Photoluminescence of CaS:Pb Phosphors Grown by Atomic Layer Deposition

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Abstract

CaS:Pb thin film used as phosphor layer in electroluminescent devices were deposited by an atomic layer deposition (ALD). The photoluminescence emission and excitation spectra were measured at 5 and 300K for the CaS:Pb^{2+} phosphors with different Pb concentration from 0.001 at.% to 0.648 at.%. The emission spectra of these samples were characterized as UV emission and blue emission with the center of peak around 360 and 425nm, respectively. The UV emission was dominant at the low Pb^{2+} concentration of 0.001 at%, whereas with increase of Pb concentration, the blue emission became a major component and to longer wavelength.

Introduction

Calcium sulfide has been known to be one of the most possible host materials for the blue phosphor due to wide band-gap of 4.4eV. Especially, CaS:Pb has been reported to be an efficient blue photoluminescent phosphor [1]. The earlier works, however, revealed that CaS:Pb could not be a promising candidate for the blue phosphor because of the low luminance and Pb clustering [2].

The Pb^{2+} ions added into the host material of II-VI compound such as CaS, SrS, BaS, ZnS and MgS have the same cubic crystalline structure and are in the same divalent state as II family elements. The Pb^{2+} ions are added into the host material and substituted with the cations of the host materials without adding charge compensators. This results in, the Pb^{2+} ions easily form clusters or aggregate. The Pb^{2+} ion has the $6s^2$ state of the valence electron arrangement in the ground state level. When it absorbs energy, the electron of the Pb^{2+} ion transits to the $6s^16p^1$ states. The states of the energy levels are quite affected by ambient ions of host materials. The allowed $6s^16p^1 \rightarrow 6s^2$ transition leads to the efficient emission in the UV or blue wavelength region, depending on the host matrices [4].

In this study, we investigated CaS:Pb thin film phosphors deposited by atomic layer deposition (ALD). The various amounts of PbS were introduced into the host material in order to elucidate the atomic state of Pb^{2+} activator.

Experiments

The CaS and PbS films were grown on aluminum oxide-deposited Si substrate by ALD. The ALD growth of CaS:Pb was carried out by repeatedly inserting PbS thin layers in the deposition of CaS host material. CaS films were deposited by reaction of $Ca(thd)_2$(thd=2,2,6,6-tetramethyl-3,5-hepandionate) and H_2S. The precursors of tetraethyl lead and H_2S were used for the deposition of PbS. The deposition temperature was 350°C. The Pb concentration was measured by Rutherford Backscattering Spectrometry (RBS). The concentration of Pb listed in Table 1 was increased by increasing the thickness of PbS thin layer inserted in the CaS host material.

The photoluminescence (PL) measurement was carried out at the temperature of 5 and 300K. The samples were excited by a 1 kW Xe lamp and Nd-YAG laser of wavelength 266nm to obtain the excitation and the emission spectra, respectively.

Table 1. The deposition conditions of CaS:Pb thin films.

Sample No.	Concentration of Pb (at.%)	Deposition Temp. (℃)
# 1	0.001	350
# 2	0.234	350
# 3	0.455	350
# 4	0.648	350

Results and Discussion

Stoichiometric CaS:Pb films showing well-developed cubic structure were grown by ALD process (XRD data were omitted in this paper).

Figure 1 shows the excitation spectrum of CaS:Pb (#2) at 300K. In the excitation spectra, C'- and A'-bands due to aggregates including dimers are observed [5].

