Research Article

Morphology and Photoluminescence of Ba$_{0.5}$Sr$_{0.5}$MoO$_4$ Powders by a Molten Salt Method

Ling Wei, Yunfei Liu, Yinong Lu, and Tao Wu

College of Materials Science and Engineering, Nanjing University of Technology, Jiangsu, Nanjing 210009, China

Correspondence should be addressed to Yinong Lu, yinonglu@njut.edu.cn

Received 15 October 2012; Revised 6 November 2012; Accepted 7 November 2012

Academic Editor: Zhenhui Kang

Copyright © 2012 Ling Wei et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Ba$_{0.5}$Sr$_{0.5}$MoO$_4$ powders with scheelite-type tetragonal structure were successfully synthesized by a molten salt method. The structure, morphology, and luminescent property of the as-prepared powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL), respectively. The results show that the tetragonal Ba$_{0.5}$Sr$_{0.5}$MoO$_4$ powders were synthesized at 650°C for 6 h by the molten salt method. The calcining temperature, the soaking time, and the molar ratio of the salt to Na$_2$MoO$_4$ have great influence on the phase, size, morphology, and PL properties. The better crystallinity and smaller particle size, the higher PL emission peak is.

1. Introduction

The fabrication of nano- to microscale inorganic materials with special size and morphology is of great interest for the study of material chemistry because of the importance in basic scientific research and potential technology applications of such materials [1, 2]. In recent years, molybdates and tungstates have attracted the interest of many technological fields and scientific areas owing to their wide potential application, including solid-state lasers [3], optic fiber [4], stimulated Raman scatters [5], catalysts [6], and microwave applications [7].

The molybdates with scheelite-type tetragonal structure are characterized by the general formula ABO$_4$ (A = Ca, Sr, Ba, Pb; B = Mo), space group I4$_1$/a, and symmetry C$_{4h}$ [8, 9]. These materials have been prepared in both powder and film forms by means of several technologies, such as electrochemical method [10], hydrothermal [11], solid-state reaction [12], and sol-gel method [13]. However, these approaches still have some limitations, for example, the as-prepared samples are not only irregular in morphology and large in particle size, but also of small production and high cost.

Recently, researchers mostly pay attention to unit material systems and binary or multivariate molybdate thin films. Pórtio et al. [14] investigated the structure and photoluminescence of Ca$_{x}$Sr$_{1-x}$WO$_4$ system at room temperature by a soft chemical method and heat treated between 400°C and 700°C. Rangappa et al. [15] studied fabrication of Ba-rich crystalline Ba$_{1-x}$Sr$_x$WO$_4$ and Ba$_{1-x}$Ca$_x$WO$_4$ films at room temperature by mechanically assisted solution reaction. Shi et al. [16] synthesized Ca$_{0.5}$Sr$_{0.5}$MoO$_4$: Eu$^{3+}$ powder using a sol-gel method. Fewer researchers on improving the luminescent property of solid-solution powders were reported. In order to fully research their properties, the study of alkaline earth molybdate materials is necessary.

Molten salts are widely used as an effective chemical reaction medium to produce a high-temperature liquid environment for crystal growth. The ionic fluxes molten salts possess high reactivity toward different inorganic species and relatively low melting points which makes them convenient for preparation of inorganic materials. Molten salt method has advantages of simple instrumentation and easy manipulation. And it is environmentally friendly and available to a large-scale production. In this paper, we report on the synthesis of Ba$_{0.5}$Sr$_{0.5}$MoO$_4$ with perfect crystalline morphology and homogeneous chemical composition by a molten salt method. Different synthesis parameters were discussed, and a possible crystallization was proposed. Finally, the luminescent properties of Ba$_{0.5}$Sr$_{0.5}$MoO$_4$ under different soaking times were investigated.
Figure 1: XRD patterns of the products obtained at different synthesis temperatures for 6 h, with 3 : 1 molar ratio of the salt to Na₂MoO₄.
liquid phase increases gradually at high-temperature reaction system. The reaction changes from solid-state reaction to liquid phase reaction. At last, the liquid-phase reaction plays a dominant role. Thus, the size of particles decreases. When the content of salts is too much, redundant liquid phase is obtained, which depresses particle growth.

