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Optimization method for blue $Sr_2MgSi_2O_7$:Eu^{2+}, Dy^{3+} phosphors produced by microwave synthesis route

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A B S T R A C T

We report a kind of dopant (Eu^{2+}) and co-dopant (Dy^{3+}) co-doped strontium magnesium silicate phosphor synthesized via microwave irradiation in a weak reductive atmosphere of active carbon. X-ray diffraction (XRD) patterns illustrated that the samples were nearly pure $Sr_2MgSi_2O_7$ phase, in which the $Sr_2MgSi_2O_7$ host phase has the maximum fraction of tetragonal crystallography $Sr_2MgSi_2O_7$ phase. A series of long afterglow luminescent materials were synthesized to investigate the best synthetic conditions. The results showed that the optimal concentration of H_3BO_3 and the best sintering time were 5 wt% and 30 min, respectively. The phosphors made from the microwave irradiation method demonstrated excellent luminescence performance and the microwave irradiation method provide a strategy for the synthesis of other alkali earth aluminate and silicate, or other luminescent materials.

1. Introduction

Long afterglow phosphor is one kind of photoluminescent materials [1,2]. As a kind of "green light source material", people pay greater attention towards it in the recent shortage of energy. Owing to it consumes its own stored energy in the long afterglow process, it does not need external energy supply, which makes the material irreplaceable in some specific environments. The material can be widely used in traffic safety signs [3,4], sensor and detector [5–8], biomedical imaging [9,10], photocatalysis [11,12], solar cell [13,14] and in many other fields.

Rare earth doped silicate long afterglow materials have superior performance in the afterglow [15]. In addition to making up for the shortage of the aluminate long afterglow materials of poor humidity resistance, which broaden the use of long afterglow materials, it can be utilized in waterborne coatings and other moist environment directly [16,17]. Furthermore, the luminescent materials based on silicate has good chemical and thermal stability, with the sintering temperature lower than aluminates by about 100 °C, while the high-purity silica raw material is cheap and easy to obtain. The silicate long afterglow materials make up for the single issue of luminous color. In the early stage, the research results of doped silicate phosphors have laid a solid foundation for the study of long afterglow silicate materials [18–21]. The successful development of silicate long afterglow materials provides a valuable model for further exploration of new long afterglow materials. The synthesis method for long afterglow materials plays a significant role in determining the features of microstructure, afterglow properties, fluorescent quantum efficiency and the distribution of defects [1]. The conventional method is solid-state reaction [22], which require a high sintering temperature in order to obtain designed compositions, but a high sintering temperature can lead to agglomerated products with irregular morphologies. The chemical synthesis-liquid phase reaction such as sol-gel method [23], hydrothermal method [24], co-precipitation [25] and combustion methods [26], do not require high sintering temperature, however, the process is unfriendly to environment with the products possessing unsatisfactory long afterglow properties.

Like other visible light, microwaves are polarized waves and coherent waves, following the laws of light, whose interaction with matter can be transmitted, absorbed, or reflected, depending on the nature of matter. Different interactions have been involved during the microwave process, including extraction [27], sterilization [28], homogeneous precipitation and co-precipitation [29], hydrothermal method [30], sintering method [31] and solid phase synthesis [32]. Compared with the conventional synthesis method, microwave heating has the advantages of fast heating, uniform heating,

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energy saving, high efficiency and easily control.

Herein, we propose a one-step facile preparation of Eu^{2+} and Dy^{3+} co-doped long afterglow luminescent material ($Sr_2MgSi_2O_7$:Eu^{2+}, Dy^{3+}) with excellent fluorescent properties via microwave irradiation. As illustrated in Scheme 1, the $Sr_2MgSi_2O_7$:Eu^{2+}, Dy^{3+} long afterglow luminescent material (SLPLM) was synthesized in the presence of carbon powders under weak reducing atmosphere, where carbon powders acted as a wave absorbing agent and thermal reductant. In addition, a layer of mullite powder with high thermal resistance was also added outside the furnace to provide a good environment for the holding crucible, and to effectively improve the microwave heating temperature, reduce the heating time, and eliminate the damage of high temperature on the microwave furnace. The obtained SLPLM phosphor exhibited well-defined cuboid-like structures and bright blue-light emission properties as well as remarkable persistent luminescence performance.

2. Experimental section

2.1. Materials

Strontium carbonate ($Sr(CO)_3$) was purchased from Sinopharm Chemical Reagents Co. Ltd. (Beijing, China). Silicon dioxide (SiO_2), europium oxide (Eu_2O_3), dysprosium oxide (Dy_2O_3), boric acid (H_3BO_3) and carbon powders were bought from Aladdin Industrial Corporation (Shanghai, China). Basic magnesium carbonate ($4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$) was purchased from Macklin Biochemical Co. Ltd (Shanghai, China). Without otherwise stated, all other reagents and solvents were purchased from commercial suppliers and used as received without further purification.

