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Photoluminescent, electroluminescent and structural properties of CaS:Cu and CaS:Cu, Ag thin films

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Abstract. Photoluminescent, electroluminescent and structural properties of CaS thin films doped with Cu and Ag have been investigated. The emission spectrum and the crystallinity are discussed for different Cu concentrations and different annealing conditions. Codoping with Ag has been evaluated, leading to a more elaborate study of CaS:Cu, Ag layers. The morphology of these layers is investigated with AFM and SEM. Measurements of the PL intensity as a function of working temperature revealed the good quenching behaviour of the layers. For the first time, blue electroluminescent emission could be obtained from a CaS:Cu, Ag thin film system.

1. Introduction

Although SrS:Cu, Ag is the most promising blue electroluminescent (EL) emitter to date, it still has some disadvantages which prevent the breakthrough of full colour EL screens: the Ag related emission is nearly completely quenched at room temperature and the reproducibility of the emission spectra for layers made with different techniques is low [1, 2].

In this work, the possibility of using CaS as a host for Cu and Ag dopants is discussed. CaS has already been known for a long time as host in red emitting CaS:Eu alternating current thin film electroluminescent (ACTFEL) devices [3, 4] and efforts are being performed to improve photoluminescent (PL) and EL properties of Pb doped CaS films [5, 6]. Although photoluminescent [7] and electroluminescent [8] properties of Cu doped CaS powders have already been investigated, very little work has been done on CaS:Cu thin films [9]. For CaS:Cu(, Ag) both structure and morphology of the layer and PL emission spectrum have been investigated, since these are relevant parameters for both PL and EL characteristics.

First the influence of codoping CaS:Cu layers with Ag is discussed. Changes of the structure and morphology with codoping of Ag are studied. The influence of Cu concentration and annealing conditions on the emission colour and the relative brightness will be discussed briefly. Using scanning electron microscopy (SEM), correlations between PL brightness and grain size are studied. Finally, a study of the PL emission as a function of temperature is performed, greatly extending previously published results [10].

2. Specimen preparation and experimental setup

CaS:Cu(, Ag) layers were made by electron beam evaporation from pressed pellets of CaS (99.95%, CERAC), metallic Cu and (optionally) Ag₂S. The films were deposited on fused silica substrates at a substrate temperature of 773 K in H₂S ambient (partial pressure 6×10^{-3} Pa)

in a vacuum system Leybold Univex with a base pressure of 2×10^{-4} Pa. Previous work has shown that stoichiometric layers are produced in this way [11]. After deposition, the layers were rapidly thermally annealed (RTA) in an AST Superheat system in nitrogen or classically annealed (1023 K, 45 minutes) in a quartz tube furnace in nitrogen ambient. PL measurements were performed upon host excitation ($\lambda_{ex} = 254$ nm). Spectral information was obtained with an optical multichannel analyser EG&G OMA III, equipped with a gateable 1024 element microchannel plate-intensified diode array, enabling fast acquisition of spectral data with a wavelength resolution of 1 nm. Measurements at low temperatures were acquired using a cold finger helium flow cryostat with quartz windows. Film crystallinity was checked with a Siemens D5000 XRD (x-ray diffraction) spectrometer (Cu $K\alpha$ line, stepsize 0.01°). Information about the morphology of the layers was obtained from AFM (atomic force microscopy, TopoMetrix TMX 2010, Si_3N_4 tip with height $5 \mu\text{m}$ and top angle 52°) and SEM (scanning electron microscope, Philips 501) measurements.

3. Results and discussion

3.1. Comparison of CaS:Cu and CaS:Cu, Ag

3.1.1. Emission spectrum. Figure 1 shows the photoluminescent emission spectra of CaS:Cu and CaS:Cu, Ag thin films for $[\text{Cu}] = 0.6\%$ and $[\text{Ag}] = 0.6\%$ (source concentrations). The copper concentrations mentioned in the figures are concentrations in the deposition tablets. The bulk concentrations, measured with x-ray photo-electron spectroscopy (XPS), are about one fifth of the Cu concentration in the deposition source. The Ag concentration in the bulk was also measured with XPS and was about one third of the Ag concentration in the deposition source. These results are in good agreement with similar XPS measurements on doped SrS layers [12].

