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A red phosphor BaTiF$_6$·Mn$^{4+}$: reaction mechanism, microstructures, optical properties, and applications for white LEDs

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A red phosphor BaTiF$_6$·Mn$^{4+}$ with morphologies of micro rods and polyhedrons have been prepared respectively by etching TiO$_2$ and Ti(OC$_2$H$_5$)$_4$ in HF solution with optimized concentration of KMnO$_4$ at 1.5 mmol/L in hydrothermal condition. Red phosphor BaTiF$_6$·Mn$^{4+}$ exhibits a broad excitation band in blue and sharp emission peaks in red. White LED (WLED) fabricated with red phosphor BaTiF$_6$·Mn$^{4+}$ shows "warm" white light that possesses color rendering index of 93.13 at color temperature 4073.1 K.

1. Introduction

In recent years, special attention has been given on the synthesis of phosphors with broad absorption band in 380–490 nm, which show potential applications in WLEDs. The WLEDs fabricated with blue semiconductor and yellow phosphor have poor color rendering because of the scarcity of red components in their spectra. It is feasible to obtain "warm" white light with high color rendering (>80) and low color temperature (<4000 K) by mixing a red phosphor into packages of WLEDs.

The red phosphors for application in WLED coated with YAG:Ce should have a strong absorption in blue and an intense emission in red. Conventional red phosphors, such as Eu$^{2+}$ doped inorganic compounds, possess high quantum efficiency but the excitation band of Eu$^{3+}$ in blue region is too narrow due to 4f-4f transitions of Eu$^{3+}$. From a spectroscopic point of view, Eu$^{2+}$ doped sulfides and nitrides can meet the requirements for LEDs applications. However, the poor chemical stability of sulfides and critical synthetic requirements of air-sensitive metal nitrides make them unfavorable candidates for competitive products. Mn$^{4+}$ doped red phosphors have received increasing attentions due to their broad absorption band in 380–490 nm and sharp emission peaks at 610–760 nm. Among them, Mn$^{4+}$ doped dialkli hexafluorometallates in the form of A$_2$XF$_6$·Mn$^{4+}$ (A = K, Na, and Cs; X = Si, Ge, Zr, and Ti) are especially attractive due to their maximum absorption band in blue (that matches well with the electroluminescence of InGaN chip) and sharp emission peaks in red (that possesses high color purity), which shows significant potential application on WLEDs. The WLEDs show "warm" white light with a high color rendering 90 at color temperature 3088 K by coating a red phosphor K$_2$TiF$_6$·Mn$^{4+}$ together with yellow YAG:Ce phosphor on InGaN chip.
2. Experimental

2.1. Synthesis

The red phosphor BaTiF$_4$:Mn$^{4+}$ samples were prepared via a one-step method including hydrothermal and etching in a solution containing HF and K$\text{MnO}_4$. All the starting materials were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. In a typical process for synthesizing the red phosphor BaTiF$_4$:Mn$^{4+}$, the starting materials BaF$_2$ (A. R.), n-titanium butoxide Ti(O$\text{C}_3$H$_7$)$_4$ (A. R.), K$\text{MnO}_4$ (A. R.), HF (wt. 40%), and distilled water were mixed thoroughly in a Teflon cup. The molar ratio of BaF$_2$ and Ti(O$\text{C}_3$H$_7$)$_4$ were kept at 1:1. The concentration of HF was kept at 10 wt.% in all reactions. The concentration of K$\text{MnO}_4$ in the system was varied between 0.5 and 2.5 mmol/L. Hydrolyzing of titanium butoxide occurred in the mixing process. For comparison, commercially purchased TiO$_2$ (A. R.) was used for source of titanium in BaTiF$_4$:Mn$^{4+}$ in some cases. The Teflon vessel containing the suspension was closed in a stainless steel autoclave, and kept at 120°C for 24 h. After reaction, the autoclave was then cooled naturally to room temperature. The resulting white solid products were filtered, washed with distilled water, and dried under vacuum at room temperature for 24 h.

