cu Kα radiation), field-emission scanning electron microscopy (FE-SEM S-4800, Hitachi), and micro-Raman spectrometer (Jobin Yvon LabRAM HR800 UV, YGA 532 nm). The UV–vis reflection spectrum was characterized by Ultraviolet–visible spectrophotometer (Shimadzu UV3600) using an integrating sphere. Room temperature PL was measured on micro-Raman spectrometer (Jobin Yvon LabRAM HR800 UV, He–Cd 325 nm).

3. Results and discussion

The typical X-ray diffraction pattern of the as-synthesized products is shown in Fig. 1. All diffraction peaks can be indexed as the hexagonal phase of $MgCO_3$ with Rhomb-centered lattice constants $a = 0.4633$ nm, $c = 1.501$ nm, which is in good agreement with the JCPDS, No. 08-0479. Strong and sharp peaks suggest that the as-synthesized products are well crystallized. The reactions during the hydrothermal process are likely to be as follows:

$$(CH_2)_6N_4 + 10H_2O \rightarrow 6HCHO + 4NH_3{\cdot}H_2O \quad (1)$$

$$HCHO + O_2 \rightarrow CO_2 + H_2O \quad (2)$$

$$CO_2 + H_2O \rightarrow {CO_3}^{2-} + 2H^+ \quad (3)$$

$$Mg^{2+} + {CO_3}^{2-} \rightarrow MgCO_3 \quad (4)$$

Fig. 2(a) shows a low magnification SEM image of $MgCO_3$ micro-particles. It can be seen that the as-synthesized $MgCO_3$ consists of a large number of micro-particles with big size and a small quantity of particles with small size. The size of those particles ranges from hundreds of nanometers to tens of micrometers, and the mean size of those micro-particles is about 30 μm. High magnification SEM image of the as-synthesized $MgCO_3$ is shown in Fig. 2(b). It can be seen clearly that there are some small-sized particles on the surface of $MgCO_3$ micro-particles. The mean size of those small particles is

* Corresponding author. Fax: +86 717 6397559.
E-mail address: xlyang@ctgu.edu.cn (X. Yang).

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doi:10.1016/j.jallcom.2011.04.064

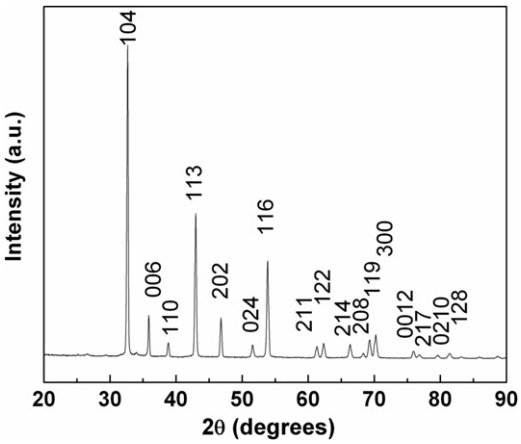

Fig. 1. X-ray diffraction pattern of the as-synthesized products.

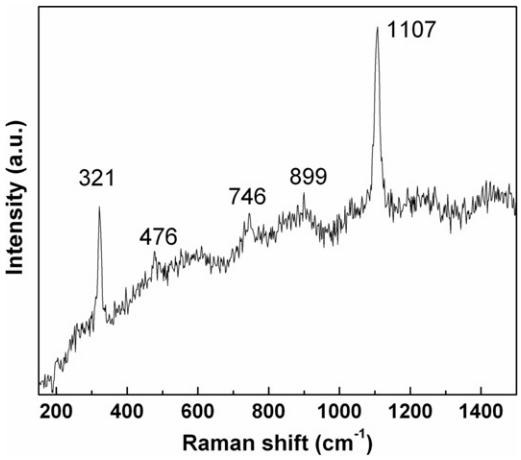

Fig. 3. Raman spectrum of the as-synthesized $MgCO_3$.

about 2 μm, and the micro-particles are of smooth surfaces with size about 30 μm.

As shown in Fig. 3, Raman spectrum of $MgCO_3$ in the wavelength range of 150–1500 cm^{-1} are dominated by the peaks located at 321, 476, 746, 899, and 1107 cm^{-1}, and these peaks are the vibration bands of $MgCO_3$. The peaks at 746 and 1107 cm^{-1} are caused by the in-plane bending and symmetry-related stretching vibration, and the peak at 321 cm^{-1} comes from librational motion of the carbonate groups relative to the divalent cation [9,13–15]. The weak peak at 476 cm^{-1} comes from Mg–O vibration, whereas the weak peak at 899 cm^{-1} originates from SO_4^{2-} [16,17].

Fig. 4 displays the UV–vis reflection of the as-synthesized $MgCO_3$. The reflection spectrum of $MgCO_3$ shows a high reflection (>70%) in the region from 450 to 900 nm, and then fell sharply in the region from 300 to 450 nm due to the onset of fundamental absorption. The optical band gap energy (Eg) was estimated by the method proposed by Wood and Tauc [18]. According to these authors the optical band gap is associated with absorbance and photon energy by the following equation:

$$h\nu\alpha \propto (h\nu - \mathrm{Eg})^2$$

where α is the absorbance, h is the Planck constant, ν is the frequency, and Eg is the optical band gap. In this case, the Eg value of $MgCO_3$ powders is evaluated by extrapolating the linear portion of the curve $(\alpha h\nu)^{1/2}$ vs $h\nu$. The obtained results are shown in insert of Fig. 4, exhibiting an indirect band gap semiconductor with band gap value of 2.89 eV (429 nm). The band gap value evaluated from UV–vis reflection is smaller than that obtained from first principle calculation [19–21]. The divergence between these two methods is likely due to the size or morphology related surface defects.

