

Correlating the Charge Trap Characteristics of ACEL Phosphor Powders ZnS:Cu,X(X=Cl,Br) with Their Electroluminescence Spectra

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Abstract: The performance of ZnS:Cu,X (X = Cl, Br, I) ACEL phosphor powders is critically dependent on the efficient injection of charge and the rates of trapping and de-trapping of these charges in the ZnS lattice, in addition to radiative recombination of the charges at luminescent Cu centres. The characterisation of the charge traps using thermoluminescence is reported and it is shown how these charge traps depend on the identities of the dopant ions and the synthetic route used in the phosphor preparation. We describe how the thermal annealing history of ACEL phosphor powders critically affects their electroluminescence performance. This is shown to be due to the dependence of the characteristics of the electron traps on the firing conditions, as is made evident from their thermally stimulated luminescence curves. As the ACEL performance of the phosphors is related to the charge traps (that are characterised by the thermoluminescence experiments) a full understanding of their origin and role is of fundamental importance if the aim is to improve phosphor performance.

Key words: ACEL phosphor powders; Charge traps; Thermally stimulated luminescence.

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ACEL 荧光粉粉末 ZnS:Cu,X 的电荷陷阱的性质与其电致发光频谱之间的联系

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摘要: ZnS:Cu,X (X = Cl, Br, I) ACEL 荧光粉的性质主要决定于 Cu 发光中心的电子发光复合、ZnS 点阵中电子的注入效率、诱捕电子和逃逸电子的比率。热致发光中的电子陷阱依赖于掺杂剂以及荧光粉制备方法。文章描述了 ACEL 荧光粉的退火过程对其电致发光性质的深远影响。从热释光发光曲线上,我们可以看到烧结条件对电子陷阱特征的作用。由于荧光粉的 ACEL 性质与电子陷阱有关,为了提高荧光粉的性能,对电子陷阱的成因和所起的作用的了解就显得尤为重要。

关键词: ACEL 荧光粉; 电子陷阱; 热释光

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Phosphor powder ACEL was first demonstrated by Destriau in 1936^[1]. He observed luminescence when an electric field was applied to ZnS:Cu phosphor powders that were suspended in castor oil. A modern conventional phosphor powder ACEL device consists of a layer of phosphor powder in a polymeric binder and one or more layers of dielectric material sandwiched between a metal back electrode and a transparent conducting oxide

front electrode.

The ZnS:Cu,X (X = Cl, Br, I) phosphor powders are carefully prepared designer materials. These sophisticated tailored particles are made so that charge in the form of electrons and holes are readily injected into the lattices under the influence of an applied AC electric field. These electrons and holes are trapped and de-trapped at sites in the ZnS lattice before recombining radiatively at lumines-

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cent copper centres. The emission spectra of ZnS:Cu,X (X = Cl, Br or I) ACEL phosphor powders have been constantly studied over the last fifty years, since the technologically important implications of the early work were realised. Blue-green emission is observed for many of these powder phosphors. It is well established that the spectra can be deconvoluted into two components, one in the blue region of the spectrum and the other in the green region. The former has been assigned to a blue copper transition originating on a copper centre that is surrounded tetrahedrally by three sulfide ions and a vacant sulfide site in the ZnS lattice (where the copper is in a Zn^{2+} lattice site). The green emission has been assigned to a similar copper site but instead of a vacancy there is a chloride ion that makes up the tetrahedral coordination of this site.

The relative proportion of these transitions in the electroluminescent (EL) emission spectrum of the phosphor can be altered using several methods to give a shift in the chromaticity between blue and green. Increasing the AC driving frequency will favour the blue emission band, or by varying the dopant ions in the ZnS:Cu,X the intensity of the bands can be altered.

It is shown herein that the ACEL emission colour is also critically dependent on the rate of cooling of the phosphors after they have been fired. Thus, the relationship between the rate of cooling and the characteristics of the charge traps is also studied in this work.

The purpose of the current work was to investigate the thermoluminescence properties in order to obtain information about these charge traps and attempt to correlate them with the phosphors' electroluminescent properties. By further investigating the deconvolution we show how the EL and PL spectra change after annealing the phosphors at various elevated temperatures followed by rapid quenching at liquid nitrogen (where significant changes in the thermoluminescence properties occur).

1 Experimental

1.1 Phosphor Synthesis

ZnS:Cu,X (X = Cl, Br, I) ACEL powder phosphors were either obtained from commercial suppliers or synthesized in-house using literature procedures^[2]. ACEL phosphor powders, ZnS:Cu,X (X = Cl, Br) have been synthesized via a two

stage firing route.

