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Well-defined barium molybdate hierarchical architectures with different morphologies: Controllable synthesis, formation process, and luminescence properties

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ABSTRACT

Uniform and well-dispersed barium molybdate ($BaMoO_4$) hierarchical microspheres and microflowers have been successfully synthesized via a hydrothermal route by using sodium dodecyl benzenesulfonate (SDBS) as surfactant. The reaction conditions, including SDBS additive, pH value of the initial solution, as well as reaction temperature, have great effect on the size and morphology of the $BaMoO_4$ products. The possible formation process of the $BaMoO_4$ microspheres has been investigated by time-dependent experiments. The as-synthesized $BaMoO_4$:Ln^{3+} (Ln = Eu, Tb, Dy, and Sm) phosphors show intense characteristic red, green, green–yellow, and orange–red emissions under ultraviolet light excitation, which might find potential applications in the fields of light emitting phosphors, advanced flat panel displays, and light-emitting diodes (LEDs).

1. Introduction

The chemical and physical properties of functional materials consisting of either inorganic compounds or inorganic/organic hybrids are fundamentally related to their size, shape, and dimensionality [1–3]. Constructing materials with fascinating hierarchical architectures are of great importance and highly demanded not only due to the fundamental scientific interest but also for potential technological applications [4]. Large-scale self-assembled hierarchical micro- and nanoparticles in phosphors have attracted great attention due to their ease of processing into devices with high resolution, high screen coverage, intense emission, and long service life [5]. Thus, many efforts have been dedicated to develop novel synthesis routes for the fabrication of high-quality hierarchical nano/micostructures. Among various synthesis routes, the hydrothermal method, due to its mild reaction conditions, ease of operation, and large-scale production capability, has been proved to be an effective and convenient synthesis technique in achieving a variety of hierarchical architectures. During the hydrothermal process, the chelating agents, and/or surfactants often provide an effective way to regulate the nucleation, growth, morphology, and orientation of the nanoparticles [6]. So they always play an important role in controlling the dynamics of crystal growth and determining the final morphology of the hierarchical nano/microstructures [7–9].

As an important class of inorganic compounds, rare earth ions doped molybdates with a scheelite structure have gained much attention due to their attractive luminescence and structural properties, supporting various promising applications such as phosphor materials in fields of light-emitting diodes (LEDs), and optical fibers, biolabels, lasers etc. [10–12]. Among the molybdates materials, barium molybdate ($BaMoO_4$) has been widely applied as an eminent candidate for the matrix of lanthanide activator ions. Up to now, many studies have been recently reported [13–16] on the luminescent properties of $BaMoO_4$ doped with different lanthanide activator ions, such as Eu^{3+}, Pr^{3+}, and Sm^{3+}. $BaMoO_4$ hierarchical micro- and nanoparticles with different morphologies have been prepared, such as hollow spheres [14], nanocrystallites [17], nanobelts [18], shuttle-like [19], nest-like [20], octahedron-like [21], and bundle-like [22] nano/microstructures. However, the synthesis of uniform and well-dispersed barium molybdate hierarchical microspheres was seldom reported. On the other hand, it is well-known that the spherical morphology with narrow size distribution and proper particle size is beneficial for high brightness because such phosphors exhibit high packing densities and low scattering of light [23,24]. Therefore, it is of significance and desirable to develop easily controllable methods for the fabrication

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of spherical lanthanide ions doped $BaMoO_4$ luminescent materials with promising novel properties.

In this paper, uniform and well-dispersed $BaMoO_4$:Ln^{3+} (Ln = Eu, Tb, Dy, and Sm) hierarchical microspheres and microflowers have been successfully synthesized through a simple and friendly hydrothermal process with SDBS as surfactant. The structure, morphology, possible formation process, and luminescence properties of the as-synthesized $BaMoO_4$ samples have been investigated in detail.

2. Experimental section

2.1. Synthesis

$Ln(NO_3)_3$ (Ln = Eu, Dy, and Sm) and $Tb(NO_3)_3$ aqueous solutions were obtained by dissolving Ln_2O_3 (99.99%) and Tb_4O_7 (99.99%) in dilute HNO_3 solution with heating with agitation. All other chemicals were of analytical grade and used directly without further purification.

In a typical synthesis, 2 mmol of $Ba(Ac)_2$ (0.511 g) was dissolved in 20 mL of deionized water. Subsequently, 2 mmol (0.697 g) of sodium dodecyl benzenesulfonate (SDBS, $C_{18}H_{29}NaO_3S$) were added into the above solution under stirring. Then, 4 mmol of Na_2MoO_4 aqueous solution (15 mL) was introduced to the former solution. The pH value of the mixture was adjusted to 5 or 4 with acetic acid solution. After additional agitation for 10 min, the as-obtained mixing solution was transferred into a 50 mL Teflon bottle held in a stainless steel autoclave, sealed, and maintained at 160 °C for 12 h. The precipitate was separated by centrifugation after the autoclave cooled to room temperature naturally. Finally, precipitate was washed with deionized water and ethanol in sequence, and then dried in air to a constant weight for further investigation.

A similar process were employed to prepare Eu^{3+}, Tb^{3+}, Dy^{3+}, or Sm^{3+} doped $BaMoO_4$ samples except for adding a stoichiometric amount (5 mol%) of $Eu(NO_3)_3$, $Tb(NO_3)_3$, $Dy(NO_3)_3$, and $Sm(NO_3)_3$ aqueous solution instead of $Ba(Ac)_2$ at the initial stage. For comparison, the experiment was performed to prepare $BaMoO_4$ sample by a similar process without using SDBS as additive. Moreover, different hydrothermal reaction temperature (200 °C, 12 h) and time (160 °C, 4 h, 8 h) were selected to investigate the formation process of the $BaMoO_4$ microspheres.

