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Fine tuning of the color of light emitted from $Sr_{1-x}Ca_xS:Mn^{2+}$ phosphors for CNT-FEDs

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ABSTRACT

$Sr_{1-x}Ca_xS:Mn^{2+}$ phosphors with calcium ion mole fraction (x) values of 0, 0.2, 0.4, 0.6, 0.8, and 1 were synthesized from CaS, SrS, and MnS by carrying out solid-state reactions. Cathodoluminescence (CL) spectra of these phosphors were acquired using moderate voltages in the range 4–10 kV in order to assess their applicability to carbon nanotube field emission displays (CNT-FEDs). The wavelength at the maximum intensity of the CL spectra of the phosphors increases gradually from 549 to 602 nm, and then slightly decreases to 599 nm, as x is increased. This increase can be interpreted in terms of the crystal structures of the phosphors. The ability to tune the color of light emitted from the $Sr_{1-x}Ca_xS:Mn^{2+}$ phosphors from greenish yellow to red confirms the promise of these phosphors for use in CNT-FEDs.

1. Introduction

Field emission displays (FEDs) have been developed for use as flat panel displays (FPDs) including plasma display panels (PDPs), liquid crystal displays (LCDs), and vacuum fluorescent displays (VFDs) [1–4]. FEDs have advantages over other FPDs such as high contrast ratios, wide viewing angles, and low power consumption [5]. The development of FEDs has been advanced by the introduction of carbon nanotubes (CNTs) as field emitters. A CNT-FED has a very simple structure, consisting of two plates, patterned phosphor layers as color emission sources, and CNTs as field emitters, which are separated by spacers with lengths of a few hundred micrometers [6,7]. The operation of CNT-FEDs requires moderate levels of electron excitation, specifically voltages ranging from 4 to 10 kV. However, most of the cathodoluminescence (CL) properties of phosphors have been examined for cathode ray tubes (CRTs) at high voltages (13–30 kV) and for Spindt-type FEDs at low voltages (<1 kV) [8–11]. Therefore, to assess the applicability of phosphors to CNT-FEDs, their CL properties should be investigated at moderate voltages (4–10 kV).

Trivalent lanthanide ions such as Tb^{3+} and Eu^{3+} are the most widely used activators for phosphors emitting green and red light [12–15]. The electrons in the 4f orbitals of these ions are strongly shielded by the outer 5s and 5p electrons, so sharp emission lines are produced by the f-f transitions within the 4f configurations [5]. Therefore, the emission wavelengths of phosphors with trivalent lanthanide ion activators do not depend strongly on the host material, and variable emission wavelengths cannot be obtained by using such activators. To solve these drawbacks, Eu^{2+} activators for the transition from the $4f^65d^1$ excited state to the $4f^7$ ($^8S_{7/2}$) energy level can be used to produce luminescent materials with a tunable emitted light color, i.e., "color-tunable" materials. For example, $BaMgAl_{10}O_{17}:Eu^{2+}$, $SrGa_2S_4:Eu^{2+}$, and $CaS:Eu^{2+}$ are phosphors emitting blue, green, and red light, respectively [16–19].

The Mn^{2+} ion has been widely used as an activator for Mn^{2+}-doped II-IV nanocrystals. The 3d states of Mn^{2+} ions are localized, atomic-like states, so the localized d-d transition of Mn^{2+}-doped II-IV nanocrystals centered at 2.12 eV (585 nm) appears regardless of changes in the size of the nanocrystals, and thus the quantum confinement effect cannot be obtained [20]. Recently, it was demonstrated that the overall color of Mn^{2+}-doped CdS nanocrystals can be tuned from red to yellow by fine tuning the host particle diameter from 1.9 to 2.6 nm. This color tunability originates in the different concentrations of Mn^{2+} ions in the surface, subsurface, and core regions of the nanocrystals [21]. The photoluminescence peak of Mn^{2+}-doped ZnSe nanocrystals can be controllably tuned over a surprisingly large optical window, from 565 to 610 nm [22]. The photoluminescence emission of Mn^{2+}-doped ZnS nanocrystals can be tuned from 567 to 594 nm by changing the cation associated with the 3-mercaptopropionic acid

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and the Mn^{2+} location in the ZnS host nanocrystals [23].