1.2 Phosphor Characterisation

The ACEL powders were characterized using electron microscopy (SEM, TEM) and XRPD.

1.3 Rapid Cooling of Phosphors

Rapid cooling studies on the phosphors were achieved by warming the sample to temperatures from 100 to 500°C and then either plunging the material into liquid nitrogen or, since liquid N₂ is not ideal for low temperature quenching, more simply quenched by quickly spreading the heated sample over a ceramic tile to allow it to quickly cool in air. We have found that both methods generate the same effect. If the temperature of the phosphor is taken above 500°C most of the emission intensity is lost and the phosphor body colour turns from off-white to yellow.

1.4 Electroluminescence

The phosphors have been studied in Destriau cells. In these cells the phosphors were mixed with castor oil in a ratio of 2:1 by mass and their ACEL emission intensities have been measured using a range of alternating voltages (110 to 200 V) and frequencies (see Fig. 1).

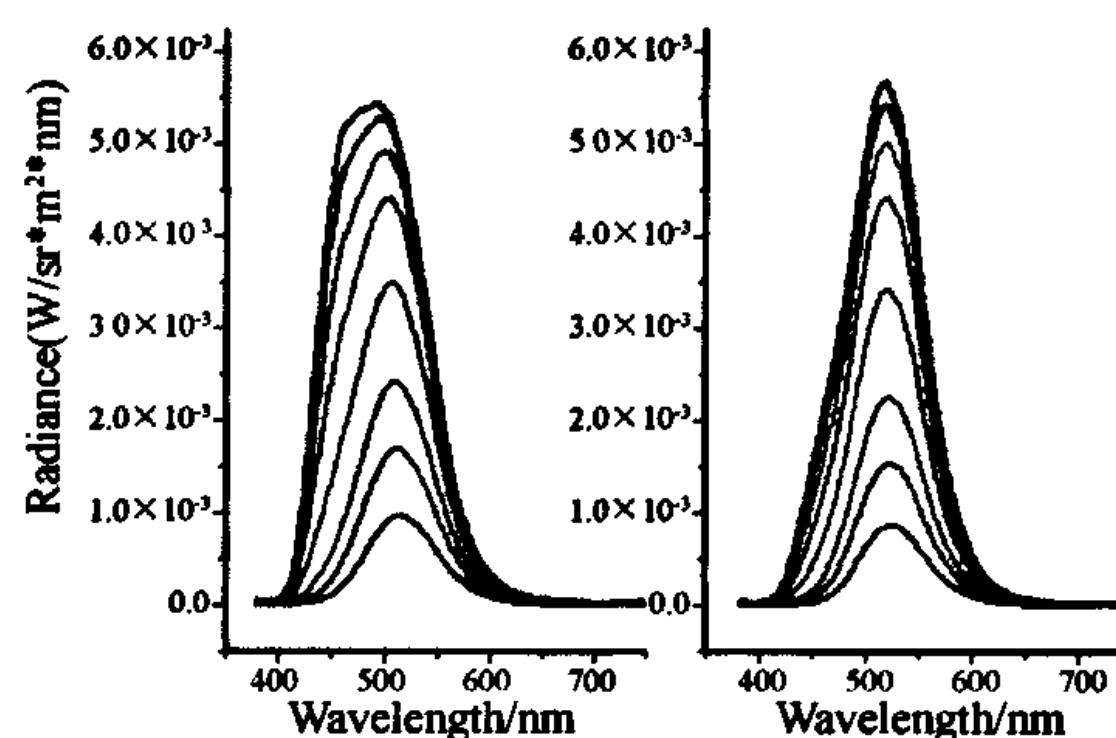


Fig. 1 ACEL emission spectra obtained from a ZnS:Cu,Cl ACEL powder phosphor synthesized via a two stage firing process and then heated to 400°C followed by cooling in air to room temperature (a) slowly (left), and (b) rapidly (right). The spectra have been obtained at frequencies (from bottom to top) of 400, 1000, 2000, 5000, 10000, 15000, 20000 and 25000 Hz and a voltage of 200 V

For the ACEL measurements on the quenched phosphor powders, the emission spectrum, obtained using an RMS voltage of 113 V and a frequency of 5000 Hz, is dominated by the green emission band with the blue emission band being almost completely eliminated after quenching (see Figure 1). This results in a reduction of the overall ACEL brightness of the material, since the blue emission is lost and the green emission shows little change in intensity after the rapid cooling treatment. When the material is allowed to cool slowly

after gentle heating, the emission is unchanged from that of the untreated material. If the rapidly quenched phosphor is once again heated to 500°C and this time allowed to cool more slowly, the blue emission band then re-appears in the ACEL emission spectrum.

