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Solid state synthesis of $SrAl_2O_4:Mn^{2+}$ co-doped with Nd^{3+} phosphor and its optical properties

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ABSTRACT

The optical properties of alkaline earth aluminates doped with rare earth ions have received much attention in the last years and this is due to their chemical stability, long-afterglow (LAG) phosphorescence and high quantum efficiency. However, there is a lack of understanding about the nature of the rare earth ion trapping sites and the mechanisms which could activate and improve the emission centers in these materials. Therefore a new phosphor material composition, $SrAl_2O_4:Mn^{2+}$, co-doped with Nd^{3+} was synthesized by a traditional solid-state reaction method. The influence of transition metal and rare earth doping on crystal structure and its luminescence properties have been investigated by using X-ray diffraction (XRD), Raman scattering, Photoluminescence (PL) and Radioluminescence (RL). Analysis of the related diffraction patterns has revealed a major phase characteristic of the monoclinic $SrAl_2O_4$ compound. Small amounts of the dopants $MnCO_3$ and Nd_2O_3 have almost no effect on the crsytalline phase composition. Characteristic absorption bands from Nd^{3+} 4f–4f transitions in the spectra can be assigned to the transitions from the ground state $^4I_{9/2}$ to the excited states. The luminescence of Mn^{2+} activated $SrAl_2O_4$ exhibits a broad green emission band 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. In photo- and radio-luminescence spectra, Nd^{3+} 4f–4f transition peaks were observed. The emitted radiations for different luminescence techniques were dominated by 560, 870, 1057 and 1335 nm peaks in the visible and NIR regions as a result of $^4I_{9/2} \rightarrow {}^4G_{7/2}$ and $^4F_{3/2} \rightarrow {}^4I_J$ ($J=9/2$, $11/2$ and $13/2$) transitions of Nd^{3+} ions, respectively. 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

Manganese (Mn^{2+}), a transition metal, has attracted much attention in recent years as an excellent luminescent ion which gives spectrum in red, blue and green wavelength regions (from 490 to 750 nm). It depends on the host-matrix crystal-field because the d–d transition in Mn^{2+} is quite sensitive to the crystal field [1–3]. Mn^{2+} has been widely utilized in variety of materials such as phosphates, aluminates, borates, sulfides and silicates [4–6] as an activator or sensitizer. In principle, red phosphors could be good candidates but their main disadvantage is that the Mn^{2+} d–d optical transition is spin- and parity-forbidden. Consequently, the emission intensity of Mn^{2+} taking place in many host materials is so low that the practical applications are limited. There are two primary methods to improve the emission spectrum of Mn^{2+}. First, the doping level of Mn^{2+} is an important factor that directly affects the emission spectrum. However, the increase of dopant contents is also restricted by other factors such as the bonding orbital of atoms, their chemical valence and the radii of ions. Second, the energy transfer from the other ion having a higher absorption coefficient could give rise to a more efficient material. As a promising sensitizer for Mn^{2+} ions, doping with lanthanide ions such as Tb^{3+} and Eu^{2+} has been widely used. This is because the absorbed energy can be transferred to Mn^{2+} by means of these ions and improves the luminescence of Mn^{2+} [7,8]. Among the rare earth, Nd^{3+} ions were recognized as one of the most popular as well as being efficient ions for obtaining near-infrared emission at 1060 nm and also at other wavelengths with the possibility of room temperature (RT) lasing at 1800, 1350 and 880 nm. This is used as amplifier material in high peak power laser applications [9]. Besides the rare earth ion-doped phosphors, Mn^{2+}-doped materials

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are good candidates for photonic sources. To the best of our knowledge, this work reports for the first time results of structural and luminescence studies of $SrAl_2O_4$:Mn^{2+},Nd^{3+}. In addition, Raman spectroscopy technique has been used to better understand the crystallographic structure and luminescence mechanism of these phosphors. Up to now, the vibrational spectra of $SrAl_2O_4$:Mn^{2+}co-doped with Nd^{3+} has not been reported. The compound has a slightly distorted crystal structure in comparison with non-activated materials, and it would be interesting to investigate the influence of activators on the Raman-PL spectra.