2.2. Characterization

X-ray powder diffraction (XRD) patterns of the as-prepared samples were examined using a diffractometer (D8 Advance, Bruker, Germany) equipped with graphite monochromatized Cu Kα radiation ($\lambda$=0.15406 nm) as the x-ray source. Identification spectra were recorded on a Shimadzu UV-1800 spectrometer with energy-dispersive x-ray spectrum (EDS). UV-visible reflectance scanning electron microscope (FEI Inc.) with an attached energy-dispersive x-ray spectrum (EDS). SEM and EDS of the as-synthesized red phosphors BaTiF$_4$:Mn$^{4+}$ obtained from starting materials BaF$_2$, HF, K$\text{MnO}_4$, and (a-c) TiO$_2$ and (d-f) Ti(O$\text{C}_3$H$_7$)$_4$ at 120°C for 20 h.

3. Results and discussion

3.1. Composition, morphology, and thermal stability

![Fig. 1 XRD patterns of the as-synthesized red phosphors BaTiF$_4$:Mn$^{4+}$ obtained from starting materials BaF$_2$, HF, K$\text{MnO}_4$, and (a) Ti(O$\text{C}_3$H$_7$)$_4$, and (b)TiO$_2$ at 120°C for 20 h.](image)

The crystal phases of the as-synthesized red phosphors BaTiF$_4$:Mn$^{4+}$ have been determined by XRD as shown in Fig. 1. The XRD patterns of the phosphors BaTiF$_4$:Mn$^{4+}$ from both TiO$_2$ and Ti(O$\text{C}_3$H$_7$)$_4$ are almost identical. All the diffraction peaks can be indexed to pure rhombohedral structure of BaTiF$_4$, with space group R-3m (166) and cell volume 340.91 Å$^3$ (JCPDS card no. 01-0508). The sharp diffraction peaks indicate that BaTiF$_4$ is crystallized in large size. No obvious phases of manganese oxides is detected, which indicates Mn$^{4+}$ ions occupy octahedral Ti$^{4+}$ sites due to the similar ionic radii and charge balance. The XRD patterns of samples prepared at different temperatures are shown in Fig. 1S in ESI† and pure BaTiF$_4$ phases can be obtained from by hydrothermal method at a temperature higher than 80°C. The diffraction peaks increase in intensity with further increase of reaction temperature, which results in higher luminescence intensity. We could not obtain red phosphor BaTiF$_4$:Mn$^{4+}$ by repeating two-step experiments for preparing BaTiF$_4$:Mn$^{4+}$ reported. The unclear phases may be attributed to BaSiF$_6$ produced by H$_2$SiF$_6$ and BaF$_2$, or starting materials which is not soluble at room temperature in previous work. It is tentatively believed that the reaction rates of etching and redox are significant for Mn$^{4+}$ doping in hexafluorometallates according to extensive research on synthesis in our work. The reaction mechanism responsible for formation of BaTiF$_4$:Mn$^{4+}$ may be due to simultaneous reactions of etching and redox expressed as the following equations:

$$\text{TiO}_2 + 2\text{BaF}_2 + 4\text{HF} \rightarrow 2\text{BaTiF}_4 + 2\text{H}_2\text{O}$$

$4\text{K}\text{MnO}_4 + 2\text{BaF}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{K}_2\text{MnF}_6 + 2\text{BaF}_2 + 10\text{H}_2\text{O} + \text{O}_2$

SEM and EDS of the as-synthesized red phosphors BaTiF$_4$:Mn$^{4+}$ obtained from starting materials BaF$_2$, HF, K$\text{MnO}_4$, and (a-c) TiO$_2$ and (d-f) Ti(O$\text{C}_3$H$_7$)$_4$ at 120°C for 20 h.