Figure 5 shows XRD patterns of the products obtained at 650 °C for different soaking patterns, with 3:1 molar ratio of the salt to Na$_2$MoO$_4$. The XRD results reveal that the soaking time plays an important role in controlling the phase structures. When the soaking time is 1 h, only BaMoO$_4$ peaks (JCPDS 08–0455) and other impurity Sr$_{0.8}$Ba$_{0.2}$CO$_3$ phase...
Figure 4: SEM images of the products obtained at 650 °C for 6 h, with different molar ratio of the salt to Na₂MoO₄.

Figure 5: XRD patterns of the products obtained at 650 °C for different soaking times, with 3:1 molar ratio of the salt to Na₂MoO₄.

peaks appear (Figure 5(a)). As the soaking time is prolonged to 2 h, no impurity phase peaks are detected and all of the diffraction peaks can be indexed to the scheelite-type tetragonal structure. The tetragonal phase of Ba₀.₅Sr₀.₅MoO₄ remained when the soaking time is controlled in the range from 4 h to 8 h (Figures 5(c)–5(e)). In addition, the strong and sharp diffraction peaks indicate a good crystallinity of the products.

According to Donnay-Harker rules [17], as to tetragonal structure, the surface of {001} faces is higher than that of {101} faces. The high-energy faces have higher reactivity and growth rate, which makes {001} faces shrink to disappear completely, so as to form octahedrons [18]. It is reported that anions play a key role in morphology [19]. In the growth process of Ba₀.₅Sr₀.₅MoO₄, Chloride could preferentially and selectively adsorb on the {101} and {001} faces of Ba₀.₅Sr₀.₅MoO₄. The faster growing rate along the [001] directions than that along the [101] directions facilitates the formation of octahedron morphology with exposed {101} faces.

Figure 6 shows SEM images of the as-prepared products obtained at 650 °C for different soaking times with 3:1 molar ratio of the salt to Na₂MoO₄. Figure 6(a) shows that micro-octahedrons are observed, and some micro-octahedrons self-assemble to big octahedrons along {111} faces at 2 h. Figure 6(b) shows that when the soaking time is 4 h, inhomogeneous octahedrons are identified, and the mean size is 5.69 μm (Figure 7). When the soaking time is 6 h, the morphology of octahedrons is more uniform and well defined. The distribution of the particles also narrows. Eventually, when the soaking time is prolonged to 8 h, the distribution broadens.

Figure 8 shows the PL spectra of Ba₀.₅Sr₀.₅MoO₄ powders obtained at 650 °C for the holding time of 2 h∼8 h, with 3:1 molar ratio of the salt to Na₂MoO₄. All Ba₀.₅Sr₀.₅MoO₄ powders with different morphologies exhibited the same blue peaks around 460 nm using a 398 nm excitation line. Wu et al. [20] verified the blue emissions of molybdates, which were attributed to the 1T₂ → 1T₁ electronic transitions into the [MoO₄] tetrahedron groups, which can be treated as excitons. Our results also indicate that with the increase of the soaking time from 2 h to 8 h, the intensity of the diffraction peaks increases gradually (Figure 5). And the mean particle size is 3.18 μm, 5.69 μm, 4.68 μm, and 6.20 μm, respectively (Figure 7). According to Figure 8, when the soaking time is 6 h, the luminescence of the particles is the best. Therefore, the better crystallinity and smaller particle size, the higher PL emission. The same conclusion has been reported before [21].

4. Conclusions

In this paper, Ba₀.₅Sr₀.₅MoO₄ powders with octahedrons can be synthesized by a molten salt method at 650 °C for 6 h. The particle size, morphology, and crystallinity of Ba₀.₅Sr₀.₅MoO₄ crystallites depend on the reaction temperature, the holding time, and the molar ratio of KCl to the Na₂MoO₄. The PL
properties are strongly dependent on their particle size and crystallinity. The better crystallinity and smaller particle size, the higher PL emission peak.

Acknowledgment

The authors acknowledge the financial support from Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.
References


Submit your manuscripts at http://www.hindawi.com