Since the 3d orbitals are strongly affected by the surrounding crystal field, the emission wavelength depends on the structure of the host crystals. The emission wavelength due to the $^4T_1 \rightarrow {}^6A_1$ electronic transition of the Mn^{2+} ion can be tuned by adjusting the composition of the host crystals through cationic substitution while preserving the crystal structure [24]. Both CaS and SrS have cubic crystal structures, and $Sr_{1-x}Ca_xS$ (x = 0–1) is a solid-solution crystal. Moreover, Mn^{2+} ions are located at the Sr^{2+} (or Ca^{2+}) sites of the cubic crystal structure of the host SrS (or CaS), with each Mn^{2+} ion coordinated by six S^{2-} ions in an octahedral geometry; the emission energy of the $^4T_1$ and $^6A_1$ electronic transition of the Mn^{2+} ion can be tuned by adjusting the crystal field through changes to the composition of the $Sr_{1-x}Ca_xS$ host. Moreover, sulfide phosphors such as $SrGa_2S_4:Ce^{3+}$, ZnS:Ag,Cl, and $ZnS:Mn^{2+}$ are considered efficient low-voltage cathodoluminescent materials [9,25]. Most of the CL properties of the sulfide phosphors have been examined at high and low voltages with a view to their applications in CRTs and Spindt-type FEDs respectively. To the best of our knowledge, there has been no examination of the CL properties of $Sr_{1-x}Ca_xS:Mn^{2+}$ phosphors at the moderate voltages appropriate to CNT-FEDs. Therefore, in this study we prepared color-tunable $Sr_{1-x}Ca_xS:Mn^{2+}$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) phosphors, and investigated their CL properties under electron excitation at moderate voltages (4–10 kV) in order assess their potential CNT-FED applications.

2. Experimental

SrS (99%, Kojundo Chemical), CaS (99.99%, Kojundo Chemical), MnS (99.9%, Aldrich), KBr (99%, Aldrich), and S (99.98%, Aldrich) were used as received. To synthesize $Sr_{0.95(1-x)}Ca_{0.95x}S{:}0.05Mn^{2+}$ (hereafter denoted as $Sr_{1-x}Ca_xS:Mn^{2+}$) phosphors, stoichiometric amounts of SrS and CaS were used, with a fixed mole fraction of 0.05 for the Mn activator. An appropriate amount of KBr (99%, Aldrich) was used as the flux. In the typical synthesis of the $Sr_{0.6}Ca_{0.4}S:Mn^{2+}$ phosphor, 1.365 g SrS, 0.548 g CaS, 0.087 g MnS, 0.060 g KBr, and 0.200 g S were mixed and ground in a mortar, and then placed in an alumina crucible. The inner crucible with reactants was nestled in an outer crucible filled with activated carbon to prevent oxidation by the air. The phosphors were prepared by performing solid-state reactions in a box-type furnace (DMF-3, Lab House) at various calcination temperatures for 3 h.

The crystal structures of the phosphors were characterized by using powder X-ray diffraction (XRD, PANalytical, X'Pert-PRO MPD) with Cu K_α radiation. The CL levels of the phosphors were measured in reflection mode in a high-vacuum (5×10^{-7} torr) chamber at various applied voltages from 4 to 10 kV under DC excitation with a current density of 2 $\mu A/cm^2$. The phosphor patches were placed on metal holders in a demountable cathode ray tube and excited with electron beams.