2.2. Synthesis of $Sr_{1.975}MgSi_2O_7$:$Eu^{2+}{}_{0.01}$, $Dy^{3+}{}_{0.015}$ powders

Polycrystalline powdered samples with the nominal composition $Sr_{1.975}MgSi_2O_7$:$Eu^{2+}{}_{0.01}$, $Dy^{3+}{}_{0.015}$ was prepared via a one-step facile microwave radiation reaction. Firstly, according to the molar ratio of 2:0.2:1.975:0.005:0.075, SiO2, $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$, $Sr(CO)_3$, Eu_2O_3 and Dy_2O_3 were accurately weighed, respectively and mixed properly. Then H_3BO_3 (the ratio of H_3BO_3 to $Sr_{1.975}MgSi_2O_7$:$Eu^{2+}{}_{0.01}$, $Dy^{3+}{}_{0.015}$ was 2 wt %~8 wt %), which is the cosolvent, was added into the above mixed material. Afterwards, the final mixed materials with zirconia beads were put together in an agate jar and mechanically, milled intensively using a high-energy ball mill. The samples, under a reduced atmosphere provided by carbon powders, were further sintered at high fire stall of a microwave oven (P70F23P-G5(B0)) for 20–30 min, and then allowed to cool to room temperature in the furnace. The reducing atmosphere was required to ensure the complete reduction of Eu^{3+} to Eu^{2+}. Note that this slow cooling also provides the formation of a ceramic structure for these materials. A series of $Sr_2MgSi_2O_7$:Eu^{2+}, Dy^{3+} long afterglow luminescent materials (SLALM) with different contents of cosolvent and different sintering time were prepared, namely SLALM-1 (5 wt % H_3BO_3, 30min), SLALM-2 (5 wt % H_3BO_3, 25min), SLALM-3 (5 wt % H_3BO_3, 20min), SLALM-4 (2 wt % H_3BO_3, 30min), and SLALM-5 (8 wt % H_3BO_3, 30min).

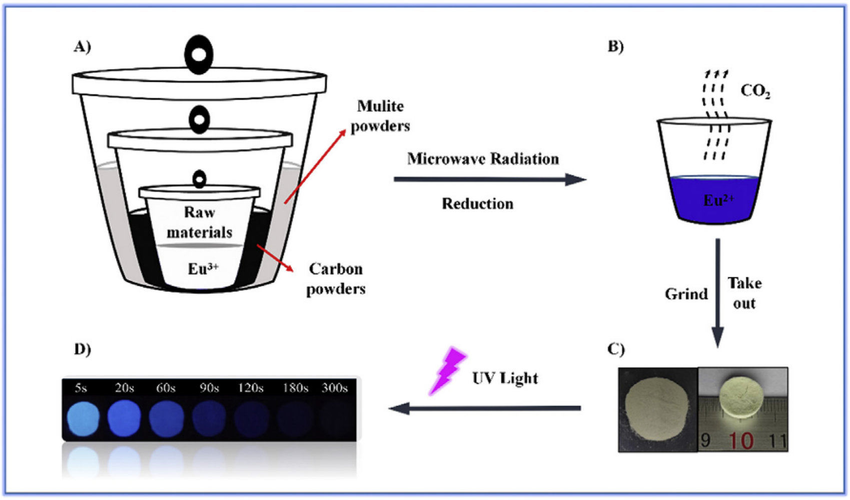
2.3. Characterization of properties

FT-IR spectra were obtained using a TENSOR27 PMA 50 (Brook, Germany). The Powder XRD data were collected on a Ultima IV (kabuskiki kaisha) X-ray diffractometer with CuKα radiation ($k = 1.5418$ Å), with a scan speed of 10 min^{-1}, scanning angle from 10°to 80°and running at 40 kV and 20 mA. The morphologies of the phosphors and films were characterized by scanning electron microscope (SEM) and the fluorescence microscopic images were taken by inverted fluorescence microscope (EVOS, America) at room temperature. The photoluminescent properties were investigated for emission and excitation spectra at room temperature with FluoroLog 3-TCSPC (Jobin Yvon Inc. USA). Afterglow properties were obtained using Screen luminance meter ST-86LA-3(Beijing, China) after the samples have been fully activated under ultraviolet (UV) light for 10 min. The decay curves were determined from an average of three independent sample measurements.

3. Results and discussion

3.1. Characterizations of the long persistent phosphors

FTIR spectra has been extensively used in the identification of organic and inorganic compounds. The $Sr_2MgSi_2O_7$:Eu^{2+}, Dy^{3+} phosphor was analyzed by FTIR and the spectra are shown in Fig. 1. The appearance of a broad band at 3430 cm^{-1} is related to the



Scheme 1. Schematic illustration for the preparation of SLPLM phosphor. The digital photograph of mixed raw materials before (a) and after microwave radiation (b), digital photograph of SLPLM phosphor (c) and the digital images of the SLPLM phosphor after excitation at 365 nm for 10 min viva an ultraviolet lamp with a power of 6 W (d).