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Luminescence of dysprosium doped strontium aluminate phosphors by codoping with manganese ion

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ABSTRACT

The authors report here the luminescence properties of strontium aluminate doped with dysprosium and manganese. The dysprosium, manganese co-doped powders were prepared by a solid state reaction at temperatures at 1600 °C under H_2 (15%)–Ar (85%) atmosphere. The dysprosium, manganese co-doped strontium aluminate phosphors have the monoclinic structure with lattice parameters $a \approx 8.440$ Å, $b \approx 8.821$ Å, $c \approx 5.157$ Å and $\beta \approx 93.4°$. The characteristic $^4F_{9/2} \to {}^6H_{15/2}$ (blue), $^4F_{9/2} \to {}^6H_{13/2}$ (yellow), $^4F_{9/2} \to {}^6H_{11/2}$ (red) and $^4F_{9/2} \to {}^6H_{9/2}$ (NIR) transitions of Dy^{3+} for different luminescence techniques (radioluminescence, photoluminescence and cathodoluminescence) were detected in the emission spectra at the room temperature. The luminescence of Mn^{2+} co-doped $SrAl_2O_4:Dy^{3+}$ exhibits a broad green–orange emission band ($^4T_1 \to {}^6A_1$ transition) from the synthesized phosphor particles under different excitation sources. This corresponds to the spin-forbidden transition of the d-orbital electron associated with the Mn^{2+} ion. Multiple emission lines observed at each of these techniques are due to the crystal field splitting of the ground state of the emitting ions. The nature of the emission lines is discussed.

1. Introduction

Solid-state lighting using light-emitting diode (LED) and phosphor material to generate white light is the current re-search focus in the lighting industry. Solid-state lighting technology has several advantages over conventional fluorescent lamps such as reduced power consumption, compactness, efficient light output, and longer lifetime. Solid-state lighting will have its impact on reducing the global electricity consumption. White light-emitting diodes (LEDs) can save about 70% of the energy and do not need any harmful ingredient in comparison with the conventional light sources, such as incandescence light bulbs and the luminescent tubes. Therefore white LEDs have a great potential to replace them and are considered as next generation solid state light devices [1,2].

Rare earth ions are characterized by an incompletely filled 4*f* shell, which can absorb the excitation energy to be at the excited state and then return to the ground state, resulting in emitting state in the visible region [3–5]. These feature transitions within the $4f^n$ configuration have been found an important application in lighting and display (color television). The syntheses of conventional rare earth phosphors primarily focused on the high-temperature solid-state reactions providing agglomerated powders. They can allow to readily alter the structural characteristics of the solid powders [6].

At present, the most of this kind phosphors have at least two luminescent centers, such as Eu^{2+}/Mn^{2+} [7–10], or Eu^{2+} (in different lattice sites) [11]. As the natural white light emission ions, Dy^{3+} ions have two dominant emission bands of blue (485 nm, $^4F_{9/2} \to {}^6H_{15/2}$) and yellow (570 nm, $^4F_{9/2} \to {}^6H_{13/2}$) [12,13]. Recently, Dy^{3+} doped alkaline earth orthosilicates ($Sr_2SiO_4:Dy^{3+}$) powders have attracted much attention due to its excellent emission characteristic, single luminescent center, and high absorption efficiency in the UV region [14,15]. As known, Mn^{2+} ions can effectively absorb UV light and then emit different colors from green to deep red depending on the surrounding crystal field strength [16]. Red or white phosphors were successfully obtained by adjusting the concentration ratios of Mn^{2+}/Dy^{3+} or Eu^{2+}/Dy^{3+} [17–19]. Therefore, there is reason to believe that the $3d^5$ configured Mn^{2+} ions may effectively compensate the emission of $SrAl_2O_4:Dy^{3+}$ phosphor as a emitting center. Among various host matrix materials, aluminates are considered to possess high energy efficiency, wide excitation wavelength range, and high quenching temperature.

In this paper, Dy^{3+} and Mn^{2+} ions co-doped $SrAl_2O_4$ powders were prepared by the solid-state reaction method using H_3BO_3 (boric acid) as the flux. Crystal structure and luminescence properties of prepared powders were investigated as well as the energy transfer process from Dy^{3+} to Mn^{2+}.