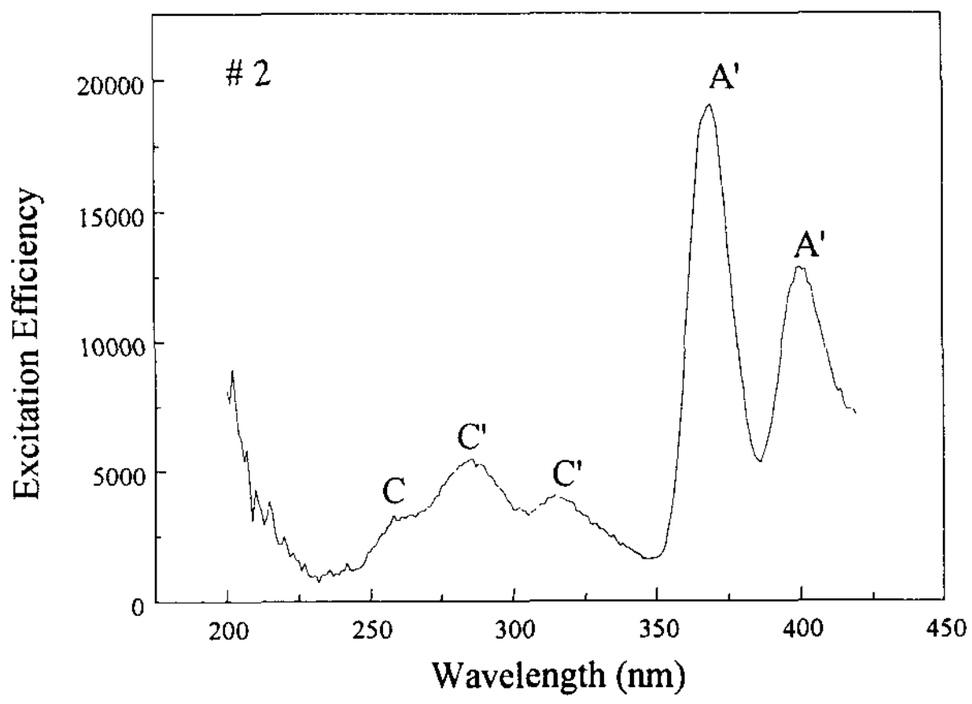

Fig. 1. Excitation spectrum of CaS:Pb observed at 300K

Figure 2 shows the PL emission spectra of CaS:Pb at 300K. At a low activator concentration of 0.001at.% (#1 in Fig. 2), the major emission band is observed in the UV region. The UV emission band corresponds to the electronic transition in the Pb^{2+} monomer centers in CaS. The UV emission band is easily observed from the CaS phosphor doped with a small amount of PbS [1, 4, 5]. This UV emission band (abbreviated as UV_L), observed at 360nm can be assigned to the electronic transition $^3A_{1u} \rightarrow {}^1A_{1g}$ [1].

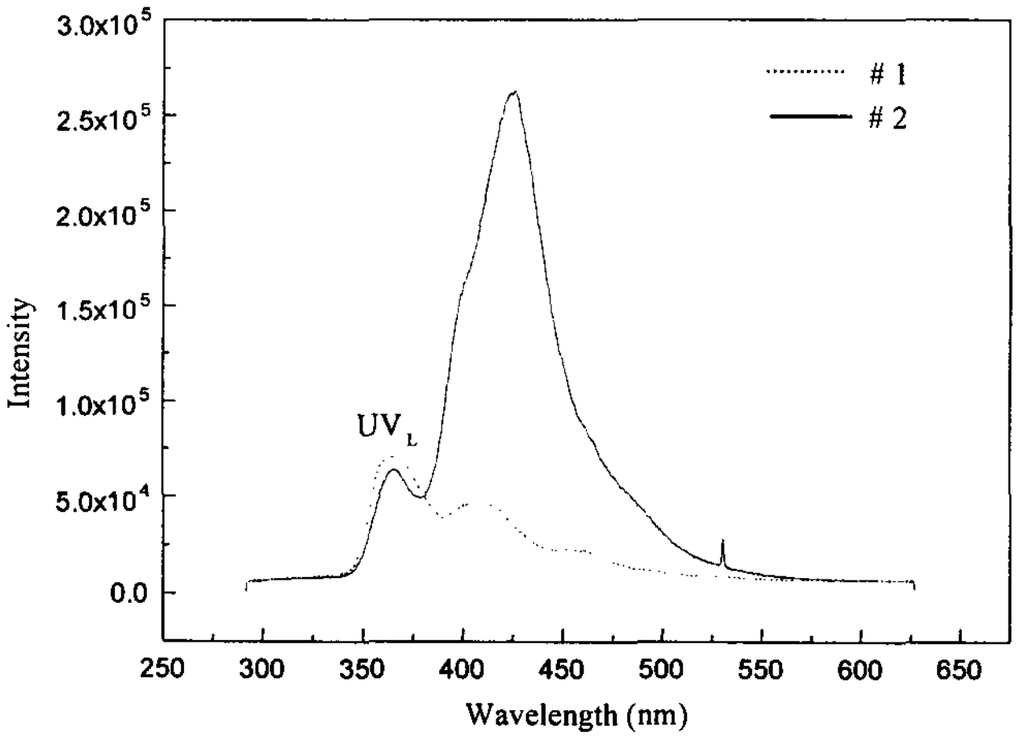

Fig. 2. PL emission spectra of CaS:Pb at 300K.

As shown in #1 and #2 of Fig. 2, the relative intensity of UV emission from monomer centers to this blue emission decreased abruptly and the blue emission increased as increasing the concentration of Pb. It has been reported that dimer centers are responsible for this blue emission [1, 4, 5].

Figure 3 shows the emission spectra of CaS:Pb with varying the concentration of Pb from 0.001 at.% to 0.648 at.% at the temperatures of 5 and 300K.

