Photoluminescence properties of Pb^{2+} centres in CaS:Pb thin films

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Yong Shin Kim[1] **and Sun Jin Yun**

Basic Research Laboratory, Electronics and Telecommunications Research Institute,
161 Kajong-dong, Yusong-gu, Daejeon, 305-350, Korea

E-mail: yongshin@etri.re.kr

Abstract
The emission and excitation spectra of CaS:Pb thin films have been obtained
at 10 K together with the emission decay curves. The CaS:Pb samples were
prepared with the variation of the concentration and the spatial uniformity of
active Pb^{2+} ions within the CaS host matrix using atomic layer deposition (ALD)
and tetraethyl lead (TEL) as the Pb precursor. The deep blue emission at
the wavelength of 400–450 nm was shown to be regulated by means of the
homogeneous distribution of the luminescent centres rather than the number
of Pb ions. At the same concentration and uniformity, the higher growth
temperature of 380 °C was found to be more advantageous for the deep blue
emission than 350 °C. These observations have been interpreted in terms of the
selective incorporation of blue-emitting Pb^{2+} dimers achieved by the controlled
ALD technique and the preferential reactivity of TEL. The excitation spectra
indicated that the absorption of Pb^{2+} monomers and CaS matrix as well as the
dimeric luminescent centres induced blue emission through efficient energy
transfer to the dimer centres. In addition, the visible emission above 450 nm is
believed to be attributable to the formation of aggregates larger than dimers in
view of the measured decay times.

1. Introduction

Inorganic thin-film electroluminescent (TFEL) devices have been extensively investigated with
a view to applications in full-colour flat-panel displays for the last few decades [1–3]. One of
the major problems for achieving a full-colour display is the lack of an efficient and stable blue
phosphor. Lead-doped calcium sulfide, CaS:Pb, known as an excellent cathodoluminescent and
photoluminescent phosphor [4–8], had been studied as a promising candidate for use in blue-
emitting TFEL devices. Unfortunately, some studies on CaS:Pb TFEL devices failed to

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[1] Author to whom any correspondence should be addressed.

obtain enough high-luminance blue emission for realizing commercialization of full-colour display panels [9, 10]. According to these studies, blue emission results from the electronic transitions in Pb^{2+} dimer centres, and the selective incorporation of Pb^{2+} dimers is difficult to control because of the preferential formation of various aggregates larger than the dimer. A CaS:Pb device fabricated previously by electron beam evaporation showed a broad bluish green emission even at Pb concentrations as low as 0.5 at.%, which indicated the formation of higher aggregates [9]. Another device deposited by atomic layer deposition (ALD) using $Pb(dedtc)_2$ (lead diethyldithiocarbamate) as the Pb precursor demonstrated weak blue emission with the luminance of 2.5 cd m^{-2} at 300 Hz [10]. In contrast to the earlier workers, Yun *et al* have recently developed a high-luminance CaS:Pb device with a deep blue colour purity using controlled ALD deposition and $Pb(C_2H_5)_4$ (tetraethyl lead, TEL) as the Pb precursor [11, 12]. The luminance at a voltage 25 V higher than the threshold voltage was reported to be higher than 80 cd m^{-2} at 60 Hz, which satisfied the requirements for a full-colour panel.

The Pb^{2+} monomer centre in a cubic crystal introduces a set of absorption bands called A, B and C bands in order of increasing energy. These absorption bands are known as arising from the transitions from the ground state $^1A_{1g}$ to the excited states $^3T_{1u}$, (^3E_u, $^3T_{2u}$) and $^1T_{1u}$, respectively. The transition from the ground state to the lowest excited state $^3A_{1u}$ is strongly forbidden, and has not been observed in an absorption measurement. Under the C-band excitation of CaS:Pb with Pb^{2+} concentration less than 0.2 at.%, the $^3A_{1u} \rightarrow {}^1A_{1g}$ emission (denoted as UV_L) is, however, observed predominantly at 362 nm in addition to the $^3T_{1u} \rightarrow {}^1A_{1g}$ emission at 356 nm (denoted as UV_H) [6, 7]. As the Pb concentration goes higher, additional absorption bands (A′, B′, C′) and visible emission peaks induced by the aggregate centres are observed. The deep blue emission in the region 400–450 nm had been assigned to the electronic transitions in the [110] dimers of Pb^{2+} ions [6].