Both layers emit blue light with CIE (Commission Internationale de l'Eclairage) (X, Y) colour coordinates (0.160, 0.063) and (0.164, 0.109) respectively. Our measurements are in

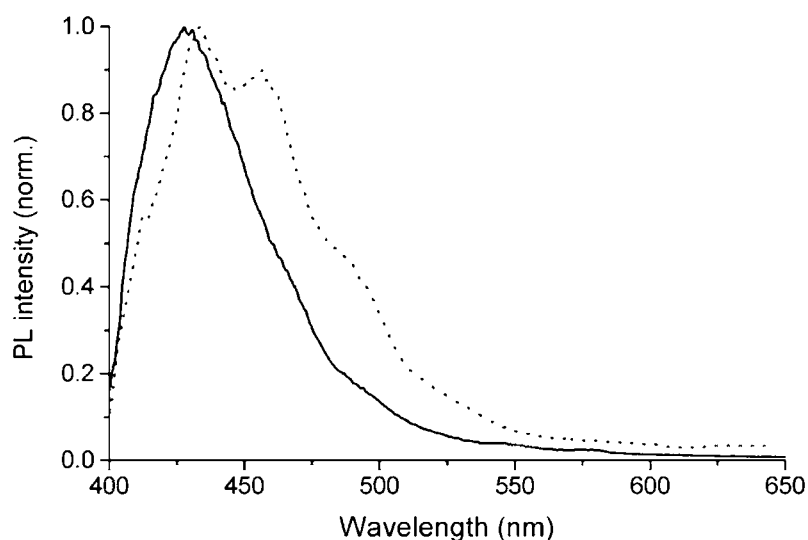


Figure 1. Photoluminescent emission spectra of CaS:Cu (full line) and CaS:Cu, Ag (dotted line) layers. $[\text{Cu}] = 0.6\%$, $[\text{Ag}] = 0.6\%$, $T_{\text{anneal}} = 1173$ K, $t_{\text{anneal}} = 2$ minutes.

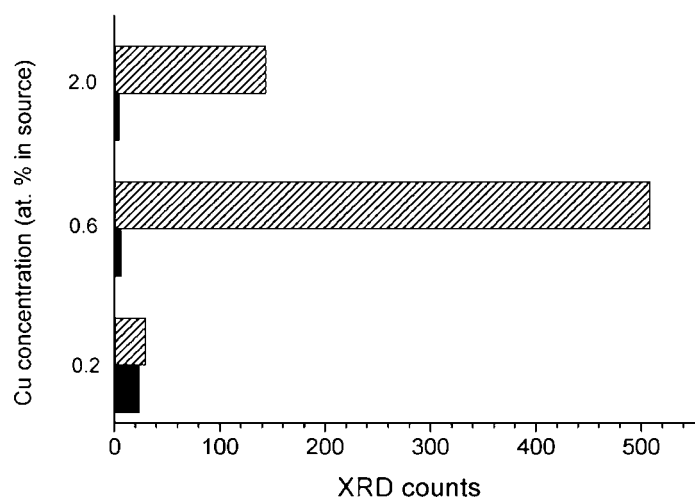


Figure 2. X-ray diffraction strongest peak intensity as a function of Cu concentration for CaS:Cu (black) and CaS:Cu, Ag (patterned) thin films. [Ag] = 0.6%, $T_{anneal} = 1173$ K, $t_{anneal} = 2$ minutes.

good agreement with the results of Yamashita [13] on CaS:Cu powder phosphors. Comparison of the emission of Cu in CaS with that in SrS [12] teaches us that the shape of the emission peaks is different. The two distinct peaks of the Cu monomer emission seen in PL spectra of SrS:Cu, Ag) are not visible in the CaS:Cu, Ag) spectra. It is not clear yet, whether these peaks are shifted towards each other and cannot be resolved or if one of the two transitions causing these peaks in SrS is forbidden in a CaS host or leads to emission in the UV range. Unexpectedly, codoping with Ag leads to a shift of the spectrum towards higher wavelengths. This phenomenon is reproducible and is also seen for layers with higher Cu concentrations. The shift towards higher wavelengths upon codoping with Ag is opposite to the situation for SrS:Cu, Ag. Both these effects show the important role played by the host lattice. The above results are achieved from measurements on rapidly thermally annealed layers. When the layers are classically annealed, the shift towards higher wavelengths upon codoping with Ag is less pronounced.

