

Eu³⁺或 Tb³⁺掺杂的 KY₂F₇ 纳米球的制备与表征

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摘要: 利用简单的室温液相反应制备了 KY₂F₇ 及镧系离子掺杂的 KY₂F₇:Eu³⁺和 KY₂F₇:Tb³⁺的纳米球, 并利用 XRD, TEM, SEM, XRF 和荧光光谱对所制备的材料进行了表征。研究表明 Eu³⁺或 Tb³⁺离子已成功地掺杂在 KY₂F₇ 纳米球中。掺杂后的 KY₂F₇:Eu³⁺和 KY₂F₇:Tb³⁺显示出 Eu³⁺或 Tb³⁺离子的特征发射峰。

关键词: 纳米球; 稀土氟化物; 液相法; 掺杂

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Preparation and Characterization of Eu³⁺ or Tb³⁺ Doped KY₂F₇ Nanospheres

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Abstract: The nanospheres of KY₂F₇ and the lanthanide doped KY₂F₇:Eu³⁺ and KY₂F₇:Tb³⁺ have been synthesized via a simple solution-based route at room temperature. The as-prepared samples were characterized by XRD, TEM, SEM, XRF and photoluminescence measurements. The results show that the luminescent lanthanide ions Eu³⁺ or Tb³⁺ is successfully doped into KY₂F₇ nanospheres. The resulting doped samples exhibit the characteristic emission peaks of Eu³⁺ or Tb³⁺ ion.

Key words: nanosphere; rare earth fluoride; solution method; doping

Recently, rare earth fluorides have attracted much attention due to their many potential applications derived from their unique properties such as luminescence^[1], ionic conductivity^[2], and scintillators^[3]. As a class of important optical materials, ternary rare earth fluorides have been extensively investigated. High-temperature solid state reactions were usually employed to prepare ternary rare earth fluorides, but these routes usually gave the product with relatively large and varied grain sizes and inhomogeneous morphologies^[4,5]. It is highly desired to develop facile preparative routes with easy control of particle sizes

and their distribution, phase homogeneity, and morphology. Recently, many reports have appeared for the preparation of nano- and microcrystals of ARF₄ (A=Li, Na, K, R=rare earth) with controlled size and shape^[6-12]. However, little work has been directed toward other types of ternary rare earth fluorides such as AR₂F₇, which were prepared by the high-temperature solid state reaction^[13,14] and hydrothermal routes^[15]. To the best of our knowledge, there has been no room-temperature preparative procedure reported for this type of ternary rare earth fluorides, nor the report concerned with nanoscaled particles of KY₂F₇. We have

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previously introduced a solution-based route to synthesize the ternary metal fluoride NaEuF₄ nanorods and Na₅Eu₉F₃₂ nanospheres by simply adjusting the reaction conditions at room temperature^[16]. Herein, we report the preparation of KY₂F₇ and the lanthanide doped KY₂F₇:Eu³⁺ and KY₂F₇:Tb³⁺ nanospheres via a room temperature simple solution-based route. The photoluminescence of KY₂F₇:Eu³⁺ and KY₂F₇:Tb³⁺ is also presented.

1 Experimental

Rare earth oxides Ln₂O₃ (Ln=Y, Eu, 99.99 %) and Tb₄O₇ (99.99 %) were purchased from Shanghai Yue Long New Materials Corporation. KF·2H₂O (A. R.) was from Shanghai Chemical Reagent Corporation. The rare earth nitrate Ln(NO₃)₃·6H₂O was made by dissolving rare earth oxide in nitric acid (63%~65%) and then evaporating the solvent. KY₂F₇ was prepared as follows. 4.0 mmol KF·2H₂O and 1.0 mmol Y(NO₃)₃·6H₂O were dissolved in 50 mL of distilled water in a plastic flask and the solution was stirred at room temperature for 6 hours. The white precipitates were collected and separated by centrifugation and washed in an ultrasonic bath several times with distilled water and ethanol. The final product was collected and dried at 70 °C for 3 h. KY₂F₇:Eu³⁺ and KY₂F₇:Tb³⁺ were prepared under the same reaction conditions except in the presence of 0.05 mmol Eu (NO₃)₃·6H₂O or Tb(NO₃)₃·6H₂O.