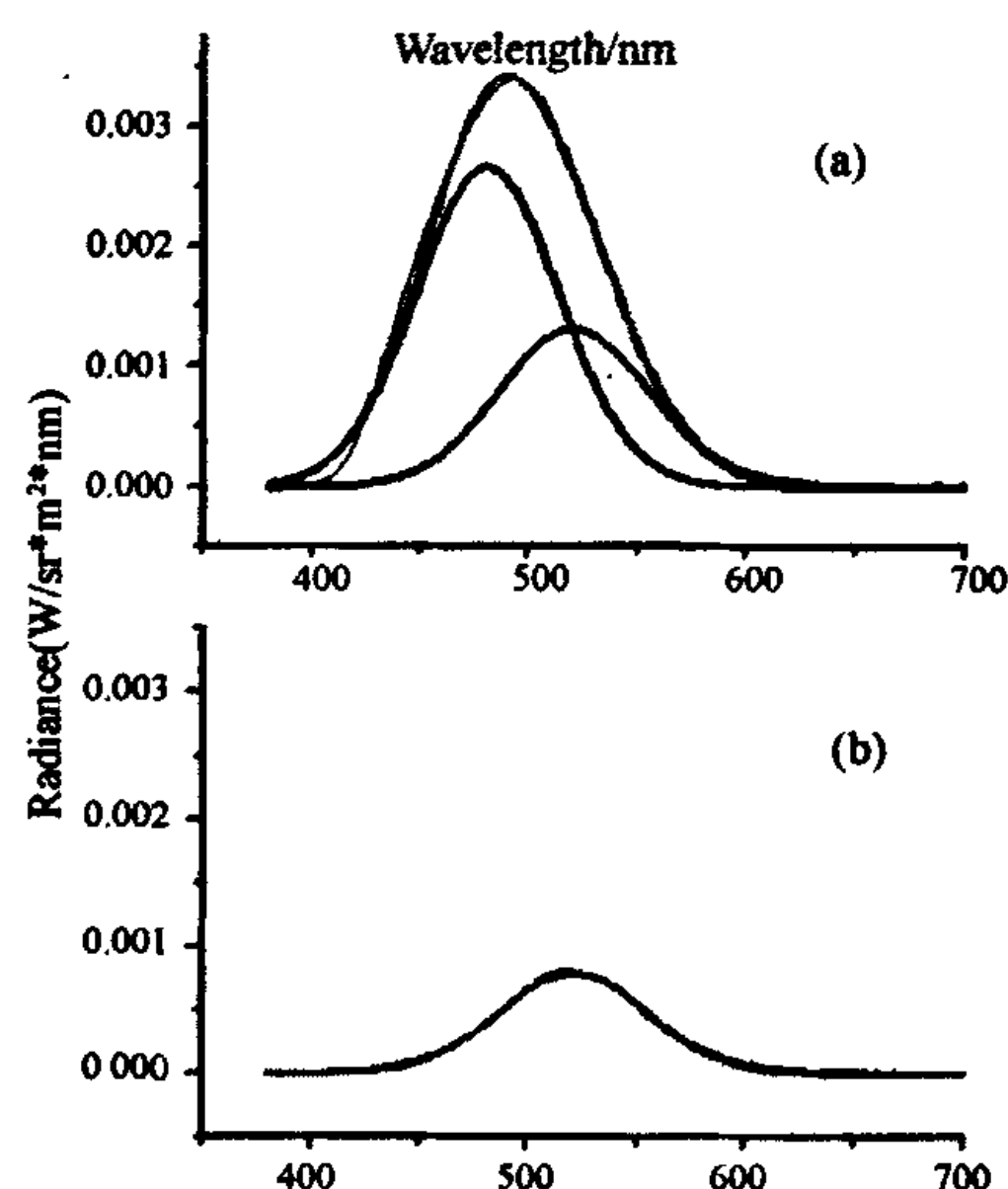


Fig. 2 ACEL spectra (thin solid lines) obtained using a voltage of 113 V RMS and a frequency of 5000 Hz from a commercial ZnS:Cu,Cl phosphor (a) before heating and (b) after heating and rapid re-cooling to room temperature. The overall fits (thick solid grey lines) consist of two Gaussian components (thick solid black lines) in (a) and one Gaussian component in (b).