3.1.2. Crystallinity. When $\theta-2\theta$ x-ray diffraction patterns of both types of layer are compared, both a difference in preferential orientation and in peak intensities are seen. While the preferential orientation for CaS:Cu is along the (220) plane, the preferential orientation for CaS:Cu, Ag is (200). However, studies on the effects of orientation have learned [14] that both types of orientation of the CaS host lead to similar emission properties. More important is the increase of the diffraction peak intensity for the Ag codoped samples (figure 2). This means that the crystallinity of these layers is much better than for CaS:Cu layers. The Cu concentration also plays an important role in this improved crystallinity: the crystallinity improvement upon Ag codoping is not significant at low Cu concentrations and is also less pronounced if Cu concentrations are high (2.0%). A more elaborate study is necessary in order to optimize the crystallinity as a function of Ag and Cu concentration. All reported XRD results are obtained from rapidly thermally annealed samples, but similar conclusions can be drawn from measurements on the classically annealed layers.

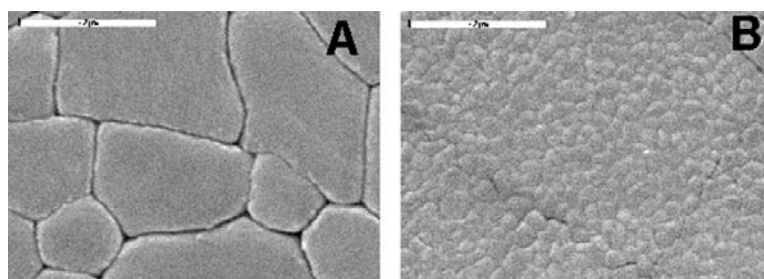


Figure 3. SEM pictures of CaS:Cu, Ag (A) and CaS:Cu (B) (magnification: $\times 20000$, scale marker = $2 \mu\text{m}$) [Cu] = 0.6%, [Ag] = 0.6%, $T_{\text{anneal}} = 1173 \text{ K}$, $t_{\text{anneal}} = 2 \text{ minutes}$.

3.1.3. Grain size. From the above measurements, it is obvious that Ag plays an important role in the crystal growth of the layer. This effect is not only visible in crystallinity but also in surface morphology. Scanning electron microscopy (SEM) pictures (magnification $\times 20000$) of CaS:Cu and CaS:Cu, Ag ([Cu] = 0.6%, [Ag] = 0.6%, $T_{\text{anneal}} = 1173 \text{ K}$, $t_{\text{anneal}} = 2 \text{ minutes}$) are shown in figure 3. The Ag codoped layer shows large, well defined grains, whereas the CaS:Cu layer shows cracks and only very small grains. We conclude that Ag acts as a flux and leads to an improved grain growth. It is not clear yet whether the influence of Ag on the emission spectrum of Cu in CaS (figure 1) is a direct effect of interaction between the emitting Cu and Ag centres or an indirect effect of improvement of the surroundings of the Cu emitting centre.

For thin film electroluminescence it is necessary that the phosphor layer has a good crystallinity in order to enable ballistic electron acceleration in the layer. Therefore, CaS:Cu, Ag is a much better candidate as an EL phosphor than CaS:Cu. Since the present work is aimed at good EL phosphor layers, further results will be focused on CaS:Cu, Ag (fixed [Ag] = 0.6%) layers.

3.2. Effect of Cu concentration and annealing process

3.2.1. Emission spectra. Figure 4 shows the influence of the copper concentration on the CIE coordinates of CaS:Cu, Ag emission spectra ([Ag] = 0.6%). The change with increasing copper concentration is probably due to the emission from clustered Cu centres as in SrS:Cu, Ag [2].

The influence of the annealing temperature on the PL emission was also studied. While no influence on the emission spectrum could be seen, the PL intensity increases with rising annealing temperature. For these measurements the annealing time was fixed at 2 minutes. Temperatures above 1173 K could not be used due to cracking of the layers and peeling off. The results, shown in figure 5, are relative to the average emission intensity (for all temperatures used).