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and structure of the as-prepared red phosphors from TiO\textsubscript{2} and Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}, the micro rods and polyhedral particles are analyzed by EDS mapping measurements (Fig. 2c,f). EDS results indicate both crystals are composed of Ba, Ti, F and Mn. The moleculeratio of Mn/Ti is less than 0.25 mol\%. Element C in the spectrum is from the grids. XPS spectrum of the sample obtained from Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} also indicates the composition of BaTiF\textsubscript{6}:Mn\textsuperscript{4+} as shown in Fig. S3 in ESI\textsuperscript{†} that is consistent with the experimental results in EDS. Fig. S4 in ESI\textsuperscript{†} exhibits SEM images of BaTiF\textsubscript{6}:Mn\textsuperscript{4+} prepared from TiO\textsubscript{2} and Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} at different temperatures. The sample prepared from Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} at 80 °C is composed of irregular particles with different sizes and the particles grow with increasing temperature. Well dispersed and uniform polyhedral particles with diameter within 10 µm are obtained from Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} at 240 °C. Increasing the reaction time does not seem to give significant changes in morphology of micro rods of BaTiF\textsubscript{6}:Mn\textsuperscript{4+} formed from TiO\textsubscript{2}.

The thermal behavior of the red phosphor BaTiF\textsubscript{6}:Mn\textsuperscript{4+} has been measured by TG-DSC analysis (Fig. S5 in ESI\textsuperscript{†}). Weight loss (~5%) on TG and an endothermic peak on DSC curve at temperature lower than 100 °C is owing to the dehydration of water molecule absorbed on the crystal surfaces. The crystals of BaTiF\textsubscript{6}:Mn\textsuperscript{4+} keep constant weight below 390 °C. An endothermic peak at 445 °C indicates that the BaTiF\textsubscript{6}:Mn\textsuperscript{4+} crystals begin to decompose with the temperature increasing further.

### 3.2. Optical properties and application in WLEDs

The vibrational structure of BaTiF\textsubscript{6}:Mn\textsuperscript{4+} and undoped BaTiF\textsubscript{6} are studied by Raman spectroscopy recorded at room temperature as shown in Fig. S6 in ESI\textsuperscript{†}. The bands at low frequencies, up to approximately 600 cm\textsuperscript{-1}, are ascribed to the Raman modes and agree with the characteristic Raman vibrations of Ti-F stretching modes in group [TiF\textsubscript{6}]\textsuperscript{4–}:22,28 The Raman peaks of BaTiF\textsubscript{6}:Mn\textsuperscript{4+} attributed to Ti-F stretching modes shift to lower wavenumbers compared to undoped BaTiF\textsubscript{6} due to a slight change in the lattice symmetry by substituting Ti\textsuperscript{4+} with Mn\textsuperscript{4+}. The maximum phonon energies of both BaTiF\textsubscript{6}:Mn\textsuperscript{4+} and BaTiF\textsubscript{6} are at 625.5 cm\textsuperscript{-1}, which is much lower than those in oxides.20 Fig. 3 exhibits diffuse reflection spectra of undoped BaTiF\textsubscript{6} and red phosphors BaTiF\textsubscript{6}:Mn\textsuperscript{4+}. It is observed that the BaTiF\textsubscript{6} host demonstrates little absorption in visible region. A strong absorption is observed in blue region with a maximum at 470 nm in the curve of red phosphors BaTiF\textsubscript{6}:Mn\textsuperscript{4+}, which is indicative of its potential application in blue semiconductor chips.

The crystal structure of BaTiF\textsubscript{6} belongs to rhombohedral structure with the lattice constant of a=b=7.368 Å, c=7.252 Å. The Ti atom is sixfold coordinated by six F ions. as shown in Fig. S7 in ESI\textsuperscript{†}. Mn\textsuperscript{4+} ions substitute octahedral Ti\textsuperscript{4+} ions sites in BaTiF\textsubscript{6} based on the similar ionic radii and charge balance. The optical properties of phosphor samples BaTiF\textsubscript{6}:Mn\textsuperscript{4+} obtained from TiO\textsubscript{2} and Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} are comparatively studied as shown in Fig. 4. Both excitation spectra have a strong broad and maximum absorption in blue region, which are ascribed to spin-allowed and parity‐forbidden transitions \( {^5}A_2 \rightarrow {^7}T_1 \) of Mn\textsuperscript{4+}. The absorption in blue region is indicative of potential application of the phosphor BaTiF\textsubscript{6}:Mn\textsuperscript{4+} in blue InGaN chips. The excitation spectrum of BaTiF\textsubscript{6}:Mn\textsuperscript{4+} obtained from Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} have two bands in UV region, which are attributed to transitions from spin \( {^4}T_2 \) levels.