1.5 Photoluminescence Studies

The PL under 365 nm excitation of these samples has also been studied and again the blue luminescence is lost after quenching (see Figure 3). This effect in the PL spectra has been previously noted^[3].

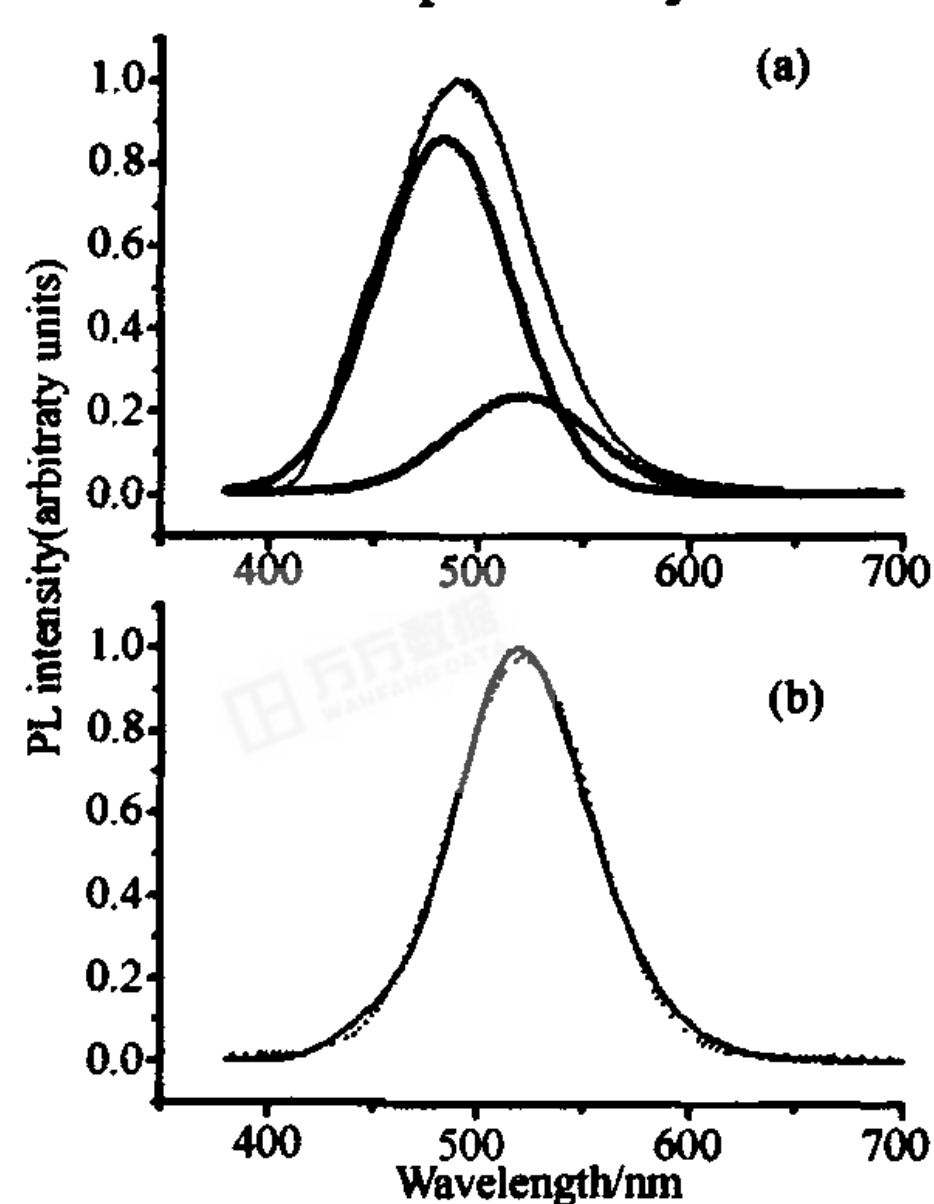


Fig. 3 PL spectra (thin solid lines) obtained under 365 nm excitation from a commercial ZnS:Cu,Cl phosphor (a) before heating and (b) after heating and rapid re-cooling to room temperature. The overall fits (dotted lines) consist of two Gaussian components (thick solid lines) in (a) and one Gaussian component in (b).

1.6 Thermoluminescence Characterisation

For thermoluminescence (TL) measurements, 0.15 g of the phosphor powder was loaded into a Linkam THMS 600 temperature programmable heater/cooler stage and cooled to 77 K. The sample was then irradiated with 365 nm light from a mercury arc source for 0.5 h before heating to 50°C at a rate of 10°C per minute. Luminance measurements were performed during the temperature ramp using a Photo Research PR880 photometer.