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2. Experimental procedures

All powder samples were synthesized by the solid-state reaction method. High purity Dy_2O_3 (>99.99%), $SrCO_3$, Al_2O_3, and H_3BO_3 (5 wt%, the flux) were used as the starting materials. Stoichiometrical amounts of starting materials were weighed out according to nominal composition and then heated in a furnace for 2 h in a platinum crucible up to the required temperature (1600 °C) in a controlled atmosphere (Ar with 15% of H_2). Phase identification was carried out using a Philips X'Pert Pro MPD diffractometer (XRD) with Cu Kα radiation line (λ = 1.5418 Å) at room temperature. The PL measurements were detected by a Jobin–Yvon monochromator system. A diode laser with a wavelength of 473 nm was used as a pump source at 300 K. Standard lock-in techniques were employed to improve the signal to noise ratio by chopping the incident beam and feeding the output signal to a lock-in amplifier. The emission spectra were recorded using a dual color Si/InGaAs uncooled detector. RL spectrum was recorded during the excitation with an X-ray tube set to 30 kV and 15 mA. Light leaving the sample was transmitted to an entrance slit and detected with a Jobin Yvon spectrometer, coupled to charge-coupled device (CCD) cooled with liquid nitrogen [20]. Wavelength accuracy is about ±0.2 nm. The samples were examined using an ESEM XL30 microscope of FEI Company. The microscope has a chemical EDS probe and a MONOCL3 Gatan probe to record CL spectra. The PMT covers a spectral range of 250–850 nm, and is more sensitive in the blue parts of the spectrum. The excitation for CL measurements was provided at 30 kV electron beam. The spectral system was calibrated with a standard mercury lamp. The used 300 mm Czerny–Turner monochromator is a standard part of the MonoCL3 system having a focal length of 300 mm, aperture f/4.2, grating size of 69 mm × 69 mm, dispersion of 1.8 nm mm^{-1} for 18001/mm grating and resolution grating dependent with a maximum of circa 0.5 nm and a wavelength accuracy of ±0.2 nm, automated backlash removal with the position determined by software.

3. Results and discussion

The analysis of XRD data of $SrAl_2O_4$ phases is usually qualitative, just based on relative peak intensities. XRD was used to identify the presence of any impurity phases of compositions different from $SrAl_2O_4$. A typical X-ray diffraction pattern of the resultant Dy^{3+}, Mn^{2+} codoped $SrAl_2O_4$: is shown in Fig. 1. The lattice parameters were calculated from the XRD data on the basis of the parent $SrAl_2O_4$. The latticed parameter calculated were for monoclinic $SrAl_2O_4$, $a \approx 8.440$ Å, $b \approx 8.821$ Å, $c \approx 5.157$ Å, $\beta \approx 93.4°$, with no measurable change in the cell volume. It is to be noted that the small amount of doped rare-earth active ions Dy^{3+} and Mn^{2+} co-doped have almost no effect on the basic crystal structure of $SrAl_2O_4$. In general, the substitution of Mn^{2+} with smaller ionic radius cannot change the crystal structure of host. However, the difference of ionic radiuses between Sr^{2+} and Mn^{2+} is 40.0% and the electro negativity of Mn^{2+} (1.55) is much bigger than that of Sr^{2+} (0.95), which make the excess Mn exist in "MnO_2" form [21].

The surface morphology and crystalline sizes of the synthesized $SrAl_2O_4$:Dy^{3+}, Mn^{2+} phosphors were observed by ESEM. It can be seen that all of the phosphor powders consisted of irregular fine grains with an average size of about 7–8 μm and have similar surface morphology of single-crystalline grains. The distribution of the crystallite sizes is not homogeneous. The morphological images of the prepared $SrAl_2O_4$:Dy^{3+}, Mn^{2+} phosphors are displayed in Fig. 2.

There are two main strengths in luminescence measurements. The first is that they are extremely sensitive and at best, in detection of rare earth impurities, they can readily respond to impurity levels minute concentrations of ppm or less. The second advantage is that the spectral dispersion can not only discriminate between different types of defect sites, but can reveal subtle variants of such lattice structures. Therefore the luminescence response of Dy^{3+}, Mn^{2+} co-doped material exposed to different excitation sources will be discussed in detail below. Although the overall energy level structure of the Dy^{3+} ion does not change greatly in different hosts due to the shielding of the 4f electrons by an outer shell $5s^2$ and $5p^6$ electrons, each energy level can be split into $2J+1$ sublevels by the local crystal field surrounding the Dy^{3+} ions.