The effect of annealing time is studied by annealing a layer at a fixed temperature (1073 K) for different times. For the briefly annealed layer (30 s) we saw some bright photoluminescent spots on the layer with no significant difference in colour (compared with the rest of the sample), on a weakly emitting background. The spots were circular areas with a diameter of a few millimetres. The number and size of the spots was correlated with the annealing time: the longer the sample was annealed, the more spots were visible. For samples annealed for 6 minutes, the spots had merged and the whole layer was strongly emitting. This study gives some information about the way in which a CaS layer becomes photoluminescent upon annealing. In the standard rapid thermal anneal process we use an annealing temperature of

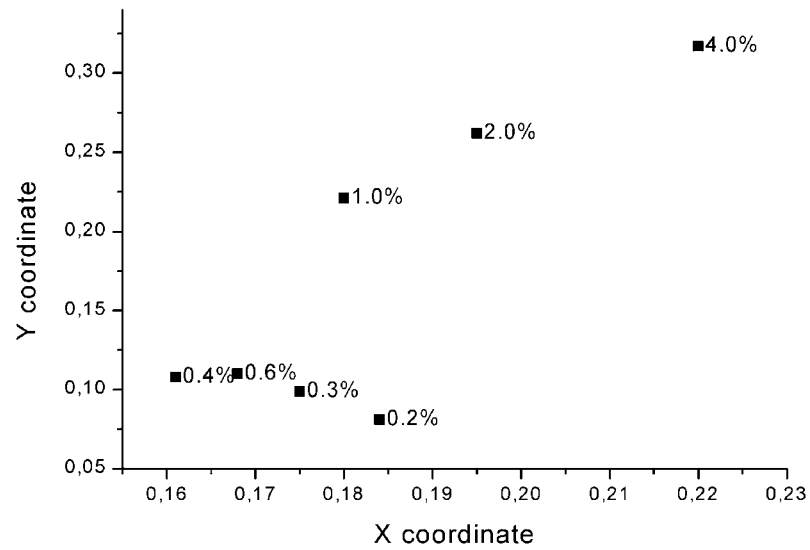


Figure 4. Average emission wavelength of photoluminescence of CaS:Cu, Ag as a function of Cu concentration. [Ag] = 0.6%.

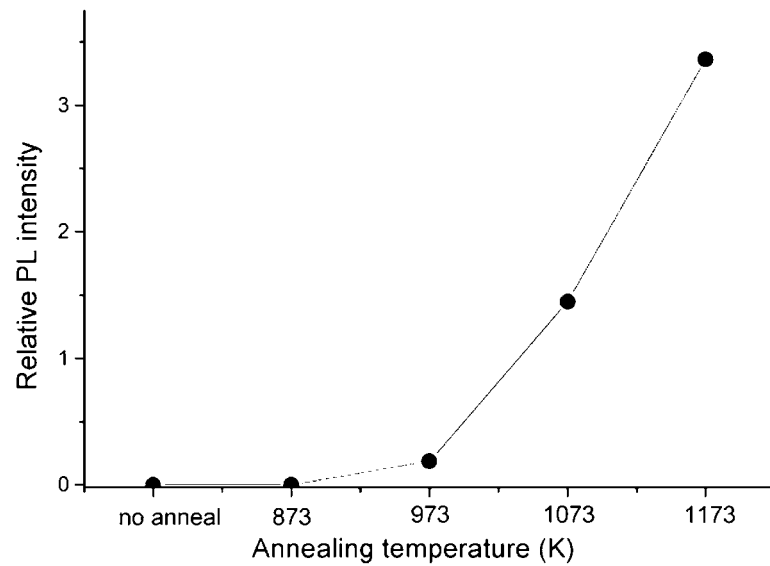


Figure 5. Relative PL intensity as a function of annealing temperature for a rapidly annealed ($t_a = 2$ minutes) CaS:Cu, Ag layer ([Cu] = 0.6%, [Ag] = 0.6%).