2 Results and Discussion

2.1 Thermoluminescence Studies

The scanning electron micrographs of the quenched material show some cracking and fracturing to reveal planar surfaces but the majority of the particles appear unaffected.

A typical thermally stimulated luminescence (TSL) curve that was obtained from a commercial ZnS:Cu powder phosphor is shown in Figure 4. This curve manifests a peak at around -130°C with a shoulder on the high temperature side. These features are due to the de-trapping of trapped charge followed by charge migration and radiative electron-hole recombination. These peaks represent the energies of the traps found in the band gaps of the phosphor powders. The electron traps lie just below the conduction band. Their energies can be obtained from TSL curve data and used to interpret EL and PL spectra.

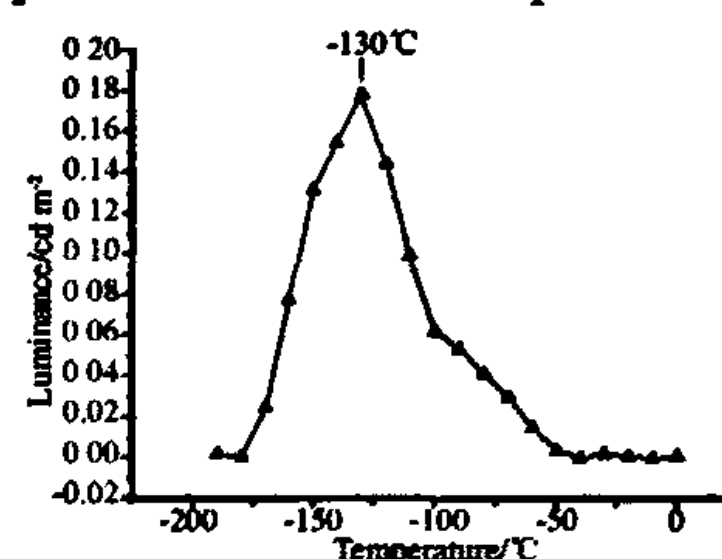


Fig. 4 TSL curve obtained from a commercial ZnS:Cu ACEL powder phosphor

Figures 5 and 6 present TSL curves and Figure 7 PL spectra of two ACEL ZnS:Cu,Br powder phosphors, one having a greater copper concentration than the other. This is manifested in the PL spectra by a larger contribution from the blue copper emission. The TSL curves are clearly different showing their sensitivity to the different copper concentrations.

The TSL curves taken from quenched samples are different to those of non-quenched samples. The latter (Figure 4) show the presence of only one broad peak centered around -130°C , whereas

the former manifest two sharper peaks, one at -160°C and the other at -100°C (see Figure 6). As the glow curve of the quenched sample (Figure 8) has two peaks, and is not the same as that of the non-quenched sample, then it provides evidence for a change in the trap levels in the band gap of the quenched powder. This change causes the difference in the emission colour. The peak at -100°C is attributed to deeper charge traps which are observed when the blue component of the ACEL emission is quenched and the phosphor shows an afterglow. When the TSL curve exhibits a single peak at -160°C , the phosphor shows no afterglow and both blue and green ACEL emission components.

