Facile Morphology-Controlled Synthesis and Luminescence Properties of BaMoO$_4$:Eu$^{3+}$ Microparticles and Micro-Rods Obtained by a Molten-Salt Reaction Route

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This work focuses on the synthesis of morphology-controlled BaMoO$_4$:Eu$^{3+}$ micro-crystals such as microparticles and micro-rods using a facile molten salt method, and their morphology, structural characterization, and luminescent properties were comparatively investigated by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and fluorescence spectra. The molten salt method synthesized products from a reaction of BaMoO$_4$ precursor obtained by a co-precipitation method of BaCl$_2$ and Na$_2$MoO$_4$ with an eutectic salt mixture of NaCl–KCl at 700°C. Detailed studies revealed that the formation of the different morphologies of the micro-crystals was strongly dependent on the weight ratio of the salt (NaCl–KCl) to the BaMoO$_4$ precursor, and the formation mechanism of the products in the present molten salt system was also investigated. Based on the investigations of the photoluminescence properties, the samples with different morphologies prepared by the molten salt method had the strongest red emission at 615 nm, corresponding to the Eu$^{3+}$ $^5D_0$–$^7F_2$ transition in the BaMoO$_4$ host lattice, and the emission intensity of BaMoO$_4$:Eu$^{3+}$ microparticles was stronger than that of BaMoO$_4$:Eu$^{3+}$ micro-rods.

Keywords: Molten Salt Synthesis, Crystal Growth, BaMoO$_4$, Luminescence.

1. INTRODUCTION

The commercialization of white GaN-based light-emitting diodes (LEDs) has created tremendous interest in both academic and industrial applications.$^{1,2}$ Especially, the red light-emitting phosphors for white LEDs based on blue LEDs are still limited commercially to sulfide-based materials like CaS:Eu$^{2+}$. The host candidates of molybdates attract much attention because of their special luminescence and structure originating from the MoO$_6^{2-}$ group.$^{4,5}$ Among them, scheelite-type BaMoO$_4$ with tetragonal structure is an important material, so that many studies have been carried out on the synthesis technique and optical properties of the BaMoO$_4$-based inorganic functional materials.$^{6-9}$ A recent trend in material synthesis is to explore new methods to control the architecture and morphology at all dimensions from the nanoscale to macroscopic scale. Therefore, dendritic BaMoO$_4$ micro-crystals were fabricated via a micro-emulsion-mediated route, and nestlike and flowerlike BaMoO$_4$ nanostructures were also synthesized by a hydrothermal method.$^{6-7}$ Further, studies into the luminescent properties of BaMoO$_4$ doped with different rare earth ions, such as Eu$^{3+}$, Sm$^{3+}$, and Pr$^{3+}$, have been recently reported.$^{8-10}$

Molten-salt synthesis is a fascinating method for preparing inorganic oxide materials with different morphologies, shapes, and sizes.$^{11,12}$ Further, this method is very simple in facility, easy in manipulation, environmentally friendly, and available to large-scale production.$^{13}$ Further, molten salt plays a critical role in the whole process as a reaction medium solvent, where reactants dissolve and precipitate in the system, and it in turn results in a tendency to minimize the energies by forming a specific morphology.$^{14}$ In this paper, much effort has been given to the morphology-controlled synthesis of BaMoO$_4$ micro-crystals. Accordingly, BaMoO$_4$:Eu$^{3+}$ microparticles and micro-rods have been successfully synthesized by a facile molten salt method, and the morphology, shape, and size of the as-obtained micro-crystals can be controlled by adjusting such reaction conditions as the weight ratio of...
the salt (NaCl–KCl eutectic mixtures) to the BaMoO₄ precursor and the calcining time. The morphology, structural characterization, formation mechanism, and luminescent properties of the micro-crystals were investigated in detail.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