The as-prepared phosphor BaTiF\textsubscript{6}:Mn\textsuperscript{4+} emits red luminescence under excitation of blue light (Fig. 5 insert). As shown in Fig. 5, the emission spectra of BaTiF\textsubscript{6}:Mn\textsuperscript{4+} are composed of three bands with maximum at 613 nm, 630 nm, and 647 nm, which are attributed to transitions between vibronic levels of \( {^4}T_2 \) and \( {^2}A_2 \) of Mn\textsuperscript{4+}. The luminescence of BaTiF\textsubscript{6}:Mn\textsuperscript{4+} obtained from Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} is more intense than that from TiO\textsubscript{2} under identical experimental conditions, which may be due to the nanosized TiO\textsubscript{2} hydrolyzed from Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} is helpful to Mn\textsuperscript{4+} doping in TiF\textsubscript{6}\textsuperscript{2–} structure. The emission spectra (Fig. 5 insert) of the as-synthesized red phosphor BaTiF\textsubscript{6}:Mn\textsuperscript{4+} excited at 250 nm, 360 nm, and 466 nm have identical spectral features, which indicates only one kind of Ti\textsuperscript{4+} site in TiF\textsubscript{6}\textsuperscript{2–} that Mn\textsuperscript{4+} can occupies.

The influence of reaction temperature and concentration of
KMnO₄ on luminescence of red phosphor BaTiF₆:Mn⁴⁺ have been investigated (Figs. S8 and Fig. S9 in ESI†). The emission intensity can be improved by increasing reaction temperature from 80 °C to 240 °C, which is due to improved crystallization at higher temperature. The optimized concentration of KMnO₄ 40mmol/L is low enough, the majority of [MnO₄]⁻² cannot be reduced into Mn⁴+ and enter [TiF₆]³⁻ to form [MnF₆]³⁻ according to EDS and XPS data. The solution becomes purple while adding NaBiO₂ solution, which indicates some of [MnO₄]⁻² may be changed into Mn²⁺ left in the solution. In our work, Mn²⁺ can be detected while the concentration of KMnO₄ as high as those in references.8-25

Fig. 6 White luminescence spectra of WLED fabricated with blue GaN chip, yellow phosphor YAG:Ce, and red phosphor BaTiF₆:Mn⁴⁺. Insert: image of WLED under current of 20 mA.

The LEDs fabricated with blue InGaN chip, yellow phosphor YAG:Ce and red phosphor BaTiF₆:Mn⁴⁺ exhibits bright "warm" white light under current of 20 mA (Fig. 6). The WLED possesses a color rendering index of 93.13, color coordinates of (0.366, 0.3331) at color temperature 4073.1 K, and an efficiency of 121 lm/W (Table 1 in ESI†).

Conclusions

A red phosphor BaTiF₆:Mn⁴⁺ with morphologies of micro-rods and polyhedral particles have been prepared from TiO₂ and Ti(OCH₃)₄ by a one-step method including hydrothermal and etching. The BaTiF₆ crystal in our experiments are not grown in situ of starting materials and the growth process of BaTiF₆ crystal is effective in controlling the particle size and morphologies of BaTiF₆:Mn⁴⁺. There are only one kind of Ti⁴⁺ site in TiF₆³⁻ that Mn⁴⁺ can occupies. The optimal concentration of KMnO₄ in reaction system for synthesis of BaTiF₆:Mn⁴⁺ is 1.5 mmol/L, which is much lower than those in reported works. The BaTiF₆:Mn⁴⁺ based WLED exhibits "warm" white light with a color rendering index of 93.13.

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Notes and references

Red phosphors BaTiF$_6$:Mn$^{4+}$ were obtained by etching (a,b) Ti(OC$_4$H$_9$)$_4$ and (c,d) TiO$_2$ with BaF$_2$ in HF and KMnO$_4$ solution. The WLED fabricated with BaTiF$_6$:Mn$^{4+}$ exhibits "warm" white light with a color rendering index of 93.13.