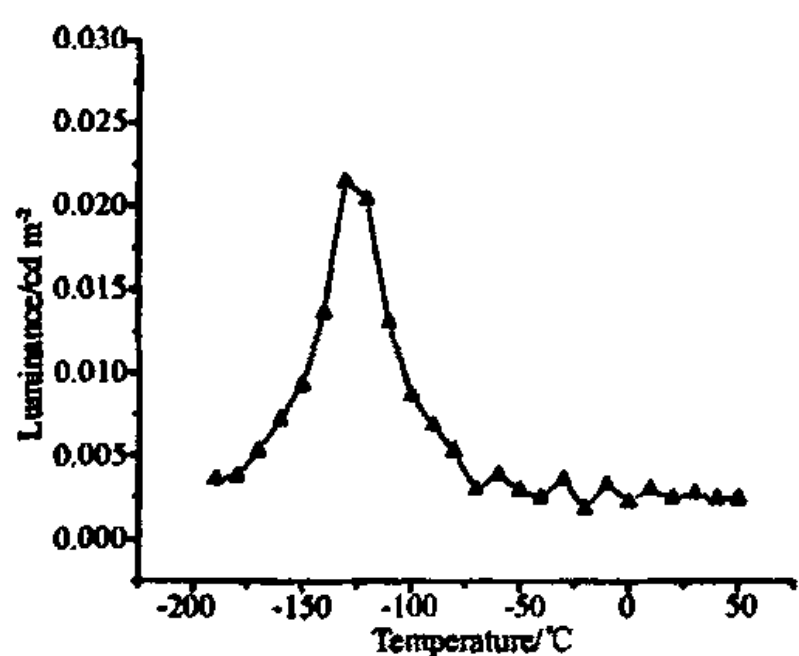


Fig. 5 TSL curve obtained from a copper rich ACEL ZnS:Cu,Br powder phosphor

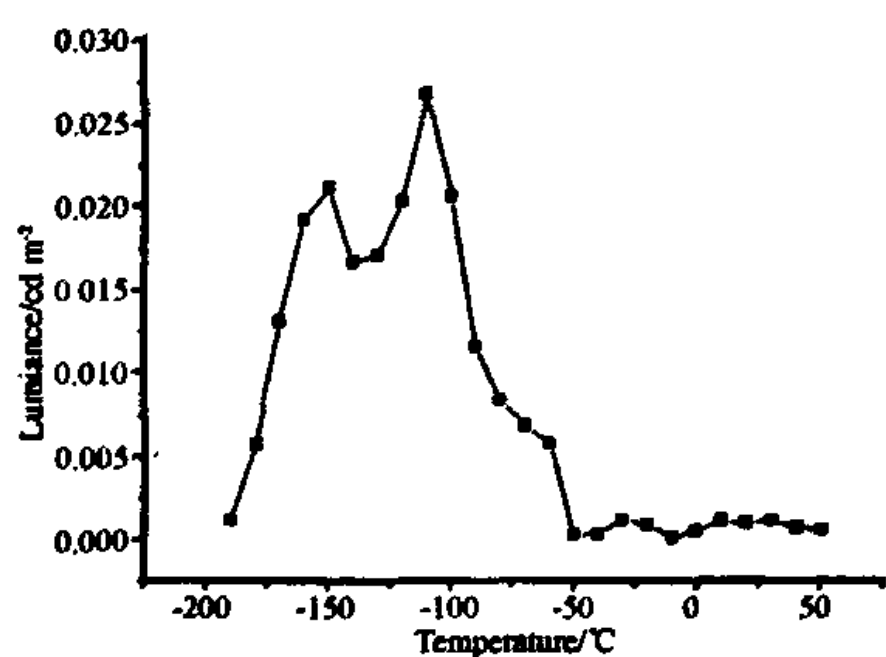


Fig. 6 TSL curve obtained from a copper deficient ACEL ZnS:Cu,Br powder phosphor

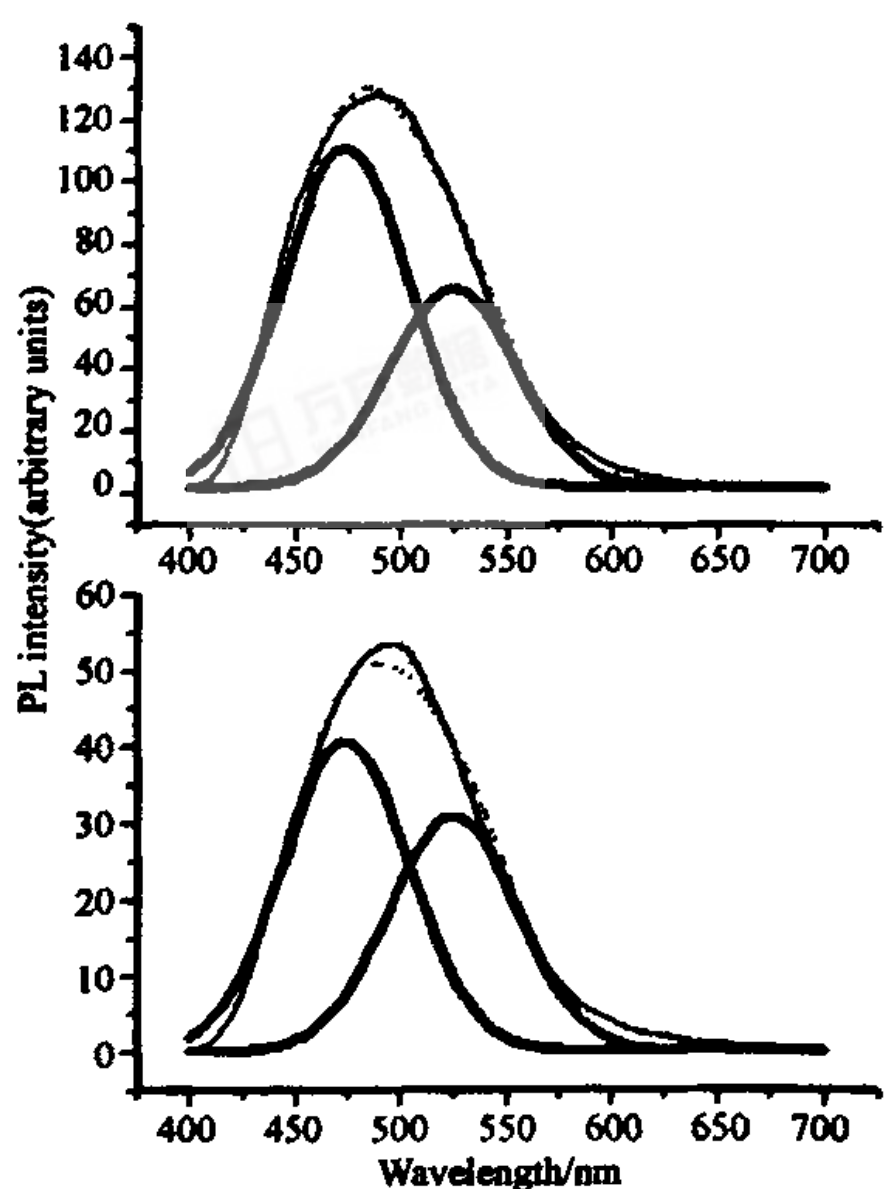


Fig. 7 Photoluminescence spectra obtained from copper rich (above) and copper deficient (below) ACEL ZnS:Cu,Br powder phosphors.

The blue emission is absent in the PL and EL spectra of the quenched sample, and there is evidence of deeper traps in the glow curve. This shows that at the elevated temperature before quenching a process has occurred that eliminates the centres that generated the blue emission. The full explanation of the structural/physical processes causing this is beyond the scope of this work.

However, this effect is partially explained by the defective nature of the ZnS lattice, which contains a higher concentration of defects at elevated temperature that are in competition as traps for electrons released in the charge injection process of ACEL. These traps are frozen into the lattice when it is rapidly quenched in temperature, in preference to the shallow traps that are responsible for the blue copper emission. However, when the phosphor is cooled slowly to room temperature, there are less defects in the ZnS lattice and a blue contribution to the ACEL emission is observed from blue copper emission originating from the shallow traps.