BaMoO₄:Eu³⁺ micro-crystals were successfully prepared by the eutectic NaCl–KCl molten salt method using BaMoO₄ co-precipitation precursor as the starting material. All chemicals were of analytical grade and used as received without further purification. Appropriate amounts of Na₂MoO₄·2H₂O (2.48 g) and BaCl₂·2H₂O (2.32 g) were dissolved in distilled water to form aqueous solutions with concentration of 1 M, respectively. 0.088 g Eu₂O₃ was dissolved in dilute HNO₃ under vigorous stirring to form the Eu(NO₃)₃ solution. Then, Eu(NO₃)₃ solution was first added to the above Na₂MoO₄ solution. Under strong magnetic stirring at room temperature, the as-mixed Na₂MoO₄ solution and BaCl₂ solutions were mixed together, and a precipitate was formed. The precipitate was filtered and washed with distilled water several times and dried in an oven at 60 °C for 5 h to obtain the BaMoO₄:Eu³⁺ precursor. By careful milling in an agate mortar, the BaMoO₄:Eu³⁺ precursor was mixed with a salt-mixture composed of 43.9 wt% NaCl and 56.1 wt% KCl, where the weight ratios of the salt to the BaMoO₄:Eu³⁺ precursor were 1:1, 2:1, 3:1, 4:1, 5:1, and 6:1. The mixtures were annealed at 700 °C for a given holding time (e.g., 1, 5, 10, and 20 h). Finally, the resultant products were thoroughly washed with hot distilled water and absolute ethanol, filtered, and dried at 60 °C for 3 h in the air to get the final products.

2.2. Characterization

The X-ray diffraction (XRD) patterns were recorded by using a SHIMADZU model XRD-6000 X-ray powder diffractometer [Cu Kα radiation, 40 kV, 30 mA and a scanning speed 2.0° (2θ)/min]. A scanning electron microscope (SEM, JEOL, JSM-6490) was employed to analyze the size and shape of the selected samples. The size, morphology, and electron diffraction (ED) pattern of the products were characterized by transmission electron microscopy (TEM, JEM-2010) with an accelerated voltage of 200 KV. The photoluminescence excitation and emission spectra were recorded by using a Perkin-Elmer LS-55 fluorescence spectrophotometer with a photomultiplier tube operating at 400 V, and a 150 W Xe lamp was used as the excitation lamp. Diffuse reflection spectra of as-synthesized phosphor powder samples were measured on an ultraviolet-visible-near infrared (UV-vis-NIR) spectrophotometer (UV-3600, SHIMADZU) attached to an integral sphere. BaSO₄ was used as a reference standard.

All the measurements for the as-synthesized samples were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1. Evolution of BaMoO₄ Crystals with Different Morphologies

It is found that the type and amount of salt, the composition, purity, initial particle size, and shape of the precursor all influence the morphologies and characteristics of the final products in the molten salt synthesis. Therefore, an eutectic salt mixture of NaCl–KCl with 43.9 wt% NaCl and 56.1 wt% KCl was used as the molten salt in the present experiment. The high reaction activity BaMoO₄ precursor obtained by a co-precipitation method was selected as the oxide source, because of its highly anisotropic growth in molten salt, as to successively synthesize anisotropic BaMoO₄ micro-crystals in the molten salt system. Further, in order to tune the growth behavior of BaMoO₄ micro-crystals in the NaCl–KCl molten salt system, changing the surface energy should be effective. Accordingly, it is believed that the weight ratios of the salt to precursor will play an important role in controlling the surface energy and crystal growth behavior. Figure 1 shows the SEM images of the as-prepared BaMoO₄:Eu³⁺ micro-crystals at 700 °C for 5 h in different weight ratios of the salt to BaMoO₄:Eu³⁺ precursor, (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4, (e) 1:5, and (f) 1:6. It can be seen from Figure 1 that there is an obvious difference in the morphology for the as-prepared BaMoO₄:Eu³⁺ products with increasing weight ratio of the salt to the precursor. When the weight ratio of the salt to the precursor is 1:1 or 1:2, the obtained BaMoO₄ crystals have the rhombohedral shape of spinel structure with particle sizes of about 2–3 μm and expose mostly (111) crystallographic planes. With increasing weight ratio of the salt to the precursor, there is an obvious morphology phase transition from particles to rods when the weight ratio is 1:3. Further, the obtained BaMoO₄ crystals appear as micro-rods with diameters of 0.5–1 µm and lengths of hundreds of micrometers when the weight ratio of the salt to the precursor is above 1:3, and the uniform micro-rods can be obtained when the weight ratio is 1:6. From the above observations, it is proved that the dissolution rate of BaMoO₄ precursor in the molten salt plays an important role that critically affects the morphology of the products in the synthesis. The SEM images shown in Figure 1 demonstrate that the weight ratio of the salt to BaMoO₄:Eu³⁺ precursor governs the final morphology of the as-prepared BaMoO₄:Eu³⁺ micro-crystals. A low weight ratio of the NaCl–KCl molten salt to the precursor tends to result in the BaMoO₄:Eu³⁺ microparticles, while a high weight ratio of the salt to the precursor will contribute to the formation of BaMoO₄:Eu³⁺ micro-rods. That is to say, the high weight ratios of the salt to the precursor
favor the crystallization and development of BaMoO$_4$:Eu$^{3+}$ micro-rods to a certain extent by the relative high dissolution rate and increasing surface energy.\textsuperscript{19}