In this work, we report on the luminescence properties of Pb^{2+} active centres in CaS:Pb thin films prepared by using controlled ALD and the TEL precursor. The CaS:Pb phosphors were deposited with variation of the concentration and the spatial uniformity of the Pb^{2+} ions together with the growth temperature in order to prepare samples with different local chemical environments for the Pb^{2+} centres. Since the electroluminescence spectra of CaS:Pb were found to be qualitatively in good agreement with the corresponding photoluminescence (PL) spectra, PL emission measurements give us a chance to evaluate whether the deposited CaS:Pb thin films are suitable for use in blue-emitting TFEL devices and to determine which experimental conditions are preferred for the incorporation of Pb^{2+} dimers. In addition, the PL excitation spectra and the emission decay times were measured in an effort to understand the luminescence characteristics of Pb^{2+} centres.

2. Experimental details

The CaS:Pb thin films were prepared by the alternating deposition of CaS and PbS layers on aluminium oxide-deposited Si substrate at the growth temperature of 350–400 °C using ALD equipment as reported previously [11, 12]. The CaS layer was grown by surface reaction between $Ca(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-hepandionate) and H_2S. And the PbS was deposited by using the precursors $Pb(C_2H_5)_4$ and H_2S. The total thickness of the CaS:Pb films was controlled by means of the total number of ALD deposition cycles used for the growth of the CaS and PbS layers. The Pb concentration and the Pb spatial uniformity within the CaS host matrix were regulated with the ratio of the total thickness of the PbS layers to the CaS total thickness and with the bilayer thickness, D_{bi}, defined as the thickness of a single pair of CaS and PbS layers. The total thickness and the Pb concentration were determined by Rutherford backscattering spectroscopy. Table 1 summarizes the growth temperature, the

Table 1. Summary on the CaS:Pb thin films used in this study.

Sample ID	Temperature (°C)	Pb concentration (at.%)	Thickness (nm)	D_{bi} (nm)
A	350	0.001	316	3.2
B	350	0.23	307	0.5
C	350	0.46	366	0.5
D	350	0.65	340	0.5
E	350	2.20	300	0.5
F	350	0.45	281	2.3
G	380	0.50	374	0.5

total thickness, the Pb concentration and the bilayer thickness for the CaS:Pb films used in this photoluminescence study. Our previous papers gave more details on the deposition conditions, the material characterization and the growth characteristics [11–14].

The PL properties of CaS:Pb samples were investigated at the temperature of 10 K. The emission spectra were obtained by using a monochromator equipped with a photomultiplier tube. The C-band excitation of Pb^{2+} monomer centres was performed with 275 nm Ar ion or 266 nm Nd/YAG lasers. The excitations at different wavelengths were carried out with the monochromated light output obtained from a xenon lamp. An Nd/YAG laser pumped optical parametric oscillator with 5 ns pulse duration and a transient recorder were used to measure PL decay times.

3. Results and discussion

3.1. Emission spectra

The emission spectra obtained under C-band excitation at 10 K are shown in figure 1 for CaS:Pb thin films with variation of the Pb concentration in the range 0.001–2.2 at.%. The Pb concentration was regulated by means of the cycle number for PbS growth for constant CaS cycle number in the alternating ALD growth process except for sample A. That is, the CaS:Pb samples were prepared with changing PbS thickness for constant CaS thickness in the CaS/PbS multilayered structure. The constant CaS thickness was calculated to be 0.45 nm by multiplication of the growth rate of 0.045 nm/cycle [12] by the cycle number used, 10. The thickness of the single PbS layer was varied in the range 0.004–0.038 nm for samples B–E. The spatial distribution of Pb^{2+} ions within CaS:Pb films is expected to be homogeneous from the fact that the Pb concentration is quantitatively regulated by the ALD cycle number for the growth of a single PbS layer under the condition $D_{bi} = 0.5$ nm [12]. There are two emission bands observed around 362 nm and in the visible region 400–550 nm. These two emissions had been assigned to the UV_L transition in the Pb^{2+} monomer centre and the analogous transitions in the aggregate centres, respectively [6]. As the Pb concentration goes higher, the relative intensity of the visible band compared with UV_L increases and its emission centre shifts to longer wavelength. These results demonstrate that the deep blue emission in the region 400–450 nm is degraded by the increase of the Pb concentration under conditions occurring with local accumulation of Pb ions. This is well interpreted in terms of the considerable amount of formation of Pb aggregates larger than dimers since the higher aggregates had been reported to conduct green emission [9].

