



Cathodoluminescence and Photoluminescence Properties of CaS Thin Film Codoped with Pb and Cu

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Luminescent properties of CaS thin films doped with Pb and Cu have been investigated. Under UV and low-voltage electron-beam excitation, the CaS:Pb, Cu thin films exhibited highly saturated blue photoluminescence centered at 430 nm and cathodoluminescence peaked at 415-425 nm at room temperature. Spectroscopic study on CaS:Pb, Cu revealed that the emission characteristics were identical to CaS:Cu, although the excitation spectra resembled that of CaS:Pb film. These results demonstrated the efficient energy transfer from Pb to Cu, confirming successful sensitization. However, the efficient energy-transfer process from Pb to Cu could not be explained by the standard energy-transfer theory. Therefore, instead of a Dexter-type energy transfer, a phonon-assisted process was proposed as a possible coupling mechanism between Cu and Pb ions in CaS.
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Manuscript submitted August 4, 2003; revised manuscript received December 18, 2003. Available electronically June 17, 2004.

The use of flat panel displays is increasing rapidly in various applications, including mobile, desktop, and home appliances, etc. The luminescent properties and improvement of phosphor materials have also gained renewed attention for flat panel display applications such as electroluminescent (EL) and field emission displays.^{1,2} Among the numerous compounds of phosphors available, luminescent center ion-doped alkaline-earth sulfides have been extensively investigated due to their high luminescent yields.³⁻⁵

Thin films of phosphor materials offer significant advantages over conventional bulk powders for display applications, such as higher resolution, more uniform density, and increased thermal stability, etc. However, polycrystalline thin-film phosphors are known to exhibit noticeably lower luminescent output than their bulk powder.⁶ It appears that the greatest challenge in the fabrication of sulfide phosphor thin films is the incorporation of the luminescent ions and/or codopants with the correct charge state uniformly within the host lattice. Deficient stoichiometry and poor crystallinity of the host lattice have also been found to affect the luminescent properties of thin-film phosphors.⁵

Calcium sulfide (CaS) and their solid solutions in polycrystalline form have been the subject of much interest for large-area displays. The introduction of rare earth and/or other dopants in these large-bandgap host matrices permits them to be tuned as narrow or broad-band visible light-emitting phosphors. Although CaS, a wide-gap semiconductor material, has been commercially used as a host material of phosphor and the photoluminescent (PL) and EL properties of Cu-doped CaS (CaS:Cu) powders have already been investigated, little work on CaS:Cu thin films has been carried out.⁷⁻⁹

Although the correct mechanism of the luminescent transition of CaS:Cu has not been determined, the fact that CaS:Cu exhibited efficient PL and cathodoluminescence (CL) indicates that the main reason for poor EL performance of CaS:Cu could be poor excitation efficiency under EL excitation conditions.^{3,7,8,10} Therefore, improvement of EL performance was attempted by changing the structure of a CaS:Pb EL device which had exhibited efficient EL.¹¹

CaS:Pb has been known to exhibit efficient blue PL. Pb^{2+} is a so-called S^2 -ion, having a $6s^2$ ground state. The $6s^16p^1-6s^2$ transition is efficient, allowed, and luminescent in the UV or blue wavelength regions, depending on the host lattice.¹² The use of two different types of ions to obtain high excitation efficiency and desirable color adds great flexibility to phosphor development.¹³ In the present article, we report on the PL and CL characteristics of CaS

thin films codoped with Pb and Cu ions (CaS:Pb,Cu) for the first time. The unique luminescent property of CaS:Pb, Cu, such as stable blue emission at 430 nm wavelength at room temperature, is also presented.

Experimental

Beginning with a CaS:Pb thin film deposited by atomic layer deposition (ALD), the addition of Cu ions into CaS:Pb film is accomplished by chemical vapor deposition (CVD) of thin Cu film and following rapid thermal annealing (RTA). The details of sample preparation used in this study were described in a previous article and references therein.¹⁴

The 250 nm thick CaS:Pb phosphor thin films were deposited on Al_2O_3 (250 nm)-coated Si [p-type (100)] substrate using ALD, and the precursors of Ca, S, and Pb were $\text{Ca}(\text{thd})_2$ (thd = 2,2,6,6-tetramethylheptanedionate), H_2S , and $\text{Pb}(\text{C}_2\text{H}_5)_4$, respectively. The CaS:Pb films containing approximately 1 atom % Pb were deposited to emit blue PL and CL emission centered at 460 nm wavelength. The deposition temperature was 390°C and the reactor pressure was approximately 5 Torr during deposition.