In order to further understand the crystal growth behavior of the BaMoO$_4$:Eu$^{3+}$ precursor in the present NaCl–KCl molten salt system, Figure 2 shows the SEM images of the as-prepared BaMoO$_4$:Eu$^{3+}$ microparticles with weight ratio of the salt to precursor of 1:1 for different molten salt reaction times, (a) 1, (b) 5, (c) 10, and (d) 20 h. As shown in Figure 2, all the as-prepared BaMoO$_4$:Eu$^{3+}$ microparticles have the similar rhombic shape of spinel structure except for the different particle sizes depending on the different reaction time. There is an obvious grain growth trend with increasing time. For example, Figure 2(a) shows the smallest grain size (0.5–1 $\mu$m) with the reaction time of 1 h. Further, the sample grains grow up to 2–3 $\mu$m with uniform shape with the reaction times of 5 and 10 h. Finally, the BaMoO$_4$:Eu$^{3+}$ microparticles show a regular rhombic shape of spinel structure with the size of about 5 $\mu$m when the reaction time is prolonged to 20 h. Similarly, Figure 3 gives the SEM images of the as-prepared BaMoO$_4$:Eu$^{3+}$ micro-rods with the weight ratio of the salt to precursor of 1:6 for different molten salt reaction times, (a) 1, (b) 5, (c) 10, and (d) 20 h. It can be seen from Figure 3 that the same morphology as the micro-rods can be obtained for different reaction times. The obtained BaMoO$_4$ crystals appear as micro-rods with diameters of 0.5–1 $\mu$m and lengths of hundreds of micrometers. Especially, the uniform micro-rods can be obtained when the weight ratio is 1:6. It seems that the reaction time has little effect on the evolution of the BaMoO$_4$:Eu$^{3+}$ micro-rods. Therefore, we can draw a conclusion that only the large weight ratio of the NaCl–KCl molten salt, not the long reaction time helps to form the micro-rods. It is well known that, in molten salt solvents, strong electrostatic interactions between the ions