1173 K and an annealing time of 2 minutes, which seems sufficient to reach bright PL for the whole layer.

3.2.2. *Morphology of the layer.* We performed atomic force microscopy (AFM) measurements on the layers that were briefly annealed at 1073 K in order to see if there was any correlation between morphology and PL brightness. Figure 6 shows AFM surface

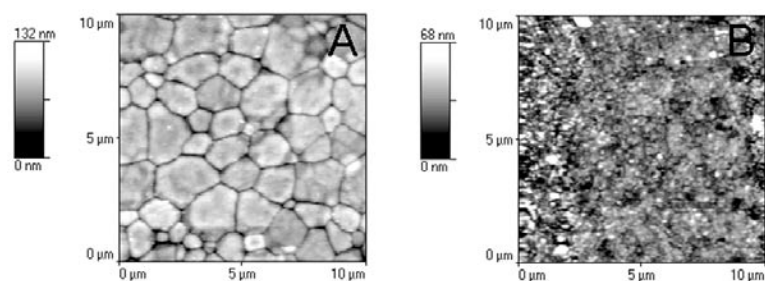


Figure 6. AFM pictures of CaS:Cu, Ag on a brightly emitting spot (A) and on a weakly emitting background (B). [Cu] = 0.6%, [Ag] = 0.6%, $T_{\text{anneal}} = 1173$ K, $t_{\text{anneal}} = 2$ minutes.

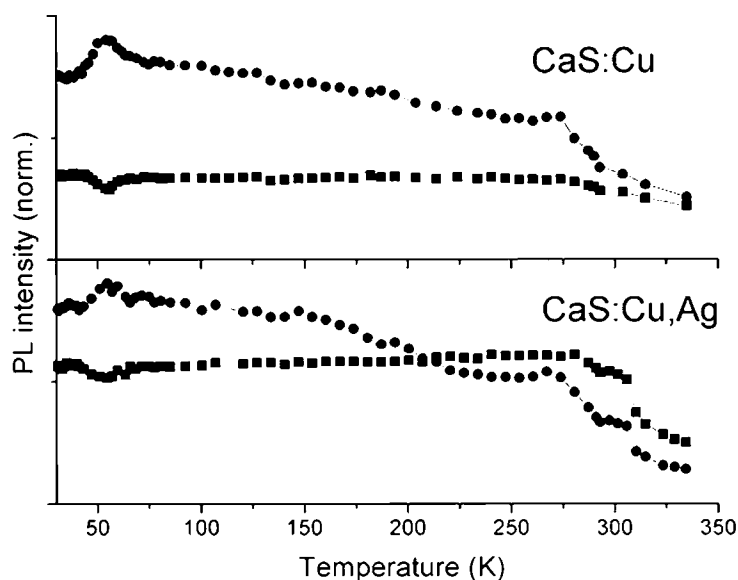


Figure 7. Temperature dependence of the PL intensity of the emission at 425 nm (circle) and at 450 nm (square) for CaS:Cu and CaS:Cu, Ag. [Cu] = 0.6%, [Ag] = 0.6%, $T_{\text{anneal}} = 1173$ K, $t_{\text{anneal}} = 2$ minutes.

profiles on a bright PL spot and on the weakly emitting background (these locations were first marked on the back of the sample and then spotted with a camera during positioning of the AFM tip). Where the weakly emitting background only shows very small grains (B), the brightly emitting PL spot shows large grains, several times the film thickness in diameter. This again shows the strong correlation between grain size and PL intensity. The Cu concentration also has its influence on the morphology of the layer (see also figure 2): at low Cu concentration (0.2%) both CaS:Cu and CaS:Cu, Ag layers show cracks. Increasing the Cu concentration leads to the formation of grains (as seen in SEM experiments). However, the grain size is mainly determined by the presence of the Ag codopant and not by the actual Cu concentration.

3.3. Temperature dependence

3.3.1. Photoluminescence. In order to study the thermal quenching behaviour of CaS:Cu, Ag, we measured the PL spectrum ([Cu] = 0.6%, [Ag] = 0.6%) at different temperatures.