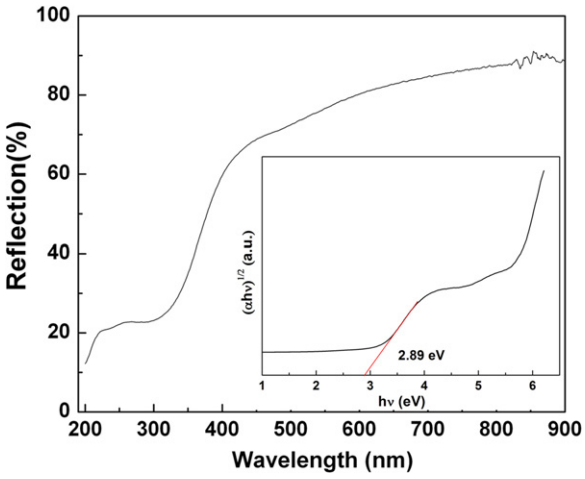

Fig. 4. UV–vis reflection spectrum of $MgCO_3$. Insert shows the optical bandgap of $MgCO_3$.

Fig. 5 shows the PL spectrum of $MgCO_3$ that measured at room temperature using an excitation wavelength of 325 nm. A wide range of visible light emission that ranges from violet to red can be found in the PL spectrum. There are three emission centers in visible light region, which consist of the violet emission center located at 425 nm, the green emission center located at 550 nm, and the red emission center located at 698 nm, respectively. Considering the band gap value of $MgCO_3$ (2.89 eV) that evaluated from UV–vis reflection spectrum, one can deduce that the violet emission cen-

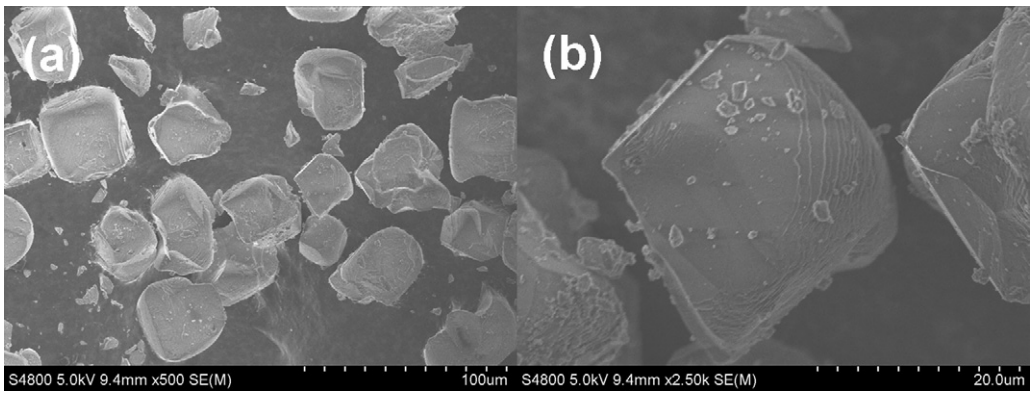

Fig. 2. SEM images of $MgCO_3$ micro-particles with low (a) and high (b) magnification.

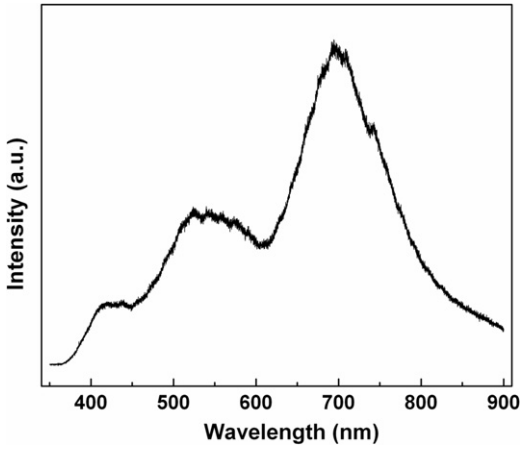

Fig. 5. PL spectrum of the as-synthesized $MgCO_3$ micro-particles.

ter of $MgCO_3$ located at 425 nm may be relevant to the electron transition from the conduction band to valence band of $MgCO_3$, which is in accordance with the indirect electronic band gap along Γ to M direction [19]. In addition, it has been well recognized that local defects such as atom vacancies or interstitials may induce new energy levels in the band gap [22,23]. $MgCO_3$ was fabricated in hydrothermal environment, defects such as O vacancies, Mg vacancies, or Mg interstitials can inevitably be formed. As the energy of the green and red emission centers (2.26 eV and 1.78 eV) are smaller than the band gap value evaluated from UV–vis reflection spectrum, it can be deduced that defects in $MgCO_3$ are due to the green and red emissions. The wide region of visible light emission of $MgCO_3$ endows it with promising application in optical field.

4. Conclusions

In conclusion, $MgCO_3$ micro-particles with mean size of about 30 μm were synthesized by a simple hydrothermal method. The structure and morphology of $MgCO_3$ micro-particles were characterized by X-ray diffraction, Raman spectrum, and field emission scanning electron microscopy. The photoluminescence properties of $MgCO_3$ micro-particles were characterized at room temperature, which shows wide region of visible light emission from violet to red. This wide region PL behavior endows it with potential applications in optical field.

Acknowledgements

We gratefully acknowledge the financial support from Natural Science Foundation of China (NSFC, 50972075), key projects of Chinese Ministry of Education (D209083), and Education Office of Hubei Province (D20081304 and CXY2009A004). Moreover, the authors are grateful to Dr. Jianlin Li at Three Gorges University for his kind support to our research.

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