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Synergistic weak/strong coupling luminescence in Eu-metal-organic framework/Zn_2GeO_4:Mn^{2+} nanocomposites for ratiometric luminescence thermometer

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ABSTRACT

Engineering novel ratiometric temperature sensors with high temperature sensitivity is still of a great challenge in versatile temperature measurement fields. Herein, a self-calibrated optical luminescent thermometer based on Eu^{3+}/Mn^{2+} dual-activator was fabricated in the same nanocomposite system, which integrated the photoluminescence originated from the temperature-insensitive Eu-metal organic framework with weak coupling effect and the temperature-sensitive Zn_2GeO_4:Mn^{2+} with strong coupling effect. Specifically, the as-prepared nanocomposites composed of lanthanide MOF Eu-BTC (BTC = 1,3,5-benzenetricarboxylic acid) and Zn_2GeO_4:Mn^{2+} nanorods possessed Eu^{3+}/Mn^{2+} dual red/green emission, which displays excellent ratiometric temperature-sensing functions and also has high relative sensitivity (S_r) of 4.1% ºC^{-1} when they are used as ratiometric luminescent thermometer in the physiological temperatures (25–45 °C). These results demonstrate that such a design strategy with synergistic weak/strong coupling luminescence is useful and the as-obtained Eu-MOF/Zn_2GeO_4:Mn^{2+} nanocomposites can be potential for temperature sensor applications.

1. Introduction

Recently, high frequency and accurate temperature measurements in both scientific and industrial fields have put forward high requirements for optical thermometers [1,2]. As one of the useful strategies, luminescence-based technique is gaining popularity attributing to its simplicity, high sensitivity, and excellent temperature resolution. Among them, various types of luminescent thermometers have been developed for temperature sensing, however, most of them belong to the single wavelength emitter, and the temperature-dependent luminescence performance may be disturbed by some unexpected factors, such as probe concentration, fluorescence efficiency, excitation intensity, and so on, further leading to the inaccurate measurements [3,4].

In contrast, ratiometric luminescent probe based on two independent luminescent centers can give rise to a highly stable self-referencing sensing performance [5]. Thus, such a fluorescence intensity ratio (FIR) based temperature sensing technology has recently attracted broad interest. Generally speaking, both high absolute and relative temperature sensitivities (S_a and S_r) are the key parameters to evaluate the desired temperature detecting properties [6]. So far, an alternative strategy involved in the design of the synergistic luminescence from Eu^{3+} and Mn^{2+} ions has been adopted. Herein, the luminescence from the lanthanide ion Eu^{3+}, with 4*f*-4*f* electronic transition, belongs to the "weak coupling" system, in which the luminescence is relatively insensitive against temperature change. However, the luminescence from Mn^{2+} belongs to the typical 3d–3d forbidden transitions with the "strong coupling" effect, and it generally presents a serious thermal quenching phenomenon [6]. Therefore, by integrating these two activators within a single system, it is possible to achieve a FIR with high temperature dependence. In addition, developing a highly sensitive thermometric material with sub-micro grain size is also a big challenge for improving the temperature detecting properties. Therefore, the following work has been conducted to develop the new FIR materials.

As is known, luminescent metal-organic frameworks (MOFs) demonstrated their great potential in temperature detection, and we can finely design the luminescent properties of the emission centers within MOFs by adjusting the constituents or by post-synthetic functionalized method [4], and many dual-emission thermometers based on lanthanide MOFs were developed [5–14]. Nevertheless, simple and feasible

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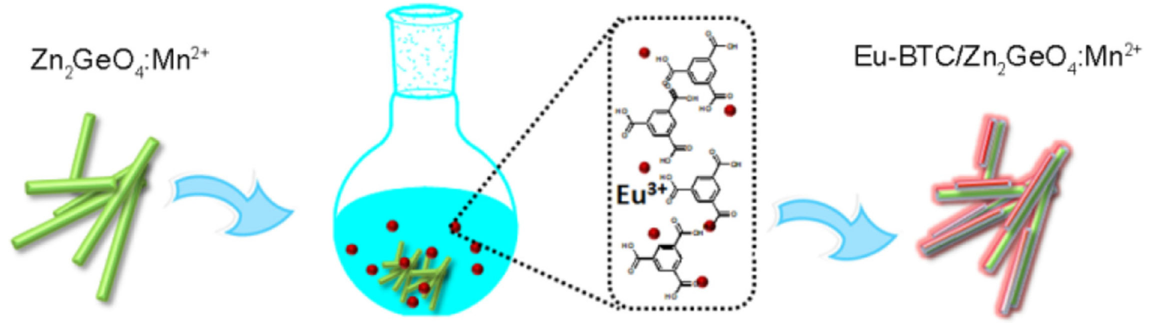

Scheme 1. Schematic illustration of Eu-BTC/Zn_2GeO_4:Mn^{2+} preparation.

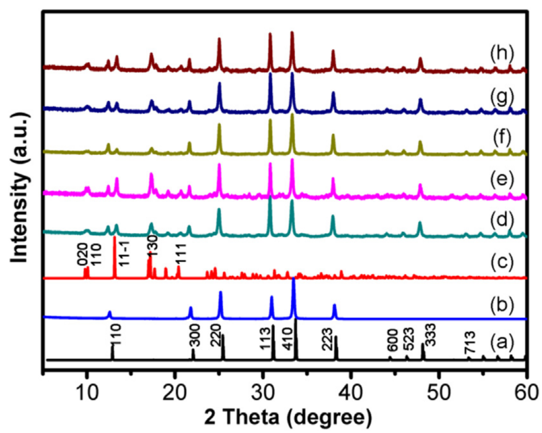

Fig. 1. Simulated (a) and experimental (b) XRD patterns of Zn_2GeO_4 and Zn_2GeO_4:Mn^{2+}; Simulated XRD pattern of Eu-BTC (c) and experimental XRD patterns of Eu-BTC/Zn_2GeO_4:Mn^{2+}-(1) (d), Eu-BTC/Zn_2GeO_4:Mn^{2+}-(2) (e), Eu-BTC/Zn_2GeO_4:Mn^{2+}-(3) (f), Eu-BTC/Zn_2GeO_4:Mn^{2+}-(4) (g), and Eu-BTC/Zn_2GeO_4:Mn^{2+}-(5) (h).