X-ray diffraction experiments were performed to confirm whether we could observe the crystal structures induced by Pb aggregates. Figure 2 shows the diffraction patterns for the three CaS:Pb samples with high Pb concentration in figure 1. The top spectrum obtained
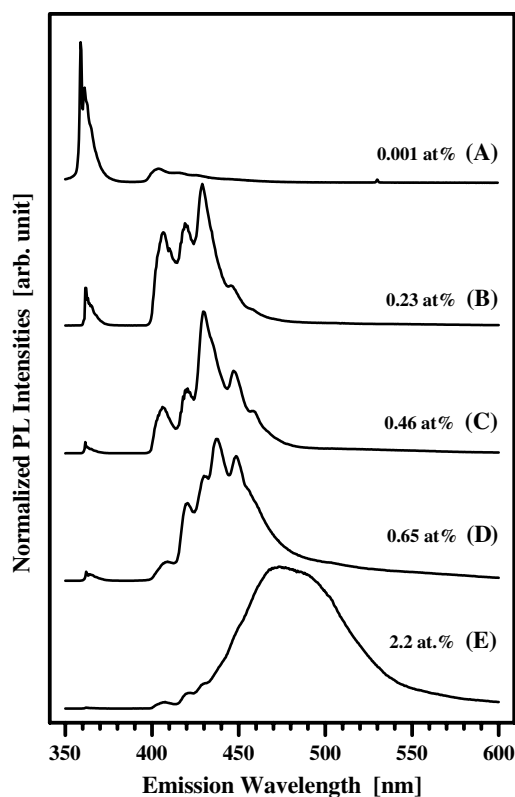
Figure 1. Emission spectra of CaS:Pb thin films prepared with change of the Pb concentration at 10 K. The spectra were obtained under C-band excitation of Pb^{2+} monomers at 266 nm for 0.001 at.% and 275 nm for other cases. The maximum intensities for each spectrum were observed to be 7.5×10^5, 4.0×10^5, 4.0×10^5, 2.4×10^5 and 1.6×10^5, respectively, with increasing Pb concentration.

from sample C (0.46 at.% Pb) shows a typical diffraction pattern of polycrystalline cubic CaS whose main peaks are [200], [220] and [420] observed at the diffraction angles of 31.1°, 45.0° and 74.5°, respectively. In addition to the strong CaS peaks, two other spectra show weak diffraction peaks, as indicated by arrows, which can be assigned to the cubic crystal structure of Pb and PbS. In the bottom spectrum for sample E (2.20 at.% Pb), the intensities of the Pb [200] and PbS [222] peaks relative to the strongest CaS [200] one were observed to be 0.03 and 0.01, respectively. On the other hand, the relative intensity of the PbS [222] peak was approximately 0.03 for sample D with 0.65 at.% Pb. Even though these diffraction peaks are difficult to correlate quantitatively with the size of Pb and PbS aggregates due to the considerable uncertainty resulting from the weak intensity being comparable to the background level, they give direct evidence for aggregate formation within CaS:Pb thin films with a high Pb concentration.