Fig. 1. SEM images of the as-prepared BaMoO$_4$:Eu$^{3+}$ microparticles and micro-rods with different weight ratios of the salt to BaMoO$_4$:Eu$^{3+}$ precursor, (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4, (e) 1:5, and (f) 1:6.
of the molten salt and the polar surfaces should occur, and surface energies of the polar planes may decrease greatly, which results in a relatively slow growth rate for these polar planes, and thus, it will obtain some exposed polar surfaces.\textsuperscript{20–21} That is to say, the BaMoO\textsubscript{4}:Eu\textsuperscript{3+} precursor is soluble in the NaCl–KCl molten salt, and the dissolution-precipitation mechanism may be the dominant mechanism throughout the synthesis. The product will readily synthesize via precipitation from the salt containing the dissolved reactants. When the weight ratio of the salt to the BaMoO\textsubscript{4}:Eu\textsuperscript{3+} precursor is lower than 1:3, the formation of the BaMoO\textsubscript{4}:Eu\textsuperscript{3+} microparticles will dominate. Comparatively, when the weight ratio of the salt to the BaMoO\textsubscript{4}:Eu\textsuperscript{3+} precursor is larger than 1:3, it will lead to the crystal growth of BaMoO\textsubscript{4}:Eu\textsuperscript{3+} micro-crystals in a preferred orientation, thus the (001) face in the spinel structure will disappear owing to the fast rate of the crystal growth of the BaMoO\textsubscript{4}:Eu\textsuperscript{3+} in the excessive molten salt solvents. Therefore, BaMoO\textsubscript{4}:Eu\textsuperscript{3+} micro-crystals with rhombic shape of spinel structure will transform to the micro-rods with widths of 0.5–1 \( \mu \)m and lengths of hundreds of micrometers. Accordingly, Figure 4 shows the digital photo and SEM images of the as-prepared BaMoO\textsubscript{4}:Eu\textsuperscript{3+} micro-rods in different magnification, respectively. It can be seen from Figure 4(a) that the as-prepared BaMoO\textsubscript{4}:Eu\textsuperscript{3+} micro-rods appear in the form of floccus lamella, and one can pick them up because the samples have some macroscopic mechanical strength. This indicates that the BaMoO\textsubscript{4}:Eu\textsuperscript{3+} micro-rods have enough length in the one-dimensional direction, and many micro-rods will get entangled to induce the existing strength, which is also shown in the SEM image in Figure 4(b). Further, as shown in Figures 4(c and d), micro-rods with regular and uniform shape can be found.

### 3.2. Growth Mechanism on the Formation of the BaMoO\textsubscript{4} Micro-crystals with Different Morphologies

From the above SEM images, the well crystallized BaMoO\textsubscript{4} crystallites in the form of microparticles and micro-rods can be obtained by the molten salt method, although the BaMoO\textsubscript{4} precursor also has a crystalline scheelite-type phase with small particle size and irregular amorphous phase. We propose that the reaction formula could be described as follows.

\[
\text{Ba}^{2+} + \text{MoO}_4^{2-} \rightarrow \text{BaMoO}_4 \downarrow \text{(precursor)} \quad (1)
\]

\[
\text{BaMoO}_4 \text{ precursor} + \text{Molten salt} \rightarrow \left( \text{NaCl} + \text{KCl} \right) \text{BaMoO}_4 \text{ crystallites} \left\{ \begin{array}{l}
\text{micro-particles} \\
\text{micro-rods}
\end{array} \right. \quad (2)
\]

That is to say, BaMoO\textsubscript{4} micro-crystals with well-crystalline and special morphology can be obtained via the molten salt treatment process. To evaluate the evolution process of the BaMoO\textsubscript{4} micro-crystals, TEM images
Fig. 3. SEM images of the as-prepared BaMoO₄:Eu³⁺ micro-rods with weight ratio of the salt to precursor of 1:6 for different molten salt reaction times, (a) 1, (b) 5, (c) 10, and (d) 20 h.