XRD analyses were carried out on a SHIMADZU XRD-6000 powder X-ray diffractometer, equipped with graphite monochromatized Cu K α radiation (λ = 0.154 06 nm), employing a scanning rate of 4.00°·min⁻¹, in the 2 θ range from 15° to 80°. The operation voltage and current were maintained at 40 kV and 30 mA, respectively. The morphologies of the as-synthesized samples were studied by transmission electron microscope (PHILIP TECNAI12) at 120 kV. The samples were ultrasonically dispersed into ethanol for several minutes prior to depositing on holey carbon-coated copper grids and allowing the excess solvent to evaporate. Energy-dispersive spectroscopy (EDS) and scanning electron microscope (SEM) analyses were

carried out on JEOL JSM-6700F at 10.0 kV. X-ray fluorescence (XRF) data were obtained from ARL-9800 spectrometer under an input power of 1 kW. The luminescent spectra of the solid samples were recorded on a luminescence spectrometer (AMINCO BOWMAN) at room temperature.

2 Results and discussion

The diffraction patterns of the as-prepared samples are shown in Fig.1. The XRD patterns of the three samples are identical and can be indexed to monoclinic KY₂F₇ (PDF No.27-0464), indicating that KY₂F₇ and Eu- or Tb- doped samples were prepared via solution reactions between Ln(NO₃)₃·6H₂O and four molar equivalent KF·2H₂O in water at room temperature. The doping of Eu³⁺ or Tb³⁺ has no effect on the phase of the monoclinic KY₂F₇. The same line widths between KY₂F₇ and the doped samples showed that they had the same grain size. The average grain size was estimated to be 10 nm by Scherrer equation using the θ values and the full-widths at half-maximum of the three observed peaks (220), (223), and (331).

Figs.2a~b show the TEM and SEM images of the

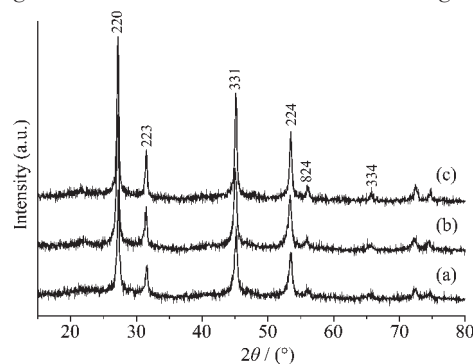


Fig.1 XRD patterns of as-obtained samples (a) pure KY₂F₇, (b) KY₂F₇:Eu³⁺, (c) KY₂F₇:Tb³⁺

pure KY₂F₇. It can be seen that the sample is composed of nanospheres with diameter of 60~150 nm. The surface of the KY₂F₇ nanospheres is not smooth. It appears that one nanosphere is composed of many small grains. The size of these small grains is ca. 10 nm, in agreement with the result of XRD estimated by Scherrer equation. Figs.2c~d show the TEM images of KY₂F₇:Eu³⁺ and KY₂F₇:Tb³⁺, respectively. It is obvious that the size and morphologies of KY₂F₇:Eu³⁺ and