Copper(I) hexafluoroacetylacetonate trimethylvinylsilane [Cu(hfac)(TMVS)] was used as the Cu precursor for the CVD process. Cu film was grown at 150°C and the chamber pressure was 5 Torr. After the deposition of Cu, the samples were annealed using RTA at temperatures of 600 and 650°C for 2 min in N_2 atmosphere. RTA was performed in order to diffuse the dopants into the CaS:Pb film and enhance the crystallinity of the phosphor film. The Pb and Cu concentrations in the films were measured by Rutherford backscattering (RBS).

PL excitation and emission spectra were recorded using an ISS PC1 photon counting spectrofluorometer. Initially an emission spectrum was obtained from excitation at 254 nm; then the excitation spectra were recorded for each important emission peak and the emission spectra were recorded for the wavelength showing the strongest excitation peak. Excitation spectra were acquired using a Hg lamp, a UV monochromator, and appropriately filtered detectors to measure both the PL intensity and the intensity of the excitation light source. A time-resolved spectroscopic technique using a pulsed laser source was used in order to elucidate the decay process at low temperatures. The emission spectra at low temperatures were obtained in a suitable cryostat. Samples were excited by a Nd-yttrium aluminum garnet (YAG) pulsed laser with pulse width of 10 ns duration.

For CL measurement, the phosphors were excited by an electron gun with an accelerating voltage of 1 kV and beam current of 10

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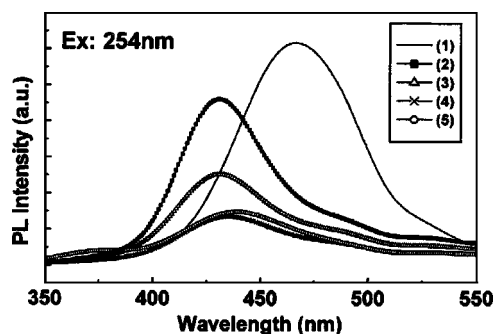


Figure 1. PL emission spectra of the CaS:Pb (1.0 atom %) thin film with various Cu concentrations: (1) none, (2) 0.3, (3) 1.0, (4) 7.9, and (5) 22.0 atom %.

μA , which could be operated in dc mode in a high-vacuum chamber ($\sim 10^{-6}$ Torr). The emission spectra under cathode ray excitation were also measured using a photon counting spectrofluorometer at room temperature.

Results and Discussion

The Cu concentration in CaS:Pb, Cu thin films was varied from 0.3 to 22.0 atom %, and the Pb concentration was approximately 1 atom %. Figure 1 shows the PL emission spectra of CaS:Pb and CaS:Pb, Cu phosphors under UV excitation at room temperature. To make a comparative study, all specimens were annealed under the same conditions. The emission spectrum of CaS:Pb (1 atom %) has a single emission peak centered at 460 nm. The deposition process of CaS:Pb was controlled to have the wavelength of PL emission be 460 nm by using a controlled ALD.¹⁴ The wavelength of CaS:Pb emission depends on the chemical binding state of Pb^{2+} ions. In earlier works, the blue emission in CaS:Pb was mainly attributed to Pb^{2+} dimers.¹⁵ Pb^{2+} monomers are thought to be responsible for UV emission, while higher Pb^{2+} aggregates yield greenish-blue emission.

Contrary to CaS:Pb, the wavelength of emission peaks of CaS:Pb, Cu samples was not sensitive to Cu content, while PL intensity decreased as Cu content increased, as shown in Fig. 1. The PL spectra of CaS:Pb, Cu films revealed peaks at 430 nm, coincident with the position of the emission band of singly doped CaS:Cu. These observations confirmed that the 430 nm emission must have originated from Cu^+ activators. The PL emission behavior of CaS:Pb, Cu films can be interpreted with the emission from the inner shell transition of $^3\text{E}_g \rightarrow ^1\text{A}_{1g}$ in the Cu^+ activator under O_h symmetry, as reported in earlier works.^{14,16}

Figure 2 shows the excitation spectrum of CaS:Cu at room temperature. On the long-wavelength side of the spectrum, the emission

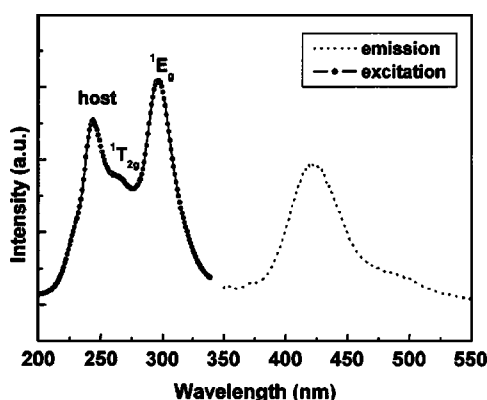


Figure 2. PL spectrum of CaS:Cu thin film at room temperature.