Fig. 4. Digital photo (a) and SEM images of the as-prepared BaMoO₄:Eu³⁺ micro-rods with weight ratio of the salt to precursor of 1:6 in different magnifications, (b) 200×, (c) 4,000× and (d) 9,000×.
of the samples obtained by different weight ratios of salt to the precursor are shown in Figures 5(a, b and c), which correspond to the weight ratios of 1:1, 1:3, and 1:6, respectively. As shown in Figure 5(a), the as-prepared BaMoO₄ microparticles have typical rhombic shape of spinel structure with particle sizes of 2–3 μm. A representative high resolution TEM (HRTEM) image of the BaMoO₄ microparticles (Fig. 5(d)) shows that the lattice fringe has a spacing of 0.35 nm belonging to the (004) lattice plane of the tetragonal BaMoO₄ phase, meaning that the microparticles grow along the (001) direction.²² The ED pattern (Fig. 5(e)) can be attributed to (010) zone axis diffraction, which suggests that the selected particle is a single crystal. As a comparison, the TEM image in Figure 5(c) also reflects the typical morphology of the micro-rods. The HRTEM image in Figure 5(f) shows that the lattice fringe has a spacing of 0.35 nm, which further proves the preferred orientation behavior, and the ED pattern indicates the good crystallinity of the micro-rods. It is more noticeable that the TEM image shown in Figure 5(b) indicates that a transition state from the microparticles to micro-rods can be found from the observation that a triangle angle corresponding to the rhombic shape is formed at the long micro-rod. In summary, Figure 5(h) gives the formation scheme of BaMoO₄:Eu³⁺ microparticles and micro-rods in the molten salt. First, when the mixtures including BaMoO₄:Eu³⁺ precursors and salts are fired at 700 °C (which is above the melting point of the salts) and form a flux, the precursor rearranges and diffuses quickly in the liquid state of the salts. Depending on different weight ratio of the salt to the precursor, BaMoO₄:Eu³⁺ microparticles and micro-rods can be formed. Then, as the calcining time increases, the as-grown microparticles and micro-rods develop to relatively big and uniform ones by consuming the small and agglomerated particles in accordance with the Ostwald ripening mechanism in the growth process.²²⁻²⁴

In order to further compare the difference of the BaMoO₄:Eu³⁺ microparticles and micro-rods, XRD investigation is also a possible method to determine the crystal structure, and one can use the difference on the relative intensities of XRD peaks to find the preferred orientation of the obtained micro-crystals with different morphologies. Therefore, Figure 6 gives the XRD patterns of the typical BaMoO₄:Eu³⁺ microparticles and micro-rods. As is shown in Figure 6, both microparticles and micro-rods have similar diffraction peaks, which are indexed according to JCPDS card 29-0193 of BaMoO₄. However, for the BaMoO₄:Eu³⁺ microparticles, the strongest diffraction peak at 26.5° is ascribed to the (112) face of the BaMoO₄ crystals. In comparison, the strongest diffraction peak at 46.0° is ascribed to the (220) face of the BaMoO₄ crystals for the BaMoO₄:Eu³⁺ micro-rods. The above observations further indicate that the difference of the crystallographic
behavior for the two different micro-crystals is very obvious. That is to say, the molten salt plays an important role in the formation of BaMoO$_4$ crystals with different morphologies, and the high weight ratios of the salt to the precursor favor the crystallization and development of BaMoO$_4$:Eu$^{3+}$ micro-rods.

### 3.3. Luminescence Properties of BaMoO$_4$

Crystals with Different Morphologies

To investigate the energy absorption of the BaMoO$_4$:Eu$^{3+}$ samples obtained in different stages, the diffuse reflectance spectroscopy (DRS) spectra of the BaMoO$_4$: Eu$^{3+}$ precursor, the typical BaMoO$_4$:Eu$^{3+}$ microparticles and BaMoO$_4$:Eu$^{3+}$ micro-rods are shown in Figure 9. From the evolution of DR spectra, the observed optical absorption edges, which are assigned to the charge-transfer (CT) band of Eu$^{3+}$ ions with the strong emission for near-UV or blue GaN-based LED chips.25–26 Especially, the weak broad bands near 240 nm are attributed to the charge-transfer (CT) transition between oxygen and molybdenum, which are consistent with the above DR spectra. The strong broad band near 285 nm should be ascribed to the CT band of Eu$^{3+}$, including the $3P_{0}$ $\rightarrow$ $3P_{2}$ transition for 395 nm and the $3P_{1}$ $\rightarrow$ $3P_{2}$ transition for 465 nm, which match well with near-UV or blue GaN-based LED chips.25–26

