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Effect of process parameters on photophysical properties and barium molybdate phosphors characteristics

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Abstract

Barium molybdate particles ($BaMoO_4$) with uniform shapes have applications in various fields such as phosphors, optical fibers, scintillators, magnets and catalysts. In this study, two synthesis methods (microwave-assisted hydrothermal (MAH) and Complex Polymerization (CP)) were used to prepare $BaMoO_4$ particles. The effect of the applied synthesis methodology and experimental parameters on the morphology, particle size, sample uniformity and optical properties of the $BaMoO_4$ were studied. Scheelite-type single crystalline structures of $BaMoO_4$ were identified by X-ray diffraction (XRD) as well as Raman and Fourier transform infrared spectroscopy (FTIR). Octahedral morphologies were characterized by field-emission scanning electron microscopy (FE-SEM). Photoluminescence (PL) spectra of the samples exhibited different emission properties which indicates a relationship with surface defect states (shallow and deep level defects) where interfaces populate additional levels in the band gap. Electronic order-disorder at short- and intermediate-ranges is generated by utilizing the synthesis method and can be modified by applied experimental parameters. If the particle size and morphology are controlled, deep and shallow defects can be controlled, and PL properties can be modified accordingly with the optical properties desired.

Keywords: A. Microwave processing; C. Optical properties; D. Transition metal oxides; Ceramics; Chemical syntheses

1. Introduction

Materials with a scheelite-type crystalline structure such as $BaMoO_4$ (BMO) have excellent optical properties which facilitates their wide use as phosphors, laser materials and scintillation detectors [1–5]. Due to their excellent thermal and chemical stability, molybdates are considered good hosts for luminescent materials [6–8]. BMO is an important material belonging to the molybdate family which attracts attention due to its ability to produce green luminescence. BMO has potential applications in various fields such as phosphors, optical fibers, scintillators, magnets and catalysts [6,7].

Barium molybdate can be synthesized by using different techniques; however, production with single crystalline structures and controlled morphology requires caution. The conventional solid-state reaction method is frequently used to obtain molybdate powders; this method produces materials with a large grain size and irregular morphology due to high annealing temperatures and long reaction times. In addition, the tendency for MoO_3 to vaporize at high temperatures can result in non-homogeneous morphologies and compositions [9].

Various techniques have been employed to obtain materials similar to $BaMoO_4$ and are discussed in this study: Czochralski, spontaneous crystallization, the CP method, MAH and calcination methods [10–16]. Nevertheless, some of these

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methods have disadvantages with high synthesis temperatures and long reaction times which destroy the morphological homogeneity. In the CP method, synthesis occurs at low temperatures. The metal complex immobilization in these rigid organic polymeric networks can reduce the metal segregation and thus ensures compositional homogeneity at the molecular scale which decreases morphological and chemical heterogeneity problems [12,16].

The MAH method is promising for fabricating ideal micro- and nanometric material with appropriate morphologies. This method generally leads to a cost reduction due to low synthesis temperatures; it also promotes high yield reactions and enables large volume processing [1,2,15]. In a recent study, Luo et al. [17] reported $BaMoO_4$ nest-like nanostructures prepared under hydrothermal conditions. Particles with a controllable size and shape, high crystallinity and low agglomeration can be obtained using this synthetic route [1,2]. In addition, a variation of this technique (i.e., hydrothermal synthesis using a microwave (microwave-hydrothermal), is an attractive growth method for single crystals which provides advantages such as low synthesis temperatures and uniform rapid heating. The microwave energy accelerates the formation of well organized nanostructures.

Studies have shown that some experimental parameters, (including the use or absence of a capping reagent and the applied synthesis methodology) influenced morphologies, sizes and PL intensity of the final products. Therefore, in this study, two synthesis methods were used to obtain $BaMoO_4$ structures; (1) the successful synthesis by the CP method which favors morphological and chemical homogeneity, and (2) the MAH method which is a fast, simple and efficient soft chemical route to prepare complex oxide materials. Various complementary characterization techniques were used, including XRD, FTIR spectroscopy, Raman spectra and PL spectroscopy. FE-SEM was used to detect particles sizes and molybdate morphologies. Based on experimental results, in this study, it is proposed that the synthesis method and applied experimental parameters can modify PL properties in accordance with the optical properties desired.

