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Luminescence temperature and pressure studies of Zn_2SiO_4 phosphors doped with Mn^{2+} and Eu^{3+} ions

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Abstract

Zn_2SiO_4:Mn^{2+}, Zn_2SiO_4:Eu^{3+} and Zn_2SiO_4:Mn^{2+},Eu^{3+} phosphors were prepared by a sol-gel process and their luminescence spectra were investigated. The emission bands from intra-ion transitions of Mn^{2+} and Eu^{3+} samples were studied as a function of pressure. The pressure coefficient of Mn^{2+} emission was found to be -25.3 ± 0.5 and -28.5 ± 0.9 meV/GPa for Zn_2SiO_4:Mn^{2+} and Zn_2SiO_4:Mn^{2+},Eu^{3+}, respectively. The Eu^{3+} emission shows only weak pressure dependence. The pressure dependences of the Mn^{2+} and Eu^{3+} emissions in Zn_2SiO_4:Mn^{2+},Eu^{3+} are slightly different from that in Zn_2SiO_4:Mn^{2+} and Zn_2SiO_4:Eu^{3+} samples, which can be attributed to the co-doping of Mn^{2+} and Eu^{3+} ions. The Mn^{2+} emission in the two samples, however, exhibits analogous temperature dependence and similar luminescence lifetimes, indicating no energy transfer from Mn^{2+} to Eu^{3+} occurs.

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Keywords: Zn_2SiO_4; Mn^{2+}; Eu^{3+}; Hydrostatic pressures; Luminescence; Crystal field

1. Introduction

Zinc silicate is an ideal host material for transition metal ions because of its chemical stability and transparency in the ultraviolet (UV)-visible range. Transition and rare-earth ions are excellent luminescent centers as a result of their inner shell electronic transitions. Consequently, transition and rare-earth ion doped zinc silicates have been studied extensively as efficient luminescent materials [1–6]. Mn^{2+} doped Zn_2SiO_4 phosphors emit green light when excited by UV light or

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cathode rays. These materials have been widely investigated as novel luminescent materials in lamps, cathode ray tubes (CRTs) and plasma display panels due to their high luminescence efficiency [7]. Similarly, $Zn_2SiO_4:Eu^{3+}$ has attracted attention because of its strong emission in the red which is in accordance with the standard made by the CIE (commission International de 1' Eclairage, France). Therefore, the phosphor has some desirable features that make it applicable to TV and CRT screen applications [5]. Co-doping of Mn^{2+} and Eu^{3+} into Zn_2SiO_4 may provide a phosphor with both green and red emissions, making it potentially useful for full-color displays.

For co-doped phosphors, it is important to reveal the interactions between the dopants in order to get high efficiency and adequate color index. Pressure and temperature dependences of the luminescence can provide useful information about the interactions between doped ions and the coupling between the dopants and the host crystal lattices. The variation in hydrostatic pressure or temperature can change the inter-atomic distance. This can change the overlap among adjacent electronic orbitals as well as the crystal field surrounding the dopant. Therefore, the study of luminescence spectral properties as a function of pressure or temperature may provide insight about the interactions between the luminescent centers or between the centers and the host lattice. In this paper, we report the pressure and temperature behaviors of Zn_2SiO_4 phosphors doped with Mn^{2+} and Eu^{3+} ions.

2. Experimental

The samples were prepared as follows. First, calculated amounts of $Zn(CH_3COO)_2$, $Mn(NO_3)_2$ $Eu(NO_3)_3$ and 0.5 g of polyvinyl alcohol (PVA) were dissolved in 50 ml water by thoroughly stirring under argon protection. Afterwards, 4.5 mM Na_2SiO_3 (2 g of 27% saturated solution) was added slowly and NaOH solution (about 10 ml of 0.1 M NaOH) was used to adjust the pH value to 10. The solution was refluxed overnight in an Argon atmosphere after which centrifugation at 5000 rpm for 15 min allowed separation of the solid samples from the solution. The resulting powders were dried at 400 °C under nitrogen overnight revealing white solids. Finally, the solids were annealed at 1000 °C under nitrogen. The glass-like solid obtained has strong green and red luminescence. Three different samples were prepared: Zn_2SiO_4 doped with 8% Mn^{2+}; Zn_2SiO_4 doped with 6% Eu^{3+}; and Zn_2SiO_4 co-doped with 8% Mn^{2+} and 3% Eu^{3+}.

The phase identity of the phosphors was examined by X-ray powder diffraction (XRPD) using a Philips X'Pert MPD system (PW3040/00 type) equipped with a 1.8 kW Cu source ($\lambda = 1.54056$ Å). The PL measurements under hydrostatic pressure were done in a diamond-anvil cell (DAC) at room temperature. The samples, together with a small piece of ruby, were placed in a stainless-steel gasket with a hole of 300 μm in diameter. A 4:1 methanol–ethanol mixture was used as the pressure-transmitting medium. The pressure was determined by using the standard ruby-fluorescence technique and varied from 0 to 6 GPa. The photoluminescence (PL) measurements at different temperatures were performed by fixing samples on the cold finger of a closed-cycle refrigeration system. The temperature varied from 10 to 300 K. The 325 nm line of a He–Cd laser and the 454.5 nm line of an Ar^+ ion laser were used as the excitation source. The emitted light was dispersed by a JY-HRD1 double grating monochromator and detected by a cooled GaAs photomultiplier tube operating in photon-counting mode. The excitation spectra under atmospheric pressure were measured with a fluorometer (FluoroMax-2 from Jobin Yvon-Spex). The sample was placed on a custom-built solid sample holder.

The lifetimes and time-resolved spectra were collected using the output of nanosecond pulsed optical parametric oscillator/amplifier (Spectra Physics MOPO-730). The output was directed onto the samples and the emission collected at right angle and focused into a monochromator equipped with either a cooled CCD detector for spectral measurements, or a standard photomultiplier tube for lifetime measurements.