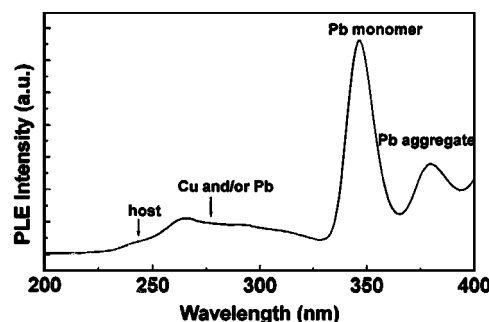


Figure 3. PLE spectrum of a CaS:Pb (1.0 atom %), Cu (1.0 atom %) thin film.

spectrum at room temperature is also presented with broken lines. The excitation spectrum shows two excitation bands associated with Cu^+ in CaS:Cu phosphor. The bands are assigned to the intraionic transitions in the isolated Cu^+ ions as described in earlier works.^{3,14}

In order to investigate the emission behavior of CaS:Pb, Cu samples, a PL excitation (PLE) study was carried out. Figure 3 shows PLE spectra of the CaS:Pb, Cu containing 1.0 atom % Cu probed at 430 nm. The high-intensity bands responsible for the excitation of Pb ions in the PLE spectrum and a single emission at 430 nm from CaS:Pb, Cu film suggest efficient energy transfer from the Pb ions to the Cu ions and emission only from Cu^+ ions.

The foregoing experimental results indicate that the emission characteristics are induced by the interaction between two activators, Pb and Cu, in CaS host. It is similar to the activator-coactivator interaction reported in ZnS-based phosphor, and it is plausible to assume that Cu is the main activator because its presence suppresses the characteristic blue emission of Pb.¹⁷

When UV light was irradiated on CaS:Pb, Cu thin film, the radiation was absorbed by both host material and Pb ions, not by the Cu ions. A small portion of excited Pb ions might emit their characteristic blue PL, while most excited Pb ions were thought to transfer their energy to Cu ions. These activated Cu ions could emit their characteristic blue emission. The strong UV absorption of the Pb ions, along with the efficient transfer of absorbed energy from Pb to Cu, must be responsible for the intensive Cu luminescence from CaS:Pb, Cu. This result is shown to be typical evidence of energy transfer.

Energy-transfer processes are often used in practical phosphors in order to enhance emission efficiency. The process is called sensitization of luminescence, and the energy donor is called a sensitizer. Dexter's theory of resonant energy transfer has elucidated that two optical centers within a certain distance may be in resonance and transfer the excitation energy from one (donor) to the other (acceptor). The mechanism of resonant energy transfer can be classified into several types based on the character of the transitions in donor and acceptor.¹⁸

In CaS:Pb, Cu phosphors, the calculated Stokes' shift value is large, $5.73 \times 10^3 \text{ cm}^{-1}$, so the resonant probability for efficient energy-transfer process is small.¹⁹ Phonon-assisted energy transfer occurs when the resonance condition is not well satisfied between donor and acceptor ion, resulting in the spectral overlap in Stokes' curve being small.¹⁸ Thus, the phonon-assisted energy transfer is thought to play an important role in CaS phosphors activated with Pb and Cu ions.

Under low-voltage-cathode ray excitation, CaS:Pb, Cu emitted an intense blue CL. The emission spectra for the samples singly Cu-doped and codoped with Pb are shown in Fig. 4. The broad emission peaks of CaS:Pb, Cu are centered at approximately 415–425 nm and are nearly similar to the PL spectra shown in Fig. 1. One of the interesting results between PL and CL emission spectra is the relative emission intensity of codoped samples. Contrary to UV excitations, under low-voltage acceleration of electron-beam, the CL

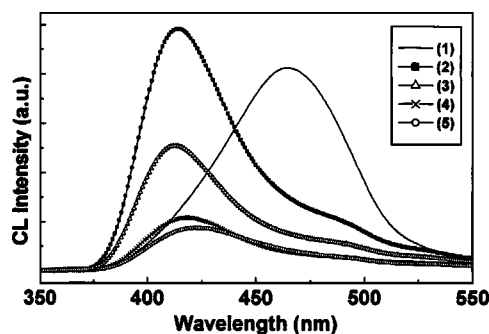
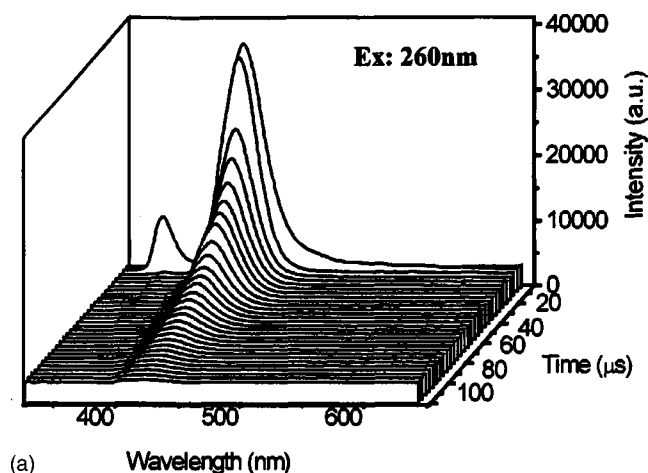