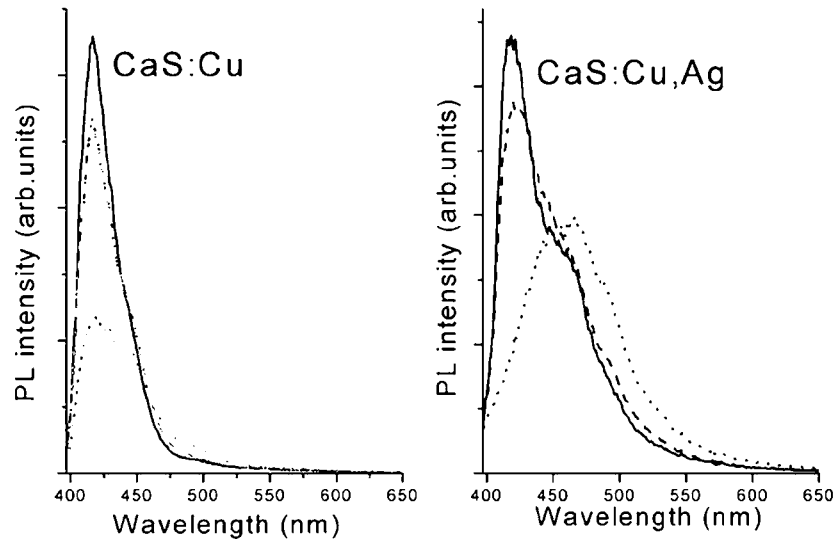


Figure 8. Temperature dependence of the PL emission spectra of CaS:Cu and CaS:Cu, Ag at 30 K (dashed), 54 K (full) and RT (dotted). [Cu] = 0.6%, [Ag] = 0.6%, $T_{\text{anneal}} = 1173$ K, $t_{\text{anneal}} = 2$ minutes.

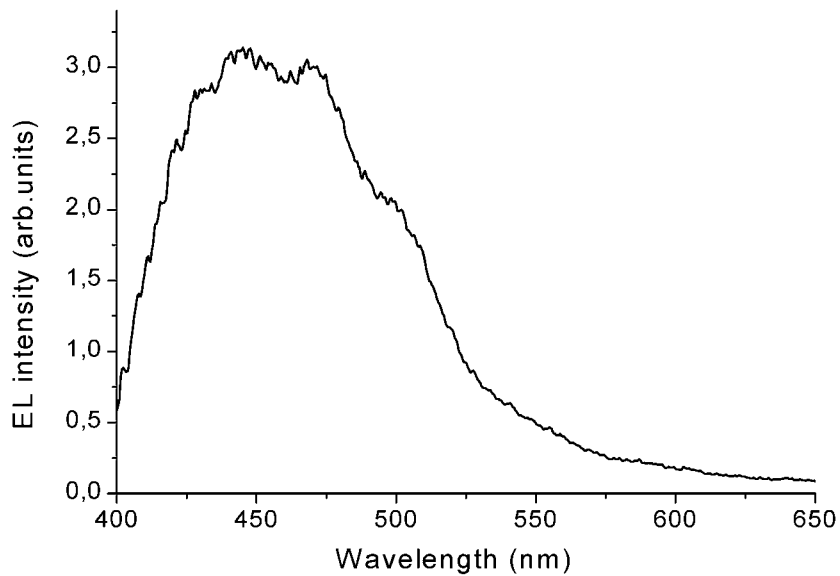


Figure 9. Electroluminescent spectrum of CaS:Cu, Ag at 1kHz sine wave excitation. [Cu] = 0.6%, [Ag] = 0.6%, $T_{\text{anneal}} = 1173$ K, $t_{\text{anneal}} = 2$ minutes.

Three different types of quenching behaviour could be found. Emission around 425 nm is strongly quenched at room temperature (RT), emission around 450 nm has almost the same intensity at RT as at 20 K and emission at higher wavelengths (around 475 nm) increases slightly. Figure 7 shows the emission intensity as a function of measurement temperature for emission at 425 and at 450 nm. This quenching behaviour makes CaS:Cu, Ag a better blue PL

emitter than SrS:Cu, Ag, in which nearly all blue emission is quenched at RT [12]. When the layer is heated up to 350 K, all emission is strongly quenched (shown in figure 7).