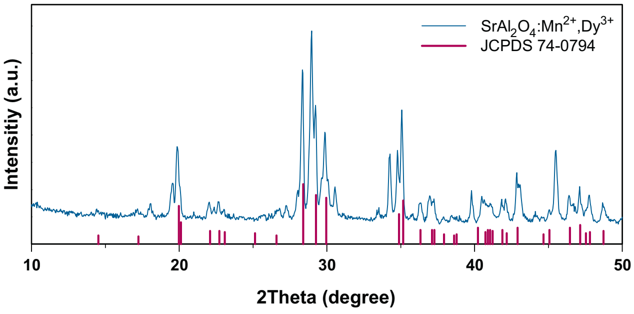

Fig. 1. X-ray diffraction pattern of Mn^{2+} co-doped $SrAl_2O_4$:Dy^{3+} phosphor.

The PL emission spectrum of $SrAl_2O_4$:Dy^{3+}, Mn^{2+} under the excitation of a 474 nm line of a diode lasers shown in Fig. 3. The spectrum contains a number of sharp lines in the range from 489 nm (blue) to 756 (NIR) nm attributed to transitions from the excited $^4F_{9/2}$ state to ^6H_J (J = 15/2, 13/2, 11/2 and 9/2) levels of Dy^{3+}. The main emission lines of the Dy used in this study are shown in Dieke diagrams near PL spectrum. PL emission peaks are observed at blue, yellow, red and NIR region of the spectrum due to Dy^{3+} ion. Thus, PL characterization of $SrAl_2O_4$:Dy^{3+}, Mn^{2+}phosphors shows that it could be applicable for LED phosphor.

The transitions involved in blue and yellow bands of Dy^{3+} ion are well known and have been identified as $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^6H_{13/2}$ transitions, respectively [22]. It is known that Dy^{3+} emission around 476 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) is of magnetic dipole origin and 573 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) is of electric dipole origin. Note that $^4F_{9/2} \rightarrow {}^6H_{15/2}$ is predominant only when Dy^{3+} ions are located at low-symmetry sites with no inversion centers. In our case this has not been observed. The optical properties of the materials are often influenced by the structure of the matrix and synthesis technique [23]. Thus, the yellow–blue ratio, known as the asymmetry ratio of Dy^{3+}, varies while locating in different host lattices. Kuang et al. [22] reported that, in the Dy^{3+} doped $SrSiO_3$ system, with increasing calcining temperature, the yellow–blue ratio increased due to the change in the local site symmetry around the Dy^{3+} ion. In our case, Dy^{3+} ion may enter the host lattice to substitute Sr^{2+} or locate on surfaces of the crystals due to the porosity of the structure. The ionic radius of Dy^{3+} (1.07 Å) is much smaller than that of Sr^{2+} (1.21 Å). Therefore, most of the Dy^{3+} ions were entered the lattice with few of them located at the surface of the $SrAl_2O_4$ host. The occupation of Dy^{3+} ion into Sr^{2+} sites in $SrAl_2O_4$ host would naturally cause a substantial number of vacant sites in the oxygen ion array and then expand the lattice to decrease crystal density. That is, the formation of Dy^{3+} due to Sr^{2+} in $SrAl_2O_4$ host induces more oxygen vacancies. Lopez et al. [24] reported that the oxygen vacancies might be sensitizers for the energy transfer to the rare earth ion due to the strong mixing of charge transfer states, resulting in highly enhanced luminescence. However, excess oxygen vacancies in the host would inevitably destroy the crystallinity, which leads to quenching of the luminescence. Of course, the more important reason is that more Dy^{3+} entered the lattice, which could enhance the $^4F_{9/2} \rightarrow {}^6H_{15/2,\ 13/2}$ transitions of the samples greatly, as shown by Fig. 3. Different dopings of activator ions can influence PL characteristics of a phosphor. Usually, a low doping gives weak luminescence, but excess doping can cause quenching of luminescence.

RL spectra were recorded at the room temperature for $SrAl_2O_4$:Dy^{3+}, Mn^{2+} under X-ray irradiation with a resolution of 0.1 nm, to gain some idea of the influence of Dy^{3+} and Mn^{2+} ions on the $SrAl_2O_4$ phosphors. Although the introduction of rare earth ion can lead to structural modifications that can alter spectral properties, in the present sample the cations from the Sr^{2+} are mainly responsible for defining the properties (e.g. effective charge) of oxygen ions. Fig. 4 shows the emission spectrum of $SrAl_2O_4$:Dy^{3+}, Mn^{2+}phosphors under the X-ray irradiation. It can