In order to investigate the dependence of the emission spectrum on the growth temperature and the Pb spatial uniformity at the same Pb concentration, additional PL measurements were carried out. The Pb uniformity was regulated by the variation of the bilayer thickness D_{bi} for a constant thickness ratio between the PbS and CaS layers. The top and middle emission spectra shown in figure 3 were obtained from CaS:Pb samples deposited at the growth temperatures of 380 and 350 °C, respectively, with the same bilayer thickness of 0.5 nm, while the middle
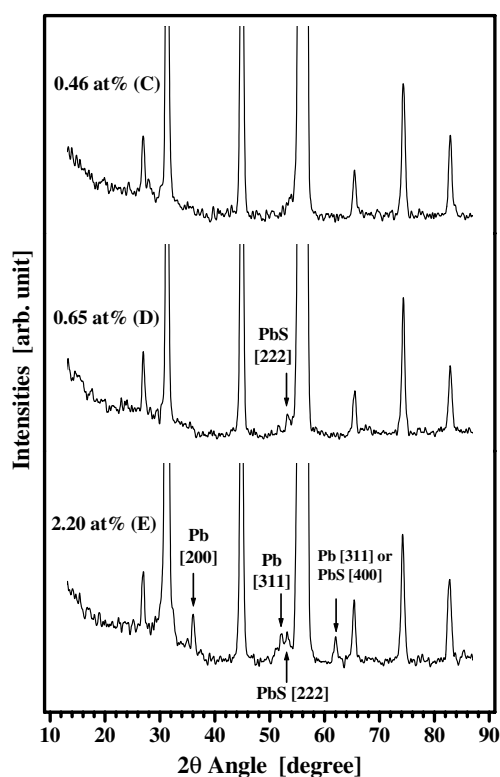
Figure 2. X-ray diffraction patterns for the three samples with a high Pb concentration in figure 1. The arrows indicate the peak positions corresponding to the observed cubic crystal structure of Pb and PbS.

and bottom spectra give us a chance to look into the effect of the Pb uniformity at the same growth temperature. In the case of $D_{bi} = 2.0$ nm (bottom), the visible emission broadens more into the long wavelength region than in the case of $D_{bi} = 0.5$ nm (middle). Since the higher bilayer thickness results in less uniform spatial distribution of Pb active centres, i.e., higher local population of Pb atoms, the emission spectrum obtained from the sample with a high bilayer thickness must have a considerable contribution from the large aggregates which lead to green-shift emission as mentioned above. From the top and middle emission spectra for the two growth temperatures, the deep blue emission is found to be better for the $380\,^{\circ}$C sample than for the $350\,^{\circ}$C. The improvement in the blue colour purity was observed up to the maximum growth temperature of $400\,^{\circ}$C above which PbS can evaporate out of the films. Therefore, the formation of blue-emitting luminescence centres seems to be favoured at high temperature even if the same number of Pb atoms exist within CaS:Pb.

3.2. Excitation spectra

The excitation spectra shown in figure 4 were obtained with the probe wavelength adjusted to the PL emission peaks. The 362 nm excitation spectrum probed for the emission corresponding to the monomer UV_L transition is different from other spectra probed at the wavelengths of the visible emission peaks resulting from the electronic transitions of aggregate centres. The UV_L excitation spectrum is well interpreted in terms of the A and C absorption bands of Pb^{2+}
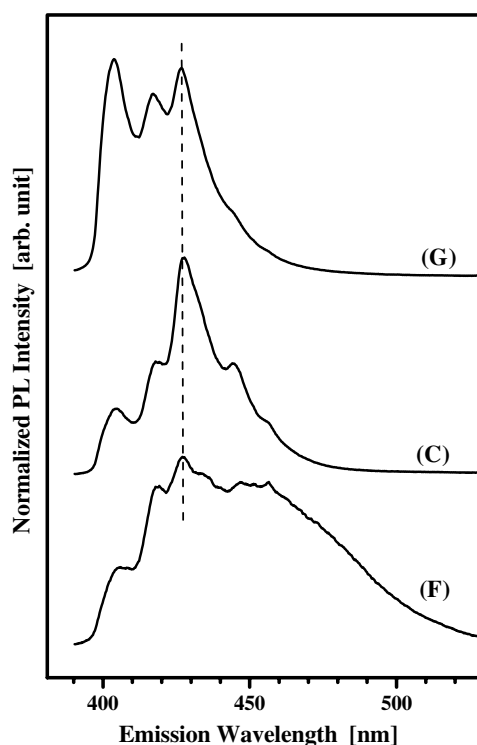
Figure 3. Emission spectra of CaS:Pb thin films with similar Pb concentrations around 0.5 at.% prepared with different growth temperatures and/or bilayer thicknesses under C-band excitation at 266 nm. The positions of maximum intensity are indicated by the dashed line at 430 nm and their magnitudes were 6.7×10^5, 5.2×10^5 and 2.9×10^5, respectively, for the top, middle and bottom spectra.

monomer centres and the absorption of the CaS host matrix below 250 nm. On the other hand, the excitation spectra for the emission induced by the aggregate centres are observed to have several additional peaks—in addition to the monomer and the host matrix absorption bands. These peaks had previously been assigned to the analogous absorption bands (A′, C′) due to the aggregate centres. The appearance of the monomer and the host matrix absorption bands in the excitation spectra for the aggregate emissions suggests efficient energy transfer from the monomer and the host matrix into the Pb^{2+} aggregates.