An intensity peak in the 425 nm emission can be seen around 54 K. This peak was also seen in EL (where the effect is very strong [2]) and PL [12] emission of SrS:Cu, Ag layers. Because of its appearance in both types of host and since it also appears in SrS:Cu (without Ag codoping), the effect is thought to be Cu related. This is confirmed by the fact that the peak is less pronounced in CaS:Cu, Ag layers, probably due to a disturbing role played by Ag, and by the fact that the effect is stronger if higher Cu concentrations are used. The influence of the host is not completely insignificant because the effect seems spectrally dependent for CaS but spectrally independent for SrS. Figure 8 shows the PL emission spectra for CaS:Cu, Ag at different temperatures. Comparison of the spectrum at 30 K and the spectrum at 54 K shows that the intensity increase mainly occurs for wavelengths around 425 nm.

3.4. Electroluminescent behaviour

Preliminary experiments were performed on CaS:Cu, Ag thin film EL devices. Standard double insulator (Al_2O_3 insulators) thin film EL devices with a Cu concentration of 0.6% and a Ag concentration of 0.6% were grown. Blue emission was observed with a brightness of about 40 Cd m^{-2} at 1 kHz. Figure 9 shows the corresponding electroluminescent spectrum. Optimization of Cu and Ag concentrations and production parameters such as deposition conditions and annealing of the EL device will be carried out in the near future.

4. Conclusions

Due to its good crystallinity and layer structure, CaS:Cu, Ag is a much better candidate as blue emitting electroluminescent phosphor than CaS:Cu. The presence of Ag leads to the formation of well defined grains, so Ag plays a role as flux in the CaS layer. The exact physical nature of its effect on the PL emission is not understood yet. The blue emission shows a good quenching behaviour, which is essential for EL phosphors. The peak in the PL intensity around 54 K is correlated with the excitation process of the Cu monomer centre. For the first time, blue EL emission from CaS:Cu, Ag was obtained. Optimization of the blue EL spectrum and intensity will be performed in the near future.

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References

- [1] Sun S S 1998 *Extended Abstracts 4th Int. Conf. on the Science and Technology of Display Phosphors (Bend, OR)* p 183
- [2] Wauters D, Poelman D, Van Meirhaeghe R L and Cardon F J. *Lumin.* at press
- [3] Tanaka S, Shanker V, Shiiki M, Deguchi H and Kobayashi H 1985 *SID 85 Digest* pp 218–21
- [4] Poelman D, Vercaemst R, Van Meirhaeghe R L, Laflère W H and Cardon F 1995 *J. Lumin.* **65** 7–10
- [5] Poelman D, Van Meirhaeghe R L, Vermeersch B A and Cardon F 1997 *J. Phys. D: Appl. Phys.* **30** 465–7
- [6] Yun S J, Kim Y S, Park S K, Kang J, Cho K and Ma D 1999 *Extended Abstracts 5th Int. Conf. on the Science and Technology of Display Phosphors (San Diego, CA)* p 149
- [7] Lehmann W 1972 *J. Lumin.* **5** 87–107

- [8] Bickerton J C, Brightwell J W, Clough S, Ray B and Viney I V F 1999 *Extended Abstracts 5th Int. Conf. on the Science and Technology of Display Phosphors (San Diego, CA)* p 61
- [9] Nakanishi Y and Shimoka G 1987 *Extended Abstracts 172nd Electrochem. Soc. Meeting* no 1224
- [10] Wauters D, Poelman D, Van Meirhaeghe R L and Cardon F 1999 *Extended Abstracts 5th Int. Conf. on the Science and Technology of Display Phosphors (San Diego, CA)* p 165
- [11] Poelman D, Vercaemst R, Van Meirhaeghe R L, Laflère W H and Cardon F 1997 *J. Lumin.* **75** 175
- [12] Poelman D, Wauters D, Van Meirhaeghe R L and Cardon F 2000 *Solid State Commun.* **113** 405–10
- [13] Yamashita N 1991 *Japan. J. Appl. Phys.* **30** 3335–40
- [14] Tanaka S, Deguchi H, Mikami Y, Shiiki M and Kobayashi H 1987 *Proc. SID* vol 28, pp 21–5