integrated systems displaying high sensitivity and resolution is still desperately needed. Accordingly, lanthanide MOF Eu-BTC (BTC = 1,3,5-benzenetricarboxylic acid) with efficient and characteristic luminescent properties is an ideal platform for fabrication of lanthanide MOF-based integrations. Moreover, Mn^{2+}-doped zinc germanate (Zn_2GeO_4:Mn^{2+}), a kind of significant green-emitting optical materials upon UV excitation, has also been found to be potential in optical sensing applications [15,16]. In this work, a dual-emitting Eu-BTC/Zn_2GeO_4:Mn^{2+} nanocomposite was designed and successfully prepared. The luminescent intensity ratio of Eu^{3+} to Mn^{2+} in the integrated composite shows a polynomial function with temperature, which can guarantee the absolute temperature measurement with a high relative sensitivity (S_r) of 4.1% $^{\circ}C^{-1}$ in the physiological temperature range (25-45 °C). The cycle-temperature sensing performance and temperature resolution of Eu-BTC/Zn_2GeO_4:Mn^{2+} composite were also studied in detail. The results demonstrate that such a design with synergistic weak/strong coupling luminescence is useful and the as-obtained Eu-MOF/Zn_2GeO_4:Mn^{2+} nanocomposites possess potential for temperature sensor applications.

2. Experimental

2.1. Synthesis of Eu-BTC/Zn_2GeO_4:Mn^{2+} nanocomposites

Zn_2GeO_4:Mn^{2+} nanorods were firstly prepared *via* a hydrothermal route. In a typical synthesis, 0.02 mmol of manganese (II) acetate tetrahydrate ($Mn(CH_3)COO)_2 \cdot 4H_2O$, 98%, Damao, Tianjin, China), 0.98 mmol of zinc(II) acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 98%, Damao, Tianjin, China) and 1 mmol of GeO_2 (99.99%, Aladdin, Shanghai, China) were used as starting materials, NaOH (96%, AR grade, Aladdin, Shanghai, China) or HCl (12 mol/L, Damao, Tianjin, China) solution (1 mol/L, aqueous solution) was used to adjust the pH at 8, and then they were treated at 140 °C for 24 h in the autoclave. For the preparation of Eu-BTC/Zn_2GeO_4:Mn^{2+} nanocomposites, 0.5 mmol of the as-prepared Zn_2GeO_4:Mn^{2+} powder was used with the fixed content (0.13 g), and 5 different ratios of Eu-BTC and Zn_2GeO_4:Mn^{2+} nanorods have been designed. 0.05, 0.10, 0.20, 0.30, 0.40 mmol of $Eu(NO_3)_3 \cdot 6H_2O$, corresponding to 0.15, 0.30, 0.60, 0.90, 1.20 mmol of 1,3,5-benzenetricarboxylic acid, and 0.025, 0.05, 0.10, 0.15, and 0.20 g of Na_2CO_3 were mixed with Zn_2GeO_4:Mn^{2+} in 30 mL of H_2O, respectively, and the solution was stirred for 12 h (Scheme 1). The resultant white precipitates having different synthetic molar ratio of Eu-BTC to Zn_2GeO_4:Mn^{2+}, including 0.1, 0.2, 0.4, 0.6, and 0.8 were defined as Eu-BTC/Zn_2GeO_4:Mn^{2+}-(1), Eu-BTC/Zn_2GeO_4:Mn^{2+}-(2), Eu-BTC/Zn_2GeO_4:Mn^{2+}-(3), Eu-BTC/Zn_2GeO_4:Mn^{2+}-(4), and Eu-BTC/Zn_2GeO_4:Mn^{2+}-(5), respectively, which were washed with distilled water and ethanol several times and dried at 60 °C in the oven.

2.2. Characterization

The phase composition of Eu-BTC/Zn_2GeO_4:Mn^{2+} nanocomposites were characterized by powder X-ray diffraction (XRD) on a X'Pert Pro MRDDY2094 diffractometer with Cu-K_{α} radiation (λ = 1.5418 Å). The sample morphology was investigated by scanning electron microscope (SEM, Hitachi SU-8010). The observation with transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) was conducted using a JEM-2100F electron microscope (JEOL, Japan) accompanied with an energy dispersive spectroscopy (EDS) to examine the chemical composition. The photoluminescence (PL) spectra were carried out on a fluorescence spectrophotometer (FluoroMax-4, HORIBA) equipped with a 150 W xenon lamp as the excitation source. The temperature-dependent luminescence performances were evaluated by an attached heating furnace (Luma 40™/Horiba4). An electric heating attachment coupled with circulating cooling water pipes were introduced into the sample chamber of the same Horiba fluorescence spectrophotometer to carry out the fluorescence measurements at different temperatures.

3. Results and discussion

Scheme 1 demonstrates the feasible and simple synthetic route used for the preparation of Eu-BTC/Zn_2GeO_4:Mn^{2+} nanocomposites. It includes two steps, firstly, the preparation of Zn_2GeO_4:Mn^{2+} nanorods by hydrothermal method and, secondly, the fabrication of the nanocomposites by precipitation method, as was also described in the