3. Results and discussion

In this study, $Sr_{1-x}Ca_xS:Mn^{2+}$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) phosphors were prepared by carrying out solid-state reactions between SrS, CaS, and MnS. To determine the optimal calcination temperatures of the $CaS:Mn^{2+}$ phosphors, i.e., those yielding the brightest emissions, various $CaS:Mn^{2+}$ phosphors were synthesized at different temperatures. The molar concentration of the Mn^{2+} ion in the $CaS:Mn^{2+}$ phosphors was fixed at 5.0%. Fig. 1 shows the CL spectra of $CaS:Mn^{2+}$ phosphors synthesized at reaction temperatures ranging from 700 °C to 950 °C. The maximum emission intensity was observed at a wavelength of 599 nm. The full width at half maximum (FWHM) for the peak at this wavelength was measured to be approximately 2300 cm^{-1}. This result indicates that the emission from $CaS:Mn^{2+}$ is broad. The intensity of the emission from the $CaS:Mn^{2+}$ phosphors increases as the calcination temperature is increased up to 850 °C, then very slightly decreases at 900 °C, and further decreases at 950 °C, as shown in the inset in Fig. 1. The CL intensity increases initially and then decreases with increases in the temperature, which is a typical temperature dependence for fluorescence quenching. This temperature dependence is probably due to the electron penetration properties of the various phosphors prepared at different temperatures, but the dominant influence on the CL intensity is not clear because of the complicated electron penetration behaviors of crystalline phosphors. In general, the optimal conditions for the brightest inorganic phosphor emissions can be found by examining the CL intensities of inorganic phosphors prepared at various calcination temperatures. The brightest CL spectrum was observed for the $CaS:Mn^{2+}$ phosphor calcinated at 850 °C, as shown in Fig. 1.

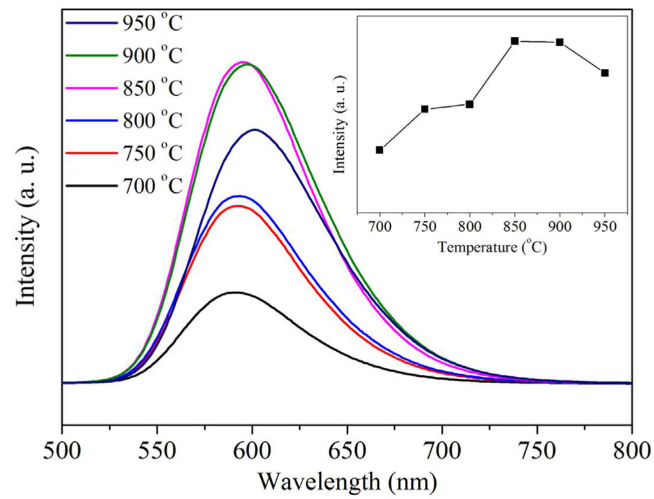

Fig. 1. CL spectra of $CaS:Mn^{2+}$ phosphors prepared at reaction temperatures ranging from 700 °C to 950 °C. The inset shows the variation with reaction temperature in the emission intensity at 599 nm of these phosphors.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the $CaS:Mn^{2+}$ phosphors prepared at various reaction temperatures between 700 °C and 950 °C. At each of the tested reaction

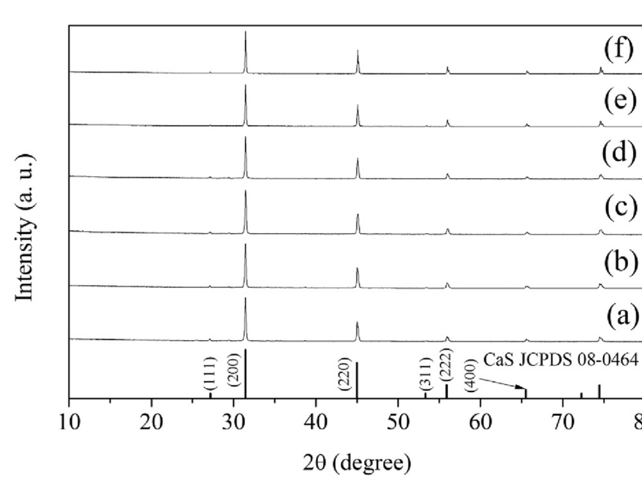

Fig. 2. XRD patterns of $CaS:Mn^{2+}$ phosphors prepared at various reaction temperatures: (a) 700 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C, (e) 900 °C, and (f) 950 °C. The XRD patterns and Miller indices of CaS (JCPDS 08-0464) are shown for comparison.