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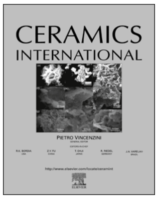

Effect of H_3BO_3 flux on the morphology and optical properties of $Sr_2MgAl_{22}O_{36}:Mn^{4+}$ red phosphors for agricultural light conversion films

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ABSTRACT

H_3BO_3 was added during the preparation of $Sr_2MgAl_{22}O_{36}:Mn^{4+}$ phosphors by a high-temperature solid-state reaction method. The influence of H_3BO_3 flux on the crystal structure, particle morphology and photoluminescence properties of the $Sr_2MgAl_{22}O_{36}:Mn^{4+}$ phosphors was investigated by employing X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence spectroscopy, respectively. The results indicate that adding H_3BO_3 flux can improve the luminescence intensity and morphology, and reduce the synthesis temperature of the $Sr_2MgAl_{22}O_{36}$ phosphor. The formation temperature of pure-phase $Sr_2MgAl_{22}O_{36}$ was significantly decreased when H_3BO_3 flux as introduced. The excited state lifetime of the $Sr_2MgAl_{22}O_{36}$:1.2 mol% Mn^{4+} phosphor by the addition of 2.0 wt% H_3BO_3 was ~1.02 ms. We demonstrated the potential of these phosphors to enhance sunlight harvesting by agricultural light conversion film testing. We propose that films containing the $Sr_2MgAl_{22}O_{36}$:1.2 mol% Mn^{4+} phosphor can be applied to increase the production of agricultural plants.

1. Introduction

In the 21st century, the world is faced with an energy crisis. To maintain sustainable economic development, it is very important to improve the efficiency of energy consumption. Solar energy is widely accepted as a free, abundant and endlessly renewable source of clean energy. Countless efforts have been dedicated to develop methods to leverage this cheap energy source. The agricultural light conversion film, as an important factor in plant production, can significantly improve the land utilization rate, production efficiency and economic efficiency. We know that plants harness solar energy via photosynthetic processes to produce sugar and other life-essential compounds [1]. Agricultural crops harvest sunlight primarily through green-pigment chlorophyll antenna complexes. However, these compounds only absorb blue and red light, leaving the other components of the solar spectrum unused. Converting unused sunlight to blue and red light is a valuable method to improve the sunlight conversion efficiency of the photosynthetic process [2]. The addition of a light conversion agent to the films can greatly improve the utilization of sunlight for crops and thus increase agricultural production. Currently, the function of light conversion can be achieved by adding the sunlight conversion agent to a plastic film. This type of agricultural light conversion film requires blue or red phosphors with a high quantum efficiency. A large number of red- and blue-emitting phosphors excited by NUV light, such as $CaZnOS:Eu^{2+}$, $MZnOS:Mn^{2+}$ (M=Ca, Ba), $KBaBP_2O_8:Eu^{3+}$, $M_2Si_5N_8:Eu^{2+}$ (M=Ca, Sr and Ba), $NaSrBO_3:Ce^{3+}$, $Ba_5(BO_3)_2(B_2O_5):Sm^{3+}$, have been reported and generally possess excellent chemical and physical stabilities [3–11]. Among the red-emitting phosphors, the most used activators are Eu^{2+} and Eu^{3+}, followed by Ce^{3+} and Sm^{3+}, among others. Noticeably, most of these rare earth ions are very expensive, and some of their chlorides, citrates, and oxides are toxic and harmful, which substantially limits their widespread application. At the same time, a high demand also stimulates the search for rare-earth ion doping schemes, for instance, Eu^{2+}-doped oxynitrides and nitrides have to be synthesized under high-temperature, high-pressure, or reducing conditions. Additionally, for Eu^{3+}- and Sm^{3+}-doped red phosphors, the sharp absorption peaks in the UV region limit their application in agricultural light conversion films because of their low energy converting efficiency [12]. Consequently, research into environment-friendly, cost-effective and rare-earth-free phosphors that can be prepared at relatively low temperatures and in air remains an

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important issue. As a transition metal ion, Mn^{4+} has been widely used as an activator for red phosphors. The typical spin-forbidden ^2E_g-$^4A_{2g}$ transition is capable of generating a bright red emission with a high quantum efficiency [13]. Thus, for example, the Mg-germanate:Mn^{4+} phosphor has been applied as a color correcting phosphor in high-pressure mercury vapor lamps and in fluorescent lamps to provide light for plant growth. On the other hand, phosphors such as $3.5MgO \cdot 0.5MgF_2 \cdot GeO_2$:$Mn^{4+}$ and ZnS:Mn^{2+}, contain no rare-earth ions. However, toxic and harmful elements, such as arsenic (As) and sulfur (S), in phosphors have a long-term adverse effect on the environment [14,15]. Recently, a novel highly efficient red-emitting $Sr_2MgAl_{22}O_{36}$:Mn^{4+} (SMA:Mn^{4+}) phosphor has been investigated, and is regarded as a potential phosphor for UV-based W-LEDs [16]. Based on the d-d transitions of the manganese ion with a $3d^3$ electron configuration, Mn^{4+}-doped $Sr_2MgAl_{22}O_{36}$ has been identified as a red phosphor with a broad absorption band in the visible region and superior chromaticity in the deep red region. However, to meet the practical application of current agricultural light conversion films, it is necessary to further enhance the luminescent intensity. At the same time, a conventional SMA:Mn^{4+} phosphor is prepared by solid-state methods at temperatures above 1400 °C, which leads to large particle sizes and hard particle agglomerates. The luminescent efficiency and stability of phosphors can be reduced due to the irregular shape of particles and crystal damage by subsequent ball milling. Therefore, it would be worthwhile to synthesize SAM:Mn^{4+} at a relatively lower temperature. There have been many research efforts directed towards the development of promising methods and the improvement of the luminescent intensity. To sufficiently improve the luminescent intensity and morphology, while reducing the reaction temperature, fluxes are used to stimulate the diffusion of ions and the formation of a host lattice at a low temperature [17]. It has become a popular research topic to investigate the effect of fluxes on the properties of luminescent materials.

