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A spectroscopic study on SrS : Cu,Ag two-component electroluminescent phosphors

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Abstract

Under 4.507 eV excitation, the SrS : Cu,Ag thin films exhibited a saturated blue emission at 2.876 eV at room temperature and two additional emission bands at 3.443 and 2.398 eV were also observed at 10 K. By comparing with singly doped SrS : Cu and SrS : Ag, the two bands at 3.443 and 2.876 eV were assigned to the Ag emission bands and the 2.398 eV band to Cu emission. The enhancement of the 2.876 eV Ag emission band and the simultaneous suppression of the 2.398 eV Cu emission band are indicative of the presence of strong energy transfer from Cu to Ag ions in SrS : Cu,Ag. Low-temperature PLE spectrum of the 2.876 eV emission band was found to exhibit Cu excitation bands, confirming the presence of energy transfer from Cu to Ag. However, the energy transfer process from Cu to Ag exhibited anomalous properties that cannot be explained by the standard energy transfer theory. Therefore, instead of a Dexter-type energy transfer, electron transport was proposed as a possible coupling mechanism between the Cu and Ag ions in SrS. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: SrS : Cu,Ag; Electroluminescence; Photoluminescence; Energy transfer

One of the most exciting developments in electroluminescent (EL) phosphors in recent years was the development of SrS : Cu,Ag two-component phosphors [1]. This development was preceded and motivated by the discovery that SrS : Cu exhibited efficient EL emission with a good blue chromaticity [2]. The broad emission of SrS : Cu centered at 2.61 eV was attributed to the $3d^94s^1 \rightarrow 3d^{10}$ ionic transition of the Cu^+ ion occupying the Sr site with an octahedral symmetry. A fine structure was also observed in the excitation spectrum of the Cu^+ emission and was studied by using crystal-field theory [3,4]. The success of SrS : Cu naturally directed attention to SrS : Ag, which has the same outer shell electronic structure. Despite the fact that SrS : Ag exhibits a strong and highly saturated blue emission centered at 2.88 eV under optical excitation, the EL performance was very poor [5]. Therefore, a new system, SrS : Cu,Ag, was designed to take advantage of both the good chromaticity of Ag and the high excitation efficiency of Cu. It was observed that SrS : Cu,Ag exhibits an efficient and highly saturated blue emission under both optical and EL excitation conditions. The previous study on SrS : Cu,Ag by photoluminescence (PL) and PL excitation (PLE) spectroscopy confirmed the existence of an efficient energy transfer path from Cu to Ag [1]. Furthermore, the efficient coupling between Cu and Ag was also evident under EL excitation. A detailed study of the EL characteristics of SrS : Cu,Ag showed that the excitation characteristics of SrS : Cu,Ag were consistent with those of SrS : Cu while the emission characteristics were identical to that of SrS : Ag [6]. The success of SrS : Cu,Ag opens a pathway to develop a new class of phosphors consisting of two components, the sensitizer with a high excitation probability and the activator with a good chromaticity. The success of the two-component phosphor depends critically on the efficient coupling between the sensitizer and the activator. Therefore, it is of fundamental importance to understand the coupling mechanism. In this

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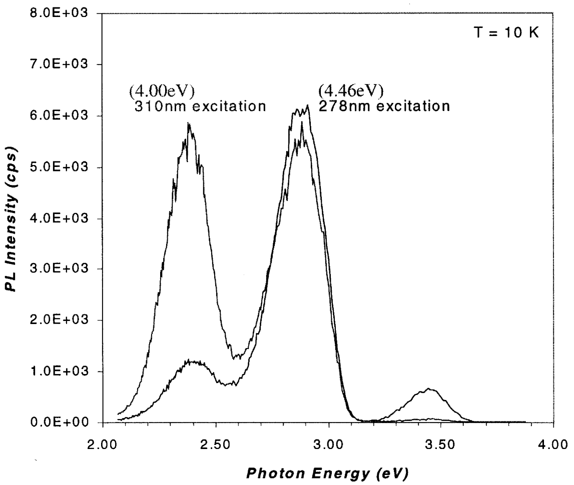

Fig. 1. Selective excitation PL spectra of a SrS : Cu,Ag thin film phosphor.

paper, we present a detailed spectroscopic study on the coupling mechanism between Cu and Ag ions in SrS.

The preparation of the samples used in this study can be found elsewhere [1]. Fig. 1 shows the selective excitation PL spectra of a thin film SrS : Cu,Ag phosphor with a Ag concentration of 0.4 at% and a Cu concentration of 0.2 at%. The spectra shows three emission bands at 3.44, 2.88 and 2.40 eV. The two bands at 3.44 and 2.88 eV were assigned to Ag ions and the 2.40 eV band to Cu emission. As shown in Fig. 1, the 2.88 eV Ag emission band dominated the spectrum under 4.46 eV excitation. However, when the excitation energy was decreased to 4.00 eV, the Cu emission band at 2.40 eV was enhanced and became comparable to the 2.88 eV Ag emission band. This result shows that the energy transfer from Cu to Ag depends on the excitation energy and that the higher excited states exhibit more efficient energy transfer. Fig. 1 also shows that the 3.44 eV Ag emission band was much weaker under 4.00 eV excitation. However, since this emission band showed little change in decay time as the excitation energy was varied, it was concluded that the suppression was due to poor direct absorption at 4.00 eV and not due to energy transfer. In order to examine the energy transfer dynamics more closely, the luminescence decay of the 2.88 and 2.40 eV emission bands was investigated. Fig. 2(a) shows the decay curves for the 2.88 eV Ag emission band. The effective decay time changed from 28 to 21 μs as the excitation energy was varied from 4.46 to 3.60 eV. It is clear that the Ag emission was not seriously influenced by the change in excitation energy. In sharp contrast, the decay of the 2.40 eV Cu luminescence showed a drastic change as the excitation energy was varied. As shown in Fig. 2(b), the effective decay time of the Cu emission was 9 μs under 4.46 eV excitation and was increased up to 80 μs when the excitation energy was decreased to 4.00 eV. First, it should be noted that at all excitation energies the decay time of the Cu emission was much smaller than that of singly-doped SrS : Cu which was 144 μs. This is a clear indication that there exists a process taking energy away from the Cu ions and thus affecting the decay rate of the Cu luminescence. This energy transfer process was most efficient for the 4.46 eV excitation and least efficient for the 4.00 eV excitation, which was consistent with the selective excitation PL results.