Figure 5 shows the emission spectra of CaS:Pb (0.23 at.% Pb) excited at the centre wavelength of the absorption bands in the excitation spectrum. The blue emission is observed as a major component for all the excitation wavelengths. On the other hand, the emission intensities for the UV_L and UV_H bands seem to be considerably dependent on the excitation wavelength. In order to compare the intensity of the two UV bands quantitatively, the relative intensity ratios at the peak positions of 362 and 356 nm with respect to the peak intensity of the 430 nm visible band are calculated and these are summarized in table 2. The relative intensity of the UV_L emission is found to become stronger in the order of band excitation A, C, CaS, C′, while the UV_H emission is only observed under A-band excitation, significantly. It is worth mentioning that the excitation of the CaS host matrix leads to the more preferred blue emission rather than UV emission, which implies that the favourable energy transfer into the excited electronic states of Pb-aggregated centres occurs by means of direct energy transfer from CaS
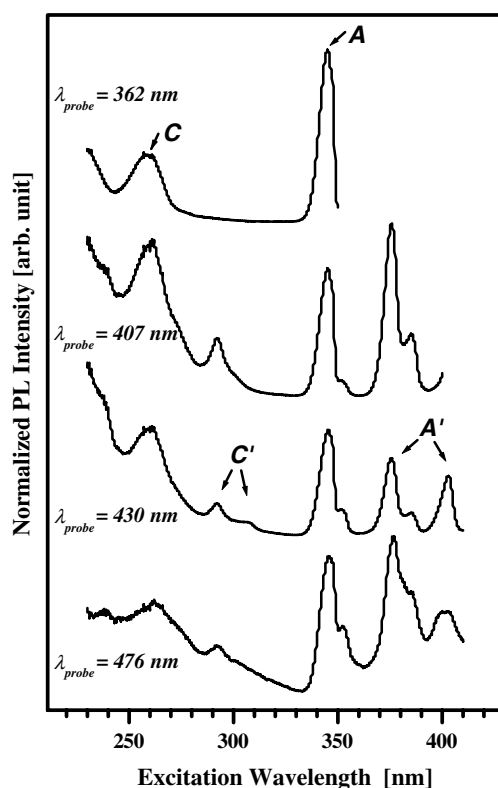
Figure 4. Excitation spectra probed at the emission wavelengths of 362, 407 and 430 nm for sample B with the Pb concentration of 0.23 at.% and at 476 nm for sample E with 2.2 at.% Pb. A and C represent the absorption bands for the Pb^{2+} monomer centres, and A′ and C′ the analogue bands for the aggregates. The A-band intensities at 345 nm were observed to be 7.1×10^3, 4.4×10^3, 8.6×10^3 and 2.7×10^3, respectively, with increasing probe wavelength.

Table 2. Intensity ratios for UV_L and UV_H emissions relative to the peak intensity at 430 nm according to the excitation band.

Intensity ratio	Excitation band			
	A band	C′ band	C band	CaS band
$\dfrac{I\ (362\ \text{nm})}{I\ (430\ \text{nm})}$	0.52	0.05	0.21	0.11
$\dfrac{I\ (356\ \text{nm})}{I\ (430\ \text{nm})}$	0.29	<0.01	<0.01	<0.01

