Luminescent properties of magnesium thiogallate phosphor with green emission for LEDs

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Abstract

A magnesium thiogallate phosphor doped with europium was prepared by solid-state method. This phosphor has green emission near 535 nm due to the allowed transition from $4f^6 5d$ at an excitation state (T_{2g}) to $4f^7$ ($^8S_{7/2}$) at a ground state of Eu^{2+} ion. This phosphor shows a wide excitation spectrum from ultra violet (300 nm) to bluish green (515 nm).

1. Introduction

A consumption of energy has been increased as human's life has been rich and developed with a improving industry. Nevertheless, the energy sources such as oil, natural gas and coal so on are limited. Interests about reducing energy spending are grown up. Methods of these are using the highly efficient equipment or unlimited energy source with solar power etc. Nowadays, a research to generate the white light from the LEDs is actively studied at many groups so as to alternate with the existing illuminations. A generation of white lights from LEDs is achieved by three methods; **i**) the combination of three diodes (red, green and blue chips), **ii**) accumulated yellow phosphor or green and red phosphors on a blue LED chip and **iii**) integrated three phosphors (red, green and blue) on a UV LED chip. Phosphor adopted with LEDs must absorb and convert the parts of the incident ultraviolet or blue light from the GaN or InGaN chips. Because of emission wavelength of those chip, these phosphors for LEDs must have long excitation wavelength as comparative as phosphors for PDP used 147 nm wavelength. Some research group reported the use of thiogallate phosphor as well as sulfide phosphor for potential materials for LEDs. Thiogallate phosphors doped with europium emit green light ($SrGa_2S_4$:Eu) and yellow light ($CaGa_2S_4$:Eu). In general, thiogallate phosphors were prepared by conventional preparation method based on flux method under H_2S or CS_2 gas atmosphere. However, these gases are well known for a long time as toxic gases and they can cause serious pollution. For those reason, the exhausted gas must be handled very carefully.

2. Experimental

2.1 Synthesis

In this research, novel europium doped magnesium thiogallate phosphors were prepared by a solid-state method. Raw materials were MgS (99%), Ga_2S_3 (99.99%) and EuS (99.9%) from High Purity Chemicals. Those reagents were appropriately weighed and mixed with additional sulfur and acetone in the agate mortar. These precursors were fired in a tube furnace at 950℃ under mild hydrogen gas atmosphere and those were grinded.

2.2 Characterization

Optical properties of those were obtained by using a Perkin Elmer LS50B luminescence spectroscopy composed of a Xe-lamp, monochrometer, photo multiplier tube and attenuator. Their emission wavelengths were scanned from 480 nm to 750 nm under excitation wavelength of 465 nm at room temperature. The excitation spectrum was obtained in the range 300 ~ 510 nm at emission wavelength.

3. Results and discussion

The mixed raw materials with sulfur were heat-treated at high temperature under reducing atmosphere by using mild hydrogen gas. Figure 1 depicts emission and excitation spectra of europium doped magnesium thiogallate phosphor. It shows a broad green emission with wavelength maximum at 535 nm. Some research groups explained the emission of Eu^{2+} ions in host materials is due to f-d transition. To be more particular, the electrons of Eu^{2+} ions occupied an outmost shell, $4f^7$. This electron will excited to the upper level, $4f^6 5d$ when the Eu^{2+} ion is affected by outer energy source such as photon, electron and electric field, so on. The energy levels of 5d orbital are split into two levels that are composed of E_g and T_{2g} set of orbitals by host crystal field. The broad green emission is owing to the allowed transition from the excitation state (T_{2g}) of $4f^6 5d$ configuration to the ground state ($^8S_{7/2}$) of $4f^7$ configuration of Eu^{2+} ions. The excitation spectrum was obtained by monitoring the Eu^{2+} emission at 535 nm. This is characteristic of transition from $4f^7$ ($^8S_{7/2}$) to $4f^6 5d$ (T_{2g}) band in Eu^{2+}. The excitation spectrum has wide range between ultra violet (300 nm) and bluish green (515 nm). It is optimized to adapt a phosphor for LEDs, because emission wavelength of LEDs chip is shifted from 370 nm (GaN) to 470 nm (InGaN) by increasing indium concentrations in GaN.

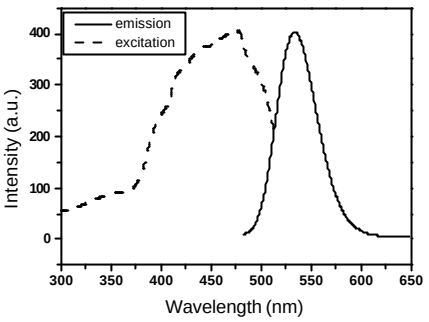

Figure 1 The emission and excitation spectra of the $MgGa_2S_4$:Eu phosphor

The maximum emission intensity obtained at 950℃. The changes of emission spectra and intensities were investigated at various Eu concentrations. Figure 2 shows emission intensities of those manufactured on the various europium concentrations. It shows a maximum intensity is obtained to 0.07 mol. Above this concentration, it is decreasing depend on the europium concentration owing to concentration quenching. In a word, emission light of Eu^{2+} ions at high concentration (>0.07 mol) absorbs the nearest neighbor Eu^{2+} ion and this causes diminution of emission efficiencies.

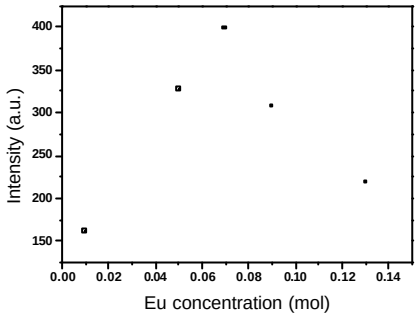

Figure 2 Changes of emission intensities of $Mg_{1-x}Ga_2S_4:Eu_x$

A change of the europium concentration affects a emission wavelength as well as efficiency. It is expressed in Fig. 3. The emission wavelength shifts from 526 nm at 0.01 mol to 538 nm at 0.13 mol. As mentioned above, one of the valence electrons (5d) with Eu^{2+} in the excited state locates the $5s^25p^6$ electron cloud and affects by crystal field. Eu^{2+} ions are larger than Mg^{2+} ion and those are substituted to some parts of Mg site. The crystal field of surrounding Eu^{2+} is increased at high concentration and it causes shift of emission wavelength.

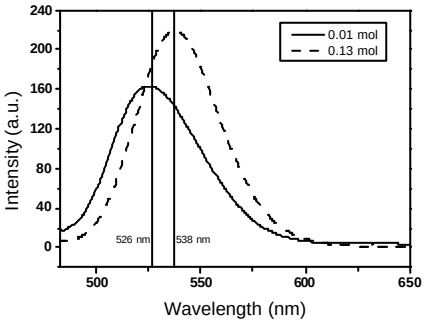

Figure 3 Shifts of emission spectra on various Eu concentrations

4. Conclusion

In this study, a magnesium thiogallate phosphor doped with europium was prepared by solid-state method. This phosphor has green emission near 535 nm due to the allowed transition from $4f^65d$ at an excitation state (T_{2g}) to $4f^7$ ($^8S_{7/2}$) at a ground state of Eu^{2+} ion. This phosphor shows a wide excitation spectrum from ultra violet (300 nm) to bluish green (515 nm). This phosphor has enough possibility with the green phosphor for LEDs.

5. References

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