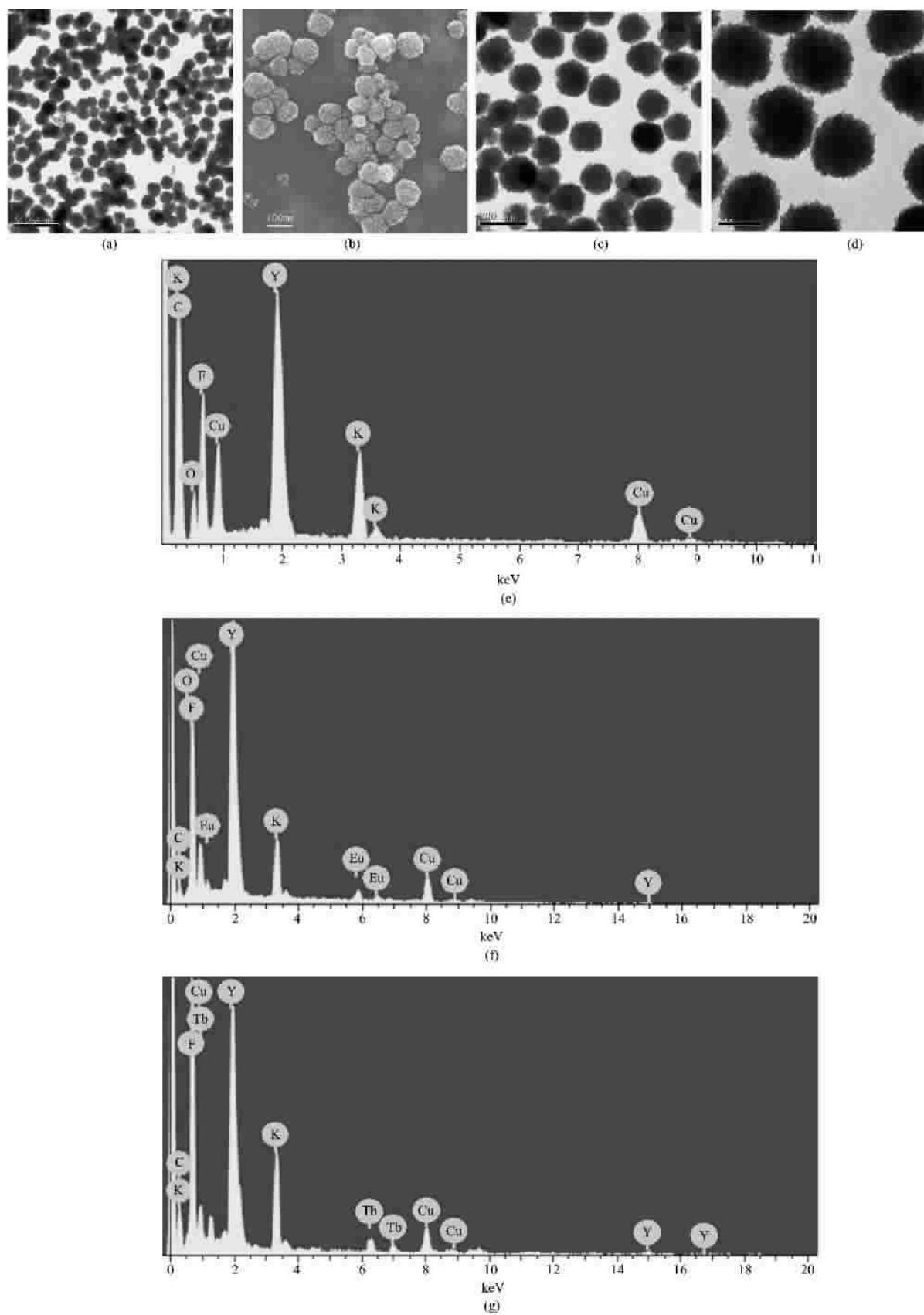


Fig.2 (a) TEM image of pure KY_2F_7 ; (b) SEM image of pure KY_2F_7 ; (c) TEM image of $\text{KY}_2\text{F}_7:\text{Eu}^{3+}$; (d) TEM image of $\text{KY}_2\text{F}_7:\text{Tb}^{3+}$; (e~g) EDS spectra of pure KY_2F_7 , $\text{KY}_2\text{F}_7:\text{Eu}^{3+}$ and $\text{KY}_2\text{F}_7:\text{Tb}^{3+}$

KY₂F₇:Tb³⁺ are identical with that of the pure KY₂F₇. As shown in Figs.2e~g, the as-prepared pure KY₂F₇ contains K, Y and F with atomic ratio of 1:1.9:7.6, in agreement with the theoretical value. Meanwhile, Eu³⁺ and Tb³⁺ ions are found in the rare earth doped KY₂F₇ nanospheres by EDS (Figs.2f~2g).