2. Experimental

2.1. Materials

All chemical reagents are analytical grade and were used without further treatments: Molybdenum trioxide (MoO_3) (Alfa Aesar, 99.95%), barium acetate ($(CH_3CO_2)_2Ba$) (Alfa Aesar, 99%), citric acid ($H_3C_6H_5O_7$) (Mallinckrodt, 99%) and polyethylene glycol ($HOCH_2CH_2OH$) (Mw 200) (PEG 200) (Sigma-Aldrich, 99.9%).

2.2. Synthesis of barium molybdate ($BaMoO_4$)

2.2.1. Synthesis by the MAH method

Molybdenum trioxide (5×10^{-3} mol L^{-1}) was dissolved in 50 mL of distilled water with vigorous stirring. Then, ($Ba(CH_3CO_2)_2$) (5×10^{-3} mol L^{-1}) was added under constant stirring. The pH of the solution was adjusted to 12 by adding KOH. PEG 200 was added to the BMO-3 system which required a capping reagent. In reaction system 1 (BMO-1), the solid sample was collected in this phase; this sample was washed with water and ethanol and dried at 60 °C. BMO-2 and BMO-3 samples were heat treated using the MAH method. Both reaction systems were transferred into a sealed Teflon autoclave and placed in a domestic microwave (2.45 GHz, maximum power of 800 W). The BMO-2 system (without the addition of PEG) and the BMO-3 system (with the addition of PEG were treated at 100 °C for 16 min with a heating rate fixed at 100 °C/min). The pressure in the sealed autoclave was stabilized at 2.0 atm. The autoclave was cooled to room temperature naturally, and the resulting white precipitate was collected, washed with water and ethanol and dried at 60 °C.

2.2.2. Synthesis by the CP method

Molybdenum citrate was formed by MoO_3 dissolution in an aqueous solution of $H_3C_6H_5O_7$ under constant stirring at 60–80 °C. After homogenization, a stoichiometric amount of Ba^{2+} was added to the molybdenum citrate solution. The complex which formed was stirred for several hours at 60–80 °C. Then, to produce a clear and homogeneous solution, ethylene glycol was added to promote the polyesterification. With continued heating at 80–90 °C, the viscosity of the solution increased, and phase separation was not observed. The molar ratio between barium and molybdenum cations was 1:1, and the ratio between citric acid and metals was 6:1; the citric acid/ethylene glycol mass ratio was 60:40.

After partial evaporation of the water, the resin was heat treated at 300 °C for 2 h in a static oxidizing atmosphere which precipitated the partial decomposition of the polymeric gel (the expanded resin was constituted of partially pyrolyzed material). The product was removed from the beaker and milled. The powder was annealed at 400 °C (BMO-4 400 °C) and 700 °C (BMO-4 700 °C) for 2 h in a static oxidizing atmosphere at a heating rate of 10 °C/min.

2.3. Characterization of $BaMoO_4$ samples

The samples obtained were characterized by XRD using a Rigaku-DMax/2500PC (Japan) with Cu-Kα radiation (λ=1.5406 Å) in the 2θ range from 5° to 65° with a 0.02°/min increment. Lattice parameters and unit cell sample volumes were calculated using a least-square refinement REDE93 program. The average crystallite diameter (Dcrys) of the materials after heat treatment was determined by XRD results using the (112) diffraction peak of the $BaMoO_4$ phase where 2θ is located at around 26.5° according to the procedure described elsewhere [12]. The morphology and particle sizes of the as-prepared samples were observed using FE-SEM (Jeol JSM 6330F). The FT-IR spectrum was recorded with a Bruker Equinox-55 instrument. Infrared spectroscopy was used to monitor the bonding changes occurring during the synthesis process using the KBr pellet technique. Raman spectra were recorded on a RFS/100/S Bruker FT-Raman spectrometer, and a Nd:YAG laser provided an excitation light at 1064.0 nm with