2. Material and methods

Solid state reaction method is the most common and one of the simplest ways of preparing solids. It consists of heating two non-volatile solids together in order to produce the required product. This method is commonly used in both industry and the laboratory, and considered to be the best way in synthesizing oxide materials. Therefore, the samples in the current study were produced by bulk materials synthesis using the conventional solid state reaction method. Stoichiometric mixtures of high purity (typically 99.9–99.999%) $SrCO_3$, Al_2O_3, $MnCO_3$ and Nd_2O_3 were weighed out according to nominal composition. The starting chemicals were mixed in the presence of an appropriate flux such as H_3BO_3 (boric acid) and then heated in a furnace for 2 h in a platinum crucible up to the required temperature (1400 °C) in a controlled atmosphere (Ar with 15% of H_2). Finally, the prepared materials are allowed to cool for about 24 h in the furnace. Phase identification was carried out using a Philips X'Pert Pro MPD diffractometer (XRD) with Cu-*K*α radiation line ($\lambda = 1.5418$ Å) at room temperature. Optical absorption properties have been tested at room temperature by means of a double beam UV–VIS–NIR Perkin Elmer spectrometer in the range from 190 to 1100 nm with 1 nm resolution. 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. A grating blazed at 500 nm and 2000 nm was used for visible and infra-red measurements, respectively. Before the samples were measured, the white light system response was taken for the spectrometer and optics. This background response was used to normalize measurements in order to better compare intensities and spectral features over a broad wavelength range [10]. 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 [11]. In the Raman experiment the micro-Raman spectrum has been recorded by means of a Thermo Fischer DXR Raman Microscope (West Palm Beach, FL 33407, USA), which has point-and-shoot Raman capability of one micron spatial resolution. We select the 20× objective of the confocal microscope together with a laser source of 780 nm at 20 mW in mode laser power at 100%. The average spectral resolution in the Raman shift ranging from 70 to 3500 cm^{-1} was 2.4–4.4 cm^{-1}, i.e., grating 900 lines/mm and spot size 2.1 μm [12].

3. Results and discussion

3.1. X-ray diffraction analysis

Two phases have been reported for $SrAl_2O_4$, namely a high temperature hexagonal phase (β phase) and a low temperature monoclinic phase (α-phase). The transition from the low temperature monoclinic to hexagonal phase occurs at a temperature ≥650 °C [13]. XRD was used to confirm the structural and phase purity of compositions different from $SrAl_2O_4$. The resulting diffraction pattern of $SrAl_2O_4$:Mn^{2+}, Nd^{3+} is shown in Fig. 1. The monoclinic phase diffraction peaks of the parent $SrAl_2O_4$ are predominant in the XRD pattern. The structure consists of Sr^{2+} ions situated within channels formed by six interconnected AlO_4 tetrahedra. The structure possesses two Sr, four Al and eight O sites. No impurity phase was observed in the XRD pattern. This fact clearly implies that the little amount of doped ions have almost no effect on the $SrAl_2O_4$ phase composition [14]. Obviously, the principal peaks corresponding to (0 3 1), (2 1 1), (2 2 0) and (2 1 1) reflection planes characterising the crystalline $SrAl_2O_4$ structure can be seen in Fig. 1. These planes are consistent with those reported in (JCPDS 74-0794). $SrAl_2O_4$ adopt a stuffed tridymite-type structure consisting of a corner sharing AlO_4 tetrahedra which connect together to form six-membered rings. Each oxygen ion is shared by two aluminium ions so that each tetrahedron has one net negative charge. The charge balance is achieved by the large divalent cation Sr^{2+}, which occupies interstitial site within the tetrahedral framework [15,16].

3.2. Raman scattering

Raman spectroscopy is a measure of the vibrational modes of a material changing the frequency of scattered light [17]. Fig. 2 shows the micro Raman spectrum of the $SrAl_2O_4$:Mn^{2+},Nd^{3+} phosphor between 50 and 1000 cm^{-1}. This spectral range usually contains bands due to metal-oxide bonds and/or lattice vibrations. In order to enhance the understanding of the doping effect from the structural point of view, Raman scattering study is a very useful tool in investigating the lattice vibrational modes, which can provide details of lattice vibrations. The Raman spectroscopy was applied in this work to complement the XRD data, particularly, when it concerns the doping and co-doping of our samples. These measurements were repeated several times from different parts of the sample and registered the same spectra as shown in Fig. 2, which confirms the homogeneity of the prepared materials. To a first approximation, we attribute modes at a frequency higher than 600 cm^{-1} to Al–O bond-stretching vibrations and the narrow low-frequency peaks below 250 cm^{-1} to tetrahedral vibrations or tilts. In the intermediate region the assignment is more difficult. However, by analogy with other compounds, band at 465 cm^{-1}

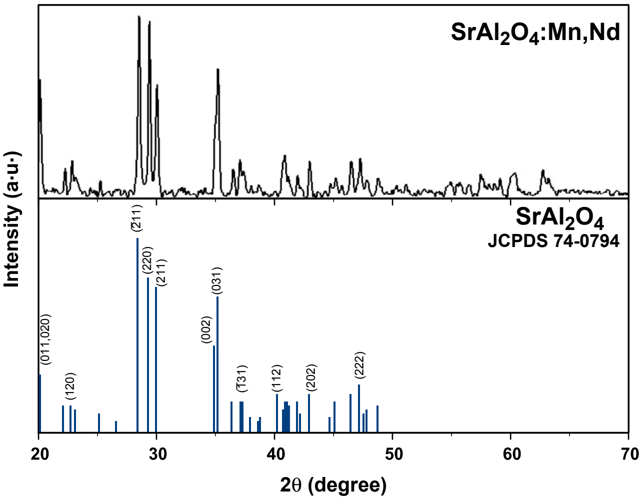

Fig. 1. Experimental XRD pattern of Nd^{3+}doped $SrAl_2O_4$:Mn^{2+} phosphor and principal peaks of crystalline planes that characterize the $SrAl_2O_4$ host structure.