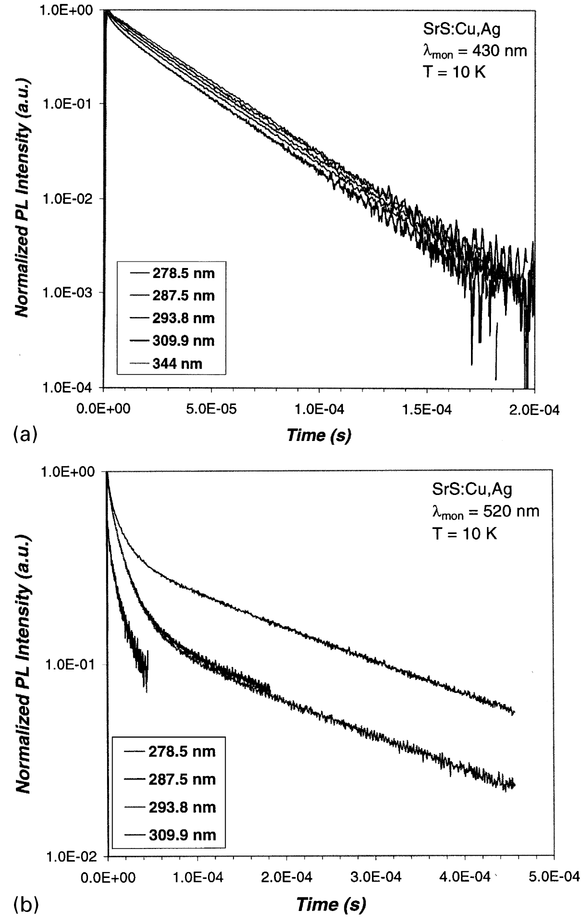

Fig. 2. Luminescence decay at various excitation wavelengths for (a) Ag emission band and (b) Cu emission band.

When the activator concentration is high or when two different types of ions are present, it is possible that two ions make a simultaneous transition in which one ion is de-excited and the other excited. This energy transfer process is commonly observed in phosphors. The energy transfer theory dictates that the energy transfer probability depends on the matrix element and the spectral overlap [7]. There are two different types of interaction that can mediate the energy transfer processes, Coulomb and exchange interaction. In case of the Coulomb interaction, the interaction Hamiltonian can be expanded into

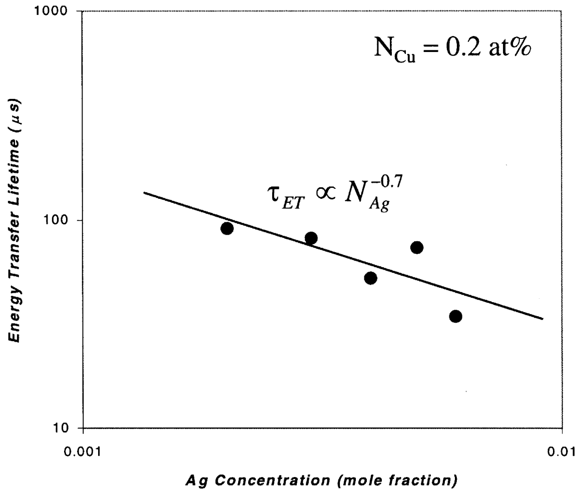

Fig. 3. The dependence of the energy transfer lifetime as a function of Ag concentration.

various multipole terms such as dipole–dipole, dipole–quadrupole, etc. The Coulomb interaction exhibits a power-law range dependence and each multipole term has a different exponent. Also, the exchange interaction has a distinct range dependence, which is an exponential dependence. This range dependence leads to different dependences on the activator concentration. Therefore, by carefully examining the concentration dependence, it is possible to determine the interaction mechanism responsible for the energy transfer [8]. Fig. 3 shows the energy transfer lifetime (τ_{ET}) as a function of Ag concentration. τ_{ET} was calculated from τ^{-1}(SrS : Cu,Ag) = τ^{-1}(SrS : Cu) + τ_{ET}^{-1}. By measuring the slope on a log–log plot, it was found that $\tau_{ET} \propto N_{Ag}^{-0.7}$. Thus, this observed concentration dependence was slightly weaker than predicted by the standard energy transfer theory, which states $\tau_{ET} \propto N_{Ag}^{-1}$.

The results of the selective excitation PL and time-resolved PL spectroscopy described above clearly show that the anomalies observed in SrS : Cu,Ag cannot be explained by energy transfer theory. First, the energy transfer seems to occur via higher excited states. Considering that the higher excited states generally exhibit short lifetimes due to fast