2.2. Characterization

The samples were characterized by powder X-ray diffraction (XRD) performed on a D8 Advance diffractometer (Bruker). Fourier transform infrared spectroscopy (FT-IR) spectra were measured with a Perkin–Elmer 580B infrared spectrophotometer with the KBr pellet technique. The morphology and composition of the samples were inspected using JSM-7500F cold field scanning electron microscope JEOL equipped with an energy-dispersive X-ray (EDX) spectrum. Transmission electron microscopy (TEM) images were obtained by an FEI Tecnai G2 S-Twin transmission electron microscope. Photoluminescence (PL) excitation and emission spectra were recorded with a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using a tunable laser (pulse width =4 ns, gate =50 ns) as the excitation (Continuum Sunlite OPO). All measurements were performed at room temperature.

3. Results and discussion

Fig. 1a and b shows the XRD patterns of the samples prepared with SDBS as surfactant at pH 5 and 4 (160 °C, 12 h). The diffraction peaks of two samples can be well indexed to the tetragonal scheelite-type structure of $BaMoO_4$ (JCPDS No. 29-0193, space group: I41/a, No. 88). No additional peaks of other phases can be detected, revealing the formation of pure tetragonal phase of $BaMoO_4$. The XRD pattern of the sample prepared without adding SDBS as additive also coincides with scheelite-type $BaMoO_4$ (Fig. 1c). Moreover, the crystallite size of the $BaMoO_4$ samples can be estimated by Scherrer's equation: $D = 0.89\lambda/\beta\cos\theta$, where D is the average grain size, the factor 0.89 is characteristic of spherical objects, λ is the X-ray wavelength (0.15405 nm), β and θ are the full-width at half-maximum and diffraction angle of an observed peak, respectively. The estimated average crystallite sizes of the spherical and flower-like $BaMoO_4$ samples are 43.9 and 38.8 nm, respectively.

The energy dispersive X-ray (EDX) spectrum was further used to investigate the as-obtained $BaMoO_4$ sample (pH 5). The EDX spectrum (Fig. 2a) of the $BaMoO_4$ sample confirms the presence

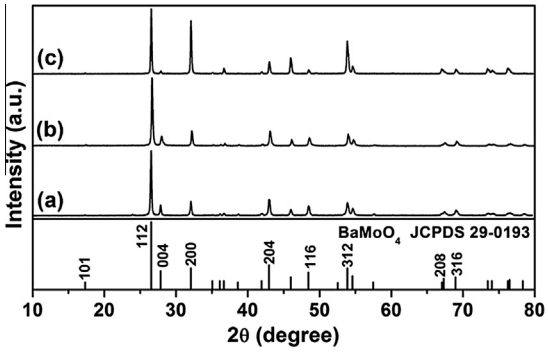

Fig. 1. XRD patterns of $BaMoO_4$ samples prepared at 160 °C for 12 h with SDBS additive at (a) pH 5, (b) pH 4 and (c) without SDBS as surfactant. The standard data of tetragonal $BaMoO_4$ (JCPDS No. 29-0193) is presented as a reference.

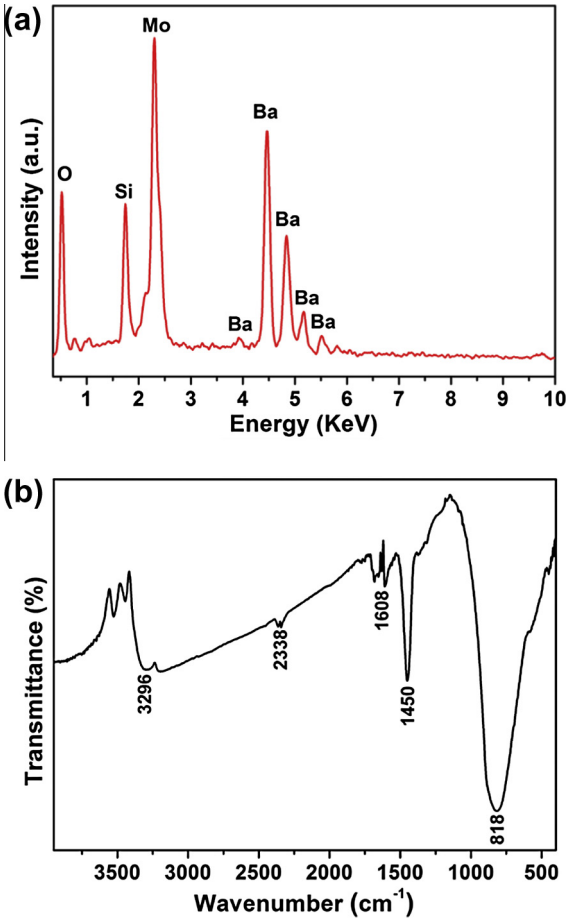

Fig. 2. (a) EDX and (b) FT-IR spectra of the $BaMoO_4$ sample prepared at pH 5.

of barium (Ba), molybdenum (Mo), and oxygen (O) elements (Si from the silicon substrate). No other impurity peaks can be detected, which confirms the pure phase of $BaMoO_4$ and can effectively support the XRD result of the sample. Fig. 2b shows the FT-IR spectrum of the $BaMoO_4$ sample prepared with SDBS as surfactant (pH 5). The absorption bands centered at 2338 and 3296 (1608) cm^{-1} are attributed to the atmospheric adsorbed CO_2 and the absorbed water on the surface of $BaMoO_4$ sample. The peak at 1450 cm^{-1} is assigned to the deformation vibration of C–H bond (δ_{CH}), which can be attributed to the characteristic frequencies of residual SDBS [25]. The intense absorption band centered at