states and the indirect pathway via the excited states of Pb^{2+} monomers. The involvement of the indirect energy transfer is reasonably understood in terms of the fact that the population of Pb^{2+} monomers is higher than that of Pb^{2+} dimers and the excitation of monomer centres also induces the preferred blue emission as shown in figure 5 and table 2.
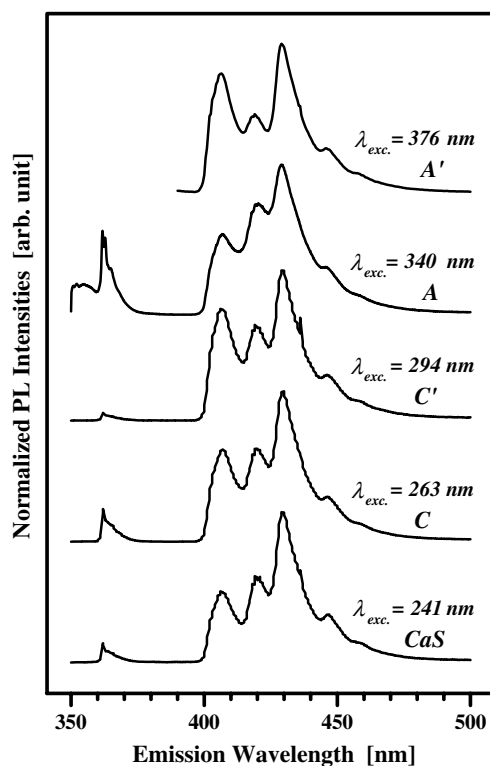
Figure 5. Emission spectra obtained at different excitation wavelengths from sample B with the Pb concentration of 0.23 at.%. The excitation wavelengths correspond to the centres of the following absorption bands: A and C transitions for Pb monomers: A′ and C′ for the aggregates; CaS for the host matrix. The emission intensities of the 430 nm peak were observed to be 5.3×10^4, 9.0×10^4, 5.9×10^4, 1.6×10^5 and 1.5×10^5, respectively, with increasing excitation wavelength.

3.3. Decay time measurements

The decay times of PL emission for sample B (0.23 at.% Pb) were measured at 10 K with excitation of the C-band absorption by 263 nm laser light. Figure 6 shows the PL decay curves obtained for the UV_L emission at 362 nm and the three visible emission peaks at 407, 430 and 460 nm. The observed curves could be fitted with an exponential decay function having three components. In the case of the UV_L emission band, there were three components with the decay lifetimes of 7, 100 and 610 μs. On the other hand, even though there is some difference, the two visible bands at 407 and 430 nm were observed to have three components with comparable decay lifetimes to the UV_L band (5, 72, 583 μs for 407 nm, and 7, 100, 700 μs for 430 nm). Previously, the excited electronic states of Pb^{2+} dimer centres were reported to be responsible for the deep blue emission in the region 400–450 nm [6]. However, the decay curve probed at 460 nm is quite different from the others. The 460 nm decay curve consists of only fast components with lifetimes less than 10 μs. Although the decay curve cannot be interpreted reasonably in terms of relevant intermediate states, it seems that the greenish blue emission is ascribable to electronic transitions of aggregates larger than Pb^{2+} dimers. Higher aggregates could lead to fast decay due to their lower local symmetry compared with monomer or dimer centres, as observed in $CaS:Mn^{2+}$ phosphor [15].

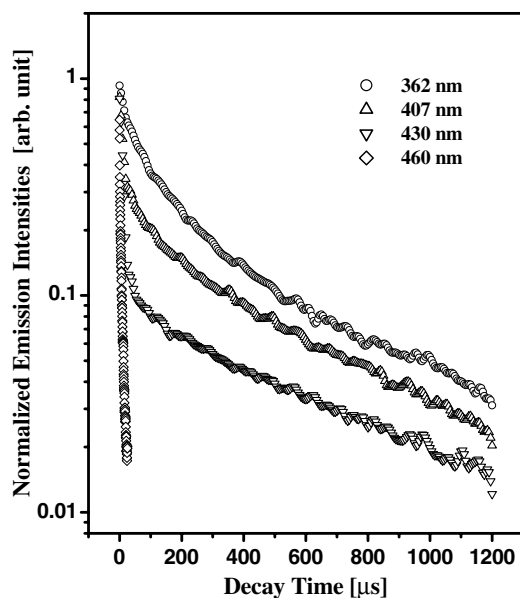**Figure 6.** Emission decay curves obtained for the UV$_L$ emission at 362 nm and three visible emission peaks from sample B (0.23 at.% Pb) at 10 K.

