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Host-sensitized phosphorescence of Mn^{4+}, $Pr^{3+,4+}$ and Nd^{3+} in $MgAl_2Si_2O_8$

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ABSTRACT

Mn^{4+} doped and $Pr^{3+,4+}$, Nd^{3+} co-doped $MgAl_2Si_2O_8$-based phosphors were first of all synthesized about 1300 °C. They were characterized by thermogravimetry (TG), differential thermal analysis (DTA), X-ray powder diffraction (XRD), photoluminescence (PL) and scanning electron microscopy (SEM). The luminescence mechanism of the phosphors, which showed broad red emission bands in the range of 610–715 nm and had a different maximum intensity when activated by UV illumination, was discussed. Such a red emission can be attributed to the intrinsic d–d transitions of Mn^{4+}.

1. Introduction

Luminescent materials with long afterglow are kinds of energy storage materials that can absorb both UV and visible light from the sun and gradually release this energy in the dark at a certain wavelength. These kinds of long lasting phosphors have been widely studied by many researchers [1–3].

Silicates therefore are suitable hosts for phosphors because of their high physical and chemical stability. The luminescence of rare earth ions in the silicate host has been studied for a long time. In recent years, silicate phosphors have been reported by researchers [4–13].

In this paper, $MgAl_2Si_2O_8$:Mn^{4+},$Pr^{3+,4+}$ and $MgAl_2Si_2O_8$:Mn^{4+},Nd^{3+} based phosphors were synthesized 1300 °C. Their thermal behavior, crystal structure, morphological characterization, photoluminescence properties and excitation mechanism were then investigated.

2. Experimental

$MgAl_2Si_2O_8$:Mn^{4+},$Pr^{3+,4+}$ and $MgAl_2Si_2O_8$:Mn^{4+},Nd^{3+} phosphors were synthesized at 1300 °C. All the starting materials, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ (A.R.), Al_2O_3 (99.0%), SiO_2 (99.8%), MnO_2 (99.0%), Pr_6O_{11} (99.99%) and Nd_2O_3 (99.99%) were weighed according to the nominal compositions of $(Mg_{0.84}Mn_{0.10}Pr_{0.06})Al_2Si_2O_8$ and $(Mg_{0.88}Mn_{0.10}Nd_{0.02})Al_2Si_2O_8$. These powders were mixed homogeneously in an agate mortar for 3 h. Small quantities of H_3BO_3 (A.R.) were added as a flux during the mixing. A small amount of each sample was taken for thermal analysis (DTA/TG) to study the phase-forming process. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out by using a DTA/TG system (Perkin Elmer Diamond type). The samples were heated at a rate of 10 °C min^{-1} from room temperature to 1300 °C, in the nitrogen atmosphere.

Afterwards, the sintering conditions of the phosphors, including the pre-firing temperature and synthesizing temperature, were determined into two steps: first, the mixtures were pre-fired at 900 °C for 3 h in a porcelain crucible in air, and then the pre-fired samples were sintered at 1300 °C for 3 h in air, in a porcelain crucible. After these procedures the phosphors were obtained and their crystal structures were examined by X-ray diffraction (XRD) analysis using a Bruker AXS D8 Advance diffractometer which was run at 20–60 kV and 6–80 mA, $2\theta = 10–90^\circ$ and a step of 0.002° using Cu Kα X-ray.

Scanning electron microscopy (SEM) images and EDX analysis were performed on a LEO 440 model scanning electron microscope using an accelerating voltage of 20 kV.

The decay time, excitation and emission spectra of the phosphors were recorded by a Perkin Elmer LS 45 model luminescence spectrophotometer with xenon lamp.

3. Results and discussion

3.1. Thermal behavior, crystallization and morphology

Fig. 1 illustrates the DTA/TG curves of nominal composition for $MgAl_2Si_2O_8$: Mn^{4+},$Pr^{3+,4+}$. The curves below 200 °C include the

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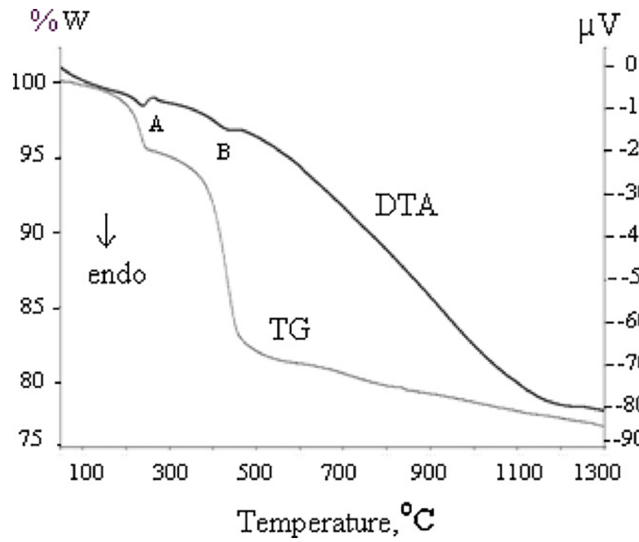

Fig. 1. TG/DTA curves of $MgAl_2Si_2O_8$: Mn^{4+},$Pr^{3+,4+}$ phosphor.

dehydration of $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ and the decomposition of H_3BO_3 which changes into B_2O_3. The first endothermic peak is (at 240 °C, point A) attributed to the deviation of the hydroxyl group from $Mg(OH)_2$. The second endothermic peak shows (at 437 °C, point B) the decomposition of $MgCO_3$ which changes into MgO.