Experimental compositions of the as-prepared KY₂F₇ and the doped samples KY₂F₇:Eu³⁺, KY₂F₇:Tb³⁺ were further determined by X-ray fluorescence (XRF). The data show that there are three elements of F, Y, K in the KY₂F₇, in agreement with the EDS result. Meanwhile, the XRF result of the doped samples indicates that there are Eu (or Tb) in KY₂F₇:Eu³⁺ and KY₂F₇:Tb³⁺ samples in addition to the existence of K, Y, and F elements.

The results of controlled experiments show that reaction time (6 h, 12 h, 24 h) has no significant effect on the phases and morphologies of the final products as long as the molar ratio of Y³⁺/KF is not less than 4 (e.g. 1:6 and 1:10). When the molar ratio of Y³⁺/KF is less than 4, no pure product would be ob-

tained as judged by the XRD results.

Figs.3a~b shows the emission spectra of the KY₂F₇:Eu³⁺ and KY₂F₇:Tb³⁺ powders at room temperature, respectively. When excited at 394 nm, the emission peaks centered at 592, 616, 651, 697 nm are observed for KY₂F₇:Eu³⁺, which could be contributed to the transitions ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₃, and ⁵D₀ → ⁷F₄, respectively^[17]. The emission peaks at 490, 544, 588 and 621 nm are observed for KY₂F₇:Tb³⁺ when excited at 374 nm, corresponding to the ⁵D₄ → ⁷F₆, ⁵D₄ → ⁷F₅, ⁵D₄ → ⁷F₄, and ⁵D₄ → ⁷F₃, respectively^[18]. These emissions are very weak, which might be due to the small size and poor crystallinity. These two as-prepared doped samples were treated at 300 °C or 400 °C for 4 h. The XRD pattern shows the same crystalline phases. Furthermore, the annealed samples have the same spherical morphology. However, the emission intensities are much stronger than those of the original samples (Fig.3). These results indicate that the heat treatment can improve the emission properties of the doped KY₂F₇ nanospheres.

3 Conclusions

A simple and efficient room-temperature solution route was used to prepare pure KY₂F₇ and lanthanide doped KY₂F₇ nanospheres, which have been characterized by XRD, TEM and SEM and XRF. This method further supports that the room-temperature solution route could be used to prepare the nanoscaled powder of the ternary rare earth fluoride. The successful doping of the luminescent lanthanide ions into KY₂F₇ nanospheres might provide an opportunity to further study their optical properties and applications.

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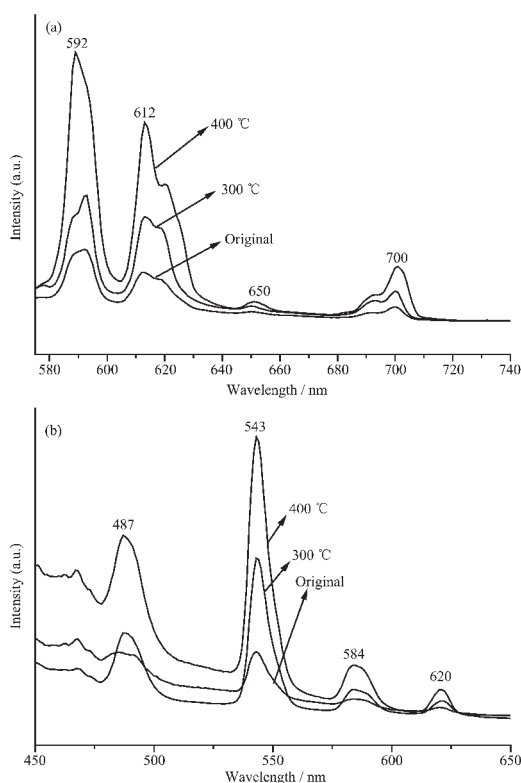


Fig.3 Photoluminescent spectra for (a) KY₂F₇:Eu³⁺ and (b) KY₂F₇:Tb³⁺: the as-prepared one and the ones calcined at 300 °C and 400 °C, respectively, for 4 h

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