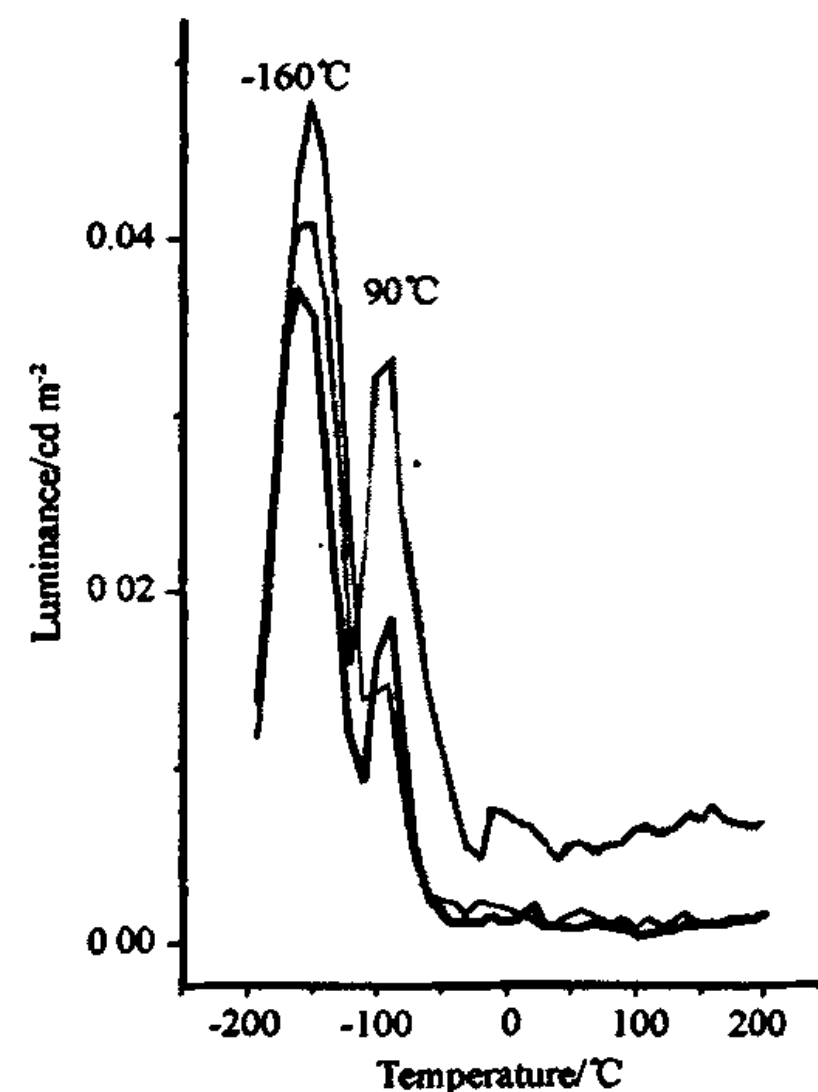


Fig. 8 TSL curves of a commercial ZnS:Cu,Cl phosphor (a) after annealing to 400°C and slow cooling to room temperature (thin black line), (b) after annealing to 400°C and rapid cooling to room temperature (thick grey line), and (c) after annealing to 400°C and rapid cooling to room temperature followed by annealing to 400°C and slow cooling to room temperature (thick black line).

2.2 Electroluminescence

The ACEL spectra on the left hand side of Figure 1 show a green emission component with a blue component growing in at higher frequencies when the ZnS:Cu,Cl phosphor has been heated to 400°C and cooled slowly in air to room temperature. In contrast, the ACEL spectra on the right hand side of Figure 1 show a green component at all frequencies with little evidence for a blue com-

ponent when the ZnS: Cu, Cl phosphor has been heated to 400°C and cooled rapidly in air to room temperature.

This is the first time, to our knowledge, that the loss of the blue component of the ACEL emission has been reported on quenching of the phosphor, although a similar effect has previously been noted in PL under 365 nm excitation^[3]. It should also be noted that the effect is reversible, because the blue ACEL component of the ACEL emission re-appears if the phosphor is re-heated to 400°C and cooled slowly.

3 Conclusions

A number of observations and conclusions can be made from the results presented in this work.

Firstly different ACEL ZnS: X phosphors have different TSL curves that give evidence for the presence of different charge trap levels being present. This allows the use of the TSL curves as finger prints to characterize the phosphors.

Secondly we have observed changes in TSL curves which tie in with changes in the electroluminescence spectra of rapidly cooled ACEL phosphor samples. The phosphor samples that are cooled rapidly to room temperature from 400°C show only

a green component in the ACEL spectra, whereas the samples that are cooled slowly show both blue and green components. This correlates with the TSL curves which show a peak at -90°C, due to deeper lying electron traps, when the phosphor has been cooled rapidly from 400°C to room temperature. This has implications for the heating and cooling of ACEL phosphors during their synthesis.

Thirdly, similar behaviour on quenching ZnS: Cu, Cl phosphors is also observed for both the PL and EL spectra. The quenched samples show the presence of only the green emission in both EL and PL. During the quenching process, a deep trap is locked into the structure in the place of shallower traps that give rise to the blue emission in non-quenched samples.

Acknowledgements

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Author's Personal Introduction

Robert Withnall holds a Chair in Materials Science and Engineering at Brunel University. He received his B. A. degree from Jesus College, Cambridge in 1980, his M. Sc. degree in Chemical Spectroscopy from the University of East Anglia in 1981, and his Ph. D. from the University of East Anglia in 1984, with John Sodeau. He carried out postdoctoral research at the University of Virginia, with Lester Andrews, from 1984 to 1987 and was awarded the Sigma Xi Visiting Scientist award in 1987. He did further postdoctoral studies at the University of California, with Ara Apkarian, and at University College London, with Robin Clark. He was appointed to a Senior Lectureship in Inorganic/Physical Chemistry in 1993 at the University of Greenwich and a Readership in Materials in 2000. His research interests embrace applications and fundamental aspects of materials science as well as applications and theoretical aspects of vibrational and electronic spectroscopy. He was appointed to an Adjunct Professorship in Chemistry at the University of Syracuse, New York in 2002.

He is hosting the International Conference on Raman Spectroscopy at Brunel University in London, 17-22 August, 2008, and serves on the editorial board of the *Journal of Raman Spectroscopy*. He has held substantial grants from the EPSRC, the Department of Trade and Industry, British Industry and the MOD, and he has published over 200 papers in refereed international journals.