In this paper, we prepared SMA:Mn^{4+} phosphors by a high-temperature solid-state reaction method using H_3BO_3 as the flux. The effects of the H_3BO_3 flux on the crystal structure, morphology and photoluminescence properties of SMA:Mn^{4+} phosphors were investigated. The results suggest that adding H_3BO_3 flux improves the morphology and luminescent intensity, and reduces the crystallization temperature. In addition, agricultural light conversion films were fabricated by blending SMA:Mn^{4+} phosphor with polyethylene. We propose that SMA:Mn^{4+} phosphors are suitable as potential light conversion agents for application in agricultural functional films.

2. Experimental

2.1. Materials and synthesis

According to the report of Cao et al. [16] a series of SMA red phosphors with the composition of SMA:1.2 mol% Mn^{4+} were synthesized by a flux-assisted conventional high-temperature solid-state reaction method. The oxides including $SrCO_3$ (99.99%), MgO (98%), Al_2O_3 (99.99%), H_3BO_3 (98%) and $MnCO_3$ (99.99%) were used as starting materials. The starting materials were thoroughly mixed in an agate mortar. The mixed raw materials were then placed in a crucible and annealed at 800 °C for 3 h and subsequently further sintered at 1000–1600 °C for 6 h in air. The calcinations were conducted at a heating rate of 5 °C/min up to the holding temperature. The products were obtained in the form of rosy powders. The sunlight conversion films were continuously prepared by pelleting and bubble film technology.

2.2. Characterizations

The crystal structure of the SMA:1.2 mol% Mn^{4+} phosphor was determined by XRD (Philips Model PW1830) with Cu-K_α radiation (λ=1.5406 Å) at 36 kV and 30 mA. A scan rate of 0.02°/s was applied to record the XRD pattern. The morphology of the SMA:1.2 mol% Mn^{4+} phosphor was characterized by SEM (ZEISS, EVO18) operating at an acceleration voltage of 15 kV. The effects of the reaction temperature and H_3BO_3 flux concentration on the photoluminescence intensity of the SMA:1.2 mol% Mn^{4+} phosphor were investigated using a fluorescence spectrophotometer (Hitachi Model F-7000) equipped with a 150 W Xenon lamp as the excitation source. The decay curve was measured by a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using a tunable laser as the excitation source. The sunlight conversion effect of the films was tested on a fiber optic spectrometer (AvaSpec-2048TEC-FI, Avantes, China) with a 150 W Xe lamp as the light source. The samples were cut into rectangular strips (1×3 cm^2). Each measurement consisted of 500 cycles, with each cycle taking 0.2 s. All of the measurements were performed at room temperature.

3. Results and discussion

3.1. X-ray diffraction analysis

The melting point and other properties of the raw materials should be taken into consideration with the high-temperature solid-state reaction method. Initially, the raw materials were boiled, dehydrated and finally decomposed with the evolution of a large amount of gases, such as CO_2 and H_2O. As is known, H_3BO_3 will lose a molecule of water at approximately 105 °C, $MnCO_3$ will decompose to MnO and CO_2 when heated to 150 °C, and $SrCO_3$ will decompose to SrO and CO_2 when the calcination temperature is above 1000 °C. Therefore, we chose 1000 °C as the minimum calcination temperature to decompose the carbonate and eliminate water, and the temperature was gradually raised to obtain the pure phase of the $Sr_2MgAl_{22}O_{36}$ phosphor.

The XRD patterns of the SMA:1.2 mol% Mn^{4+} powders prepared at various temperatures are shown in Fig. 1. The results indicate that the SMA:1.2 mol% Mn^{4+} prepared from the high-temperature solid-state reaction without flux contains a large amount of impurities, such as Al_2O_3(◆), which could greatly reduce the phosphor photoluminescence intensity. The phosphors

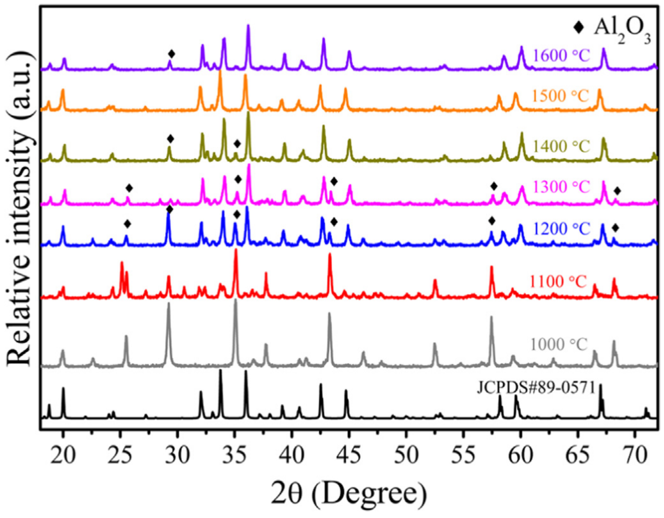

Fig. 1. X-ray diffraction (XRD) patterns of the SMA:1.2 mol% Mn^{4+} phosphor annealed at different temperatures for 6 h in air and JCPDS#89-0571.