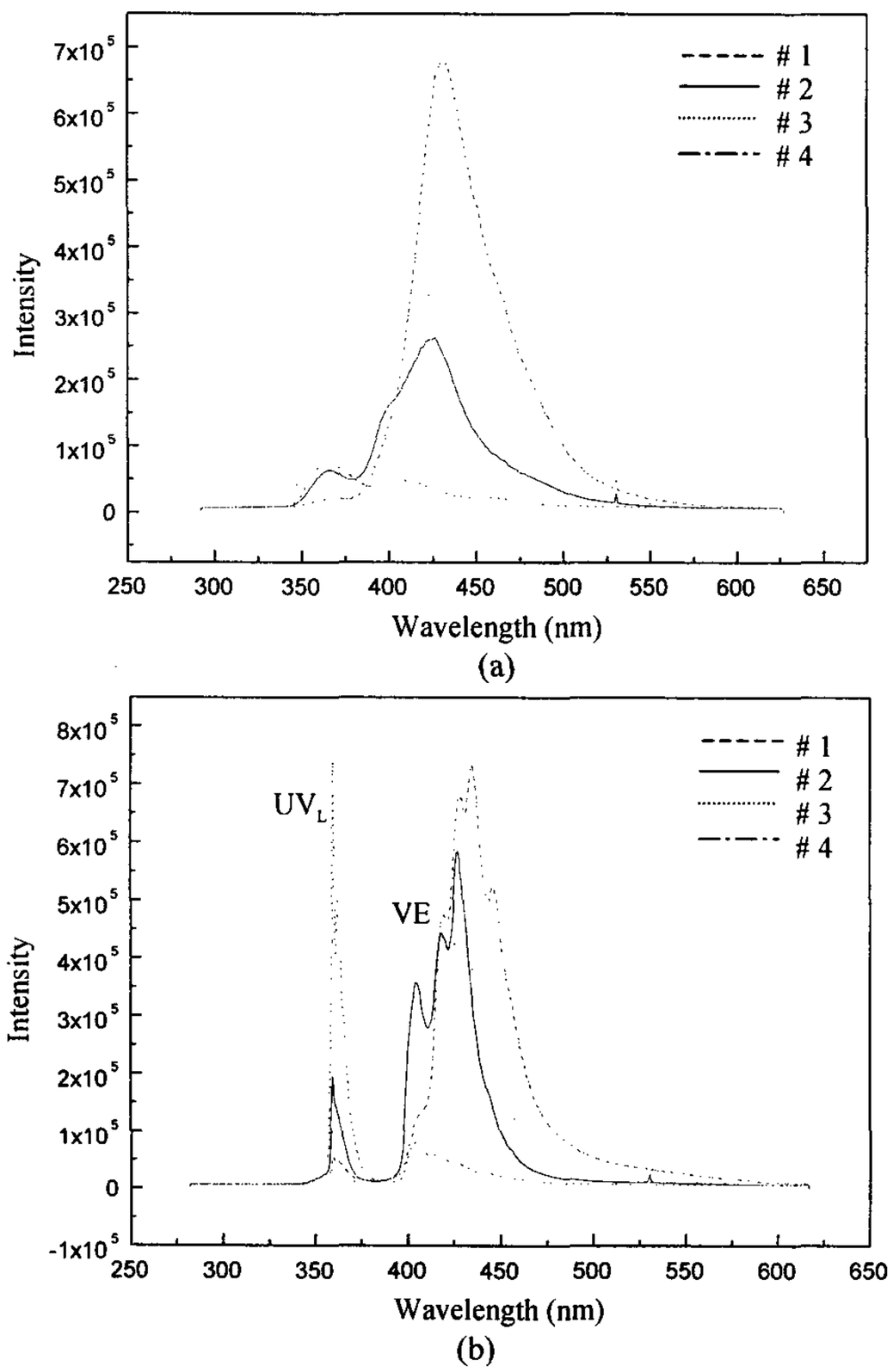

Fig. 3. PL emission spectra of CaS:Pb observed at 300K (a) and 5K (b).

At the temperature of 5K, CaS:Pb films of #2 - #4 show additional emission bands in the visible region (abbreviated as VE) at approximately 403, 417 and 426nm. The visible emission bands are inferred to be caused by the Pb^{2+} dimer centers and highly aggregated centers on the analogy of the emission spectra for the Pb^{2+} centers in calcium chalcogenides [1, 5]. Figure 3 indicates that the UV emission band at 360nm decreased abruptly while visible emission (blue emission) bands increase with increasing Pb concentration. It is considered that the Pb^{2+} ions exist as a monomer state at a concentration as low as 0.001 at.%, and they form the dimer and larger aggregates according to the increase of Pb concentration. Even if we do not have tangible evidences in favor of this shift shown in Fig. 3, this also could be originated from a change in the crystal field around Pb^{2+} ions.

Conclusion

The PL studies on CaS:Pb phosphor was carried out with Pb concentration ranging from 0.001 at.% - 0.648 at.%. At a concentration of Pb^{2+} ions as low as 0.001 at.%, a strong emission is observed at 360nm. With increasing Pb^{2+} ion, the UV emission decreases abruptly while the blue emission increases. It is considered that Pb monomer and dimer lead to UV emission and a blue emission, respectively. The PL peaks also move to longer wavelength according to the increase of Pb concentration. The PL results indicate that Pb aggregates are easily formed as increasing Pb concentration, i.e., the thickness of PbS layers in the CaS host lattices.

Acknowledgments

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