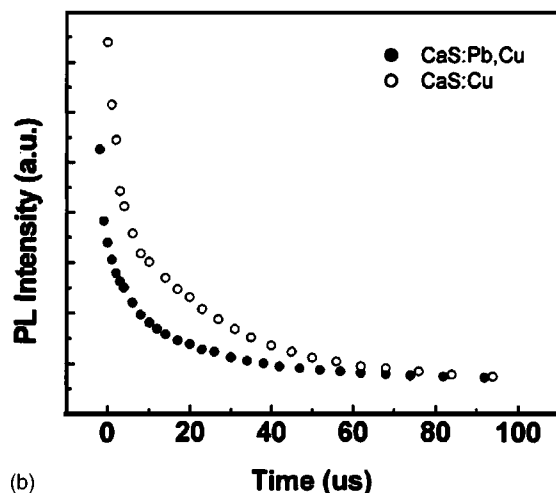
Figure 4. CL emission spectra of CaS:Pb (1.0 atom %) thin films with various Cu concentrations: (1) none, (2) 0.3, (3) 1.0, (4) 7.9, and (5) 22.0 atom %.

efficiency of the CaS:Pb film codoped with 0.3 atom % Cu increases compared to that of CaS:Pb film.

A major difference in PL and CL refers to the means of excitation: (i) CL is excited by an accelerated electron-beam which usually induces emission via all possible luminescence mechanisms available in solids.²⁰ (ii) PL, however, is induced by photons of considerably lower excitation energy, where each absorbed photon gener-



(a)



(b)

Figure 5. (a) Low-temperature, time-resolved PL emission spectra of a CaS:Pb (1.0 atom %), Cu (1.0 atom %) thin film. (b) Decay curve of CaS-based thin film.

ally excites one electron. Thus, phosphors doped with Pb and Cu are more effectively excited by cathode ray than by UV excitation.

Figure 5a shows time-resolved PL spectra of CaS:Pb, Cu at 6 K for different delay times. It is seen from this figure that PL spectra consist of two emission bands at approximately 365 and 430 nm. The UV band at 365 nm can be interpreted with the emission from the Pb^{2+} monomers, as reported in earlier works.¹⁵ It is found from the figure that the decay time of the Pb emission at 365 nm was shorter than that of the main blue emission band. The emission band at 430 nm did not shift toward longer wavelength with increasing delay time.

The decay curve of the CaS:Pb, Cu phosphor is shown in Fig. 5b and compared to that of CaS:Cu phosphor film. The curve indicated by open circles was obtained by monitoring the emission of CaS:Cu phosphors, and the curve indicated by solid circles was obtained by monitoring the 430 nm emission on the CaS:Pb, Cu film.

Their decay of luminescence following excitation is primarily determined either by the electron transition within the activator ion or by carriers temporarily captured in various traps.

The observed behavior of Pb^{2+} ions on the luminescence decay of CaS:Cu, Pb phosphor may be understood as follows. The process of excitation and emission of codoped samples is closely related to decay of luminescence. Light emission that persists after the cessation of excitation is called *afterglow*. Many investigators have tried to reduce this afterglow by incorporating a suitable chemical “killer” element in the phosphor, without resulting in an excessive reduction of the emission intensity. Time-resolved luminescence of CaS:Pb, Cu shows the same behavior as other CaS phosphors containing fast activators, and Pb ions play the role of a chemical killer as well as the role of an excitation center. A practical indication of this investigation is that CaS phosphors containing Pb ions as “afterglow killer” may advantageously replace conventional phosphors in applications where high response speed is required.

Conclusion

In summary, the luminescent properties of CaS:Pb, Cu thin-film phosphors were investigated. The CaS:Pb, Cu film exhibited highly saturated blue PL centered at 430 nm and CL peaked at 415–425 nm, identical to that of CaS:Cu, and the excitation efficiency of PL was close to that of CaS:Pb. Spectroscopic study has identified an efficient energy transfer from Pb to Cu ions, indicating that the luminescence of Cu^+ ions was successfully sensitized by activated Pb^{2+} ions. Demonstration of a successful sensitization process in CaS:Pb, Cu opens the possibility of designing and developing a new class of two-component phosphors with the potential to exhibit both better color and higher excitation efficiency than that of conventional single-activator phosphors.

Acknowledgment

The Korea Ministry of Information and Communications financially supported the accomplishment of the present work.

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