3.4. Incorporation of Pb^{2+} dimers

The intensity of a deep blue emission can be enhanced easily by increasing the number density of the blue-emitting luminescent centres, the Pb^{2+} dimers. The abundant incorporation of the dimer centre had been known to be difficult to achieve since the monomer centre is dominant at low Pb concentration and green-emitting aggregates larger than dimers are easily formed with increase of Pb ion numbers. However, our CaS:Pb devices demonstrated that the deep blue emission can be maintained even at high Pb concentration above 1 at.% [11, 14], where the emission had been reported to become greenish blue in previous studies [6, 9]. It can be interpreted in terms of the selective incorporation of Pb dimers resulting from the controlled ALD technique and the preferential reactivity of TEL for the formation of Pb^{2+} dimers.

A deposition technique is important for regulating the local chemical environment of doped Pb. The critical Pb concentration, initiating the formation of Pb aggregates in SrS:Pb thin films, was reported to increase greatly for the deposition method minimizing the formation of Pb–Pb clusters [16]. From this viewpoint, the ALD method is advantageous for incorporating blue-emitting Pb^{2+} dimer centres uniformly into the host matrix as judged against other deposition techniques due to its unique self-limiting characteristics. The CaS:Pb phosphors deposited by electron beam evaporation had been reported to suffer from substantial formation of large Pb clusters [9]. Even in the same ALD technique, the incorporation characteristics of active Pb centres are found to differ according to the Pb precursor used. The choice of Pb precursor is therefore very important for achieving high luminance and deep blue emission. Although the CaS:Pb devices fabricated with Pb(dedtc)$_2$ had been reported to conduct a more homogeneous spatial distribution of Pb ions compared with precursors such as PbCl$_2$, PbBr$_2$ and Pb(thd)$_2$ [10], the deep blue emission could be obtained in the Pb concentration range from 0.5 to 0.75 at.%. This is much narrower than the Pb concentration range of 0.3–1.25 at.% in our devices fabricated by using TEL. The increase in the maximum Pb concentration implies

that the higher number density of blue-emitting active centres can be achieved through a more homogeneous distribution in the case of TEL as compared with $Pb(dedtc)_2$. This explains well the fabrication of high-luminance and deep blue CaS:Pb devices using TEL precursor. The PbS growth rate was found to be 0.02 Å/cycle at 350 °C in the case of TEL and was 15 times smaller than the growth rate of 0.3 Å/cycle for the $Pb(dedtc)_2$ [17]. The smaller amount of PbS deposited per cycle allows Pb ions to be incorporated more homogeneously by means of the frequent repetition of the alternating deposition of CaS and PbS. Besides the small growth rate, a preferential reactivity of TEL for dimer formation seems to be operative, from the fact that the relative intensity of the blue emission with respect to the monomer UV emission is strong at the low Pb concentration around 0.2 at.% at which the UV emission had been known to be dominant in the cases of using other precursors. TEL is expected to easily form a dimeric intermediate state during the ALD process since the dimeric compound of TEL, $Pb_2(C_2H_5)_6$, is known to be isolated as a stable compound via the reaction between TEL molecules. As shown in figure 3, the incorporation characteristics of luminescent centres also depend on growth temperature. The preferential incorporation of blue-emitting centres at high growth temperature may be understood in terms of a reactivity change in the surface reactions relevant to PbS growth and Pb dimer formation.

4. Conclusion

Intensive photoluminescence studies have been performed on blue-emitting CaS:Pb thin films at 10 K. The CaS:Pb phosphors were systematically prepared by using controlled ALD and TEL as the Pb precursor with variation of the Pb concentration, the Pb spatial uniformity and the growth temperature in order to explore the optimum growth conditions for fabricating high-luminescence and deep blue CaS:Pb phosphors. For the Pb concentration range 0.3–1.25 at.%, the deep blue emission can be maintained through homogeneous spatial distributions of Pb ions and its luminescence intensity is roughly proportional to the Pb concentration. In addition, a high growth temperature is advantageous to the fabrication of good CaS:Pb films in the temperature range 350–400 °C. The maximum Pb concentration possible for emitting a blue colour is limited by the formation of aggregates larger than dimers at high Pb concentration. The larger aggregates are responsible for green emission. The blue emission is found to improve in the following order of excitation: Pb aggregate, CaS host matrix, Pb monomer absorption bands.

Acknowledgments

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