From the above DTA/TG analysis, we carried out the sintering of the phosphors in two steps: first, the samples were pre-fired at 900 °C for 3 h to achieve the dehydration and decomposition of H_3BO_3, $MgCO_3$ and $Mg(OH)_2$, and to help the doped Mn^{4+} and rare-earth ions to substitute; next the phosphors were prepared at 1300 °C for 3 h in air. Actually, the crystal systems were not observed at 900 °C, but at 1300 °C for 3 h the $(Mg_{0.84}Mn_{0.10}Pr_{0.06})Al_2Si_2O_8$ and $(Mg_{0.88}Mn_{0.10}Nd_{0.02})Al_2Si_2O_8$ triclinic crystal systems were observed (Fig. 2).

The XRD patterns of phosphors obtained at 900 °C and 1300 °C for 3 h in air are shown in Fig. 2(a) and (b). The unit cell parameters of phosphor crystallized in the triclinic system are listed in Table 1.

Figs. 3 and 4 show the images and EDX analysis obtained from the scanning electron microscopy (SEM) of the phosphors calcined at 1300 °C for 3 h. The microstructures of the phosphor consisted of regular fine grains with an average size of about 0.5–2.5 μm.

3.2. Photoluminescence properties

Fig. 5 shows the excitation and emission spectra of the $MgAl_2Si_2O_8$:Mn^{4+},$Pr^{3+,4+}$ phosphor annealed at 1300 °C. The excitation spectrum of the $MgAl_2Si_2O_8$:Mn^{4+},$Pr^{3+,4+}$ phosphor observed with Mn^{4+} emissions at 662 nm (d–d transitions) consists of an excitation band with a maximum at 258 nm. Under 258 nm UV excitation, the $MgAl_2Si_2O_8$:Mn^{4+},$Pr^{3+,4+}$ phosphor shows a strong red luminescence ranging from 600 to 750 nm with a maximum; at 662 nm and some lines (611, 634, and 710 nm) in the longer wavelength region. The red emission at 662 nm, which can be viewed as a typical Mn^{4+} emission, was ascribed to d–d transitions [14]. The emission bands at 611 nm and 634 nm are due to the transitions of Pr^{3+} ($^1D_2 \rightarrow {}^3H_4$) and Pr^{4+} ($^1D_2 \rightarrow {}^3P_0$), respectively [15]. In order to identify the origin of the emission band of the $MgAl_2Si_2O_8$:Mn^{4+},$Pr^{3+,4+}$ phosphor at 710 nm, we compared the emission spectrum of the undoped $MgAl_2Si_2O_8$ sample under the same excitation conditions (258 nm). We

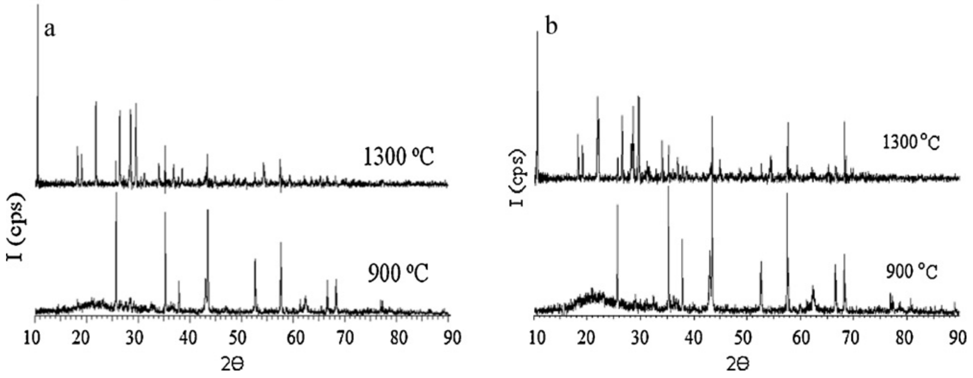

Fig. 2. XRD patterns of (a) $(Mg_{0.84}Mn_{0.10}Pr_{0.06})Al_2Si_2O_8$, (b) $(Mg_{0.88}Mn_{0.10}Nd_{0.02})Al_2Si_2O_8$.

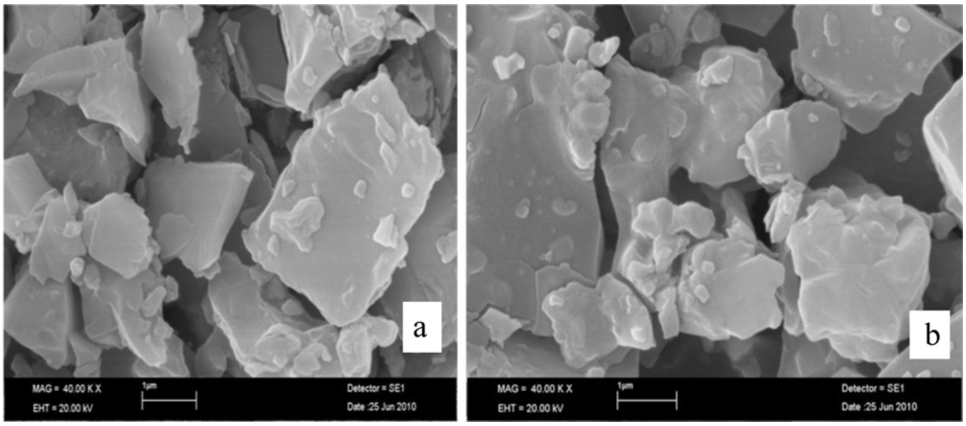

Fig. 3. SEM image of (a) $(Mg_{0.84}Mn_{0.10}Pr_{0.06})Al_2Si_2O_8$, (b) $(Mg_{0.88}Mn_{0.10}Nd_{0.02})Al_2Si_2O_8$ phosphors.