Figures 9(a and b) give the PLE spectra upon different excitation wavelength for the typical BaMoO$_4$:Eu$^{3+}$ microparticles and micro-rods, respectively. It is found that every kind of BaMoO$_4$:Eu$^{3+}$ sample has similar emission spectra, but their intensities are different. Among them, the excitation originating from the 466 nm blue light will induce the strongest red-emission light. For example, as given in Figures 9(a and b), on excitation with the 466 nm blue light irradiation, the emission spectra are described by the well-known $3D_{0}$ $\rightarrow$ $7F_{J}$ ($J = 0, 1, 2, \ldots$) emission lines of the Eu$^{3+}$ ions with the strong emission for $J = 2$ at 616 nm, which allows the Eu$^{3+}$ to occupy a center of asymmetry in the host lattice.28 Other transitions from the $5D_{1}$ excited levels to $7F_{J}$ ground states in the 570–750 nm range are relatively weak. Accordingly, Figures 9(b and c) give the variation of the emission intensities upon different excitation wavelengths for the BaMoO$_4$:Eu$^{3+}$ microparticles S1 and the micro-rods S2, it is obviously

**Fig. 6.** XRD patterns of the typical BaMoO$_4$:Eu$^{3+}$ (a) microparticles and (b) micro-rods, and the JCPDS card 29-0193 is also given as a comparison.

**Fig. 7.** UV-vis spectra of (a) the BaMoO$_4$:Eu$^{3+}$ precursor, (b) the typical microparticles, and (c) micro-rods.

**Fig. 8.** Photoluminescence excitation spectra of the typical BaMoO$_4$: Eu$^{3+}$ (a) microparticles and (b) micro-rods.
found that the emission intensity upon 466 nm is the largest. Figure 9(d) compares the emission spectra of the microparticles S1 and the micro-rods S2 upon the same excitation wavelength of 466 nm, and it is found that the emission intensity of BaMoO₄:Eu³⁺ microparticles is larger than that of BaMoO₄:Eu³⁺ micro-rods, which should be ascribed to the regular crystallographic behavior as mentioned above. Further, we can obviously find that the transition $^5D_0 \rightarrow ^7F_2$ is much stronger than the transition $^5D_0 \rightarrow ^7F_1$, which is favorable to improve the color purity of the red phosphor. Additionally, a ratio between the integrated intensity of these two transitions, $I_{593 \text{ nm}}/I_{593 \text{ nm}}$, is used in lanthanide based systems as a probe of the cation local surroundings, viz., Eu³⁺ occupies a center of asymmetry in the present BaMoO₄ host lattice.

4. CONCLUSIONS

We have developed a new route to the morphology controlled BaMoO₄:Eu³⁺ micro-crystals from microparticles to micro-rods by a molten salt process, and the morphology, shape, and size of the as-obtained micro-crystals can
be controlled by adjusting such reaction conditions as the weight ratio of the salt (NaCl–KCl eutectic mixtures) to the BaMoO₄ precursor and the calcined time. The resultant sample was in pure tetragonal BaMoO₄ structure without any other impurities. The formation of the different morphologies of the micro-crystals was strongly dependent on the weight ratio of the salt (NaCl–KCl eutectic mixtures) to the BaMoO₄ precursor. When the weight ratio of the salt to the BaMoO₄ precursor is 1:1 and 1:2, the obtained BaMoO₄ crystals have rhombic shape of spinel structure with particle sizes of 0.5–5 μm depending on the different reaction time and expose mostly (111) crystallographic planes. Further, the obtained BaMoO₄ crystals appear as micro-rods with diameters of 0.5–1 μm and lengths of hundreds of micrometers when the weight ratio of the salt to the BaMoO₄ precursor is above 1:3. Especially, the uniform micro-rods can be obtained when the weight ratio is 1:6. The formation mechanism of the products was investigated, and a heterogeneous nucleation and dissolution-recrystallization process takes place, especially the high weight ratio of the salt to the precursor supplies more driving force to form the micro-rods in the molten salt system. This novel crystal shape evolution provides insight into crystallization behavior and shape evolution process of the scheelite-type molybdate micro-crystals.

Acknowledgments: This present work was supported by the Ph.D. Programs Foundation of Ministry of Education of China (Grant No. 20090022120002), the Fundamental Research Funds for the Central Universities (2010ZY35), the Funds of the State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, and the College Student Research Innovation Program of China University of Geosciences, Beijing.

References and Notes


Received: 16 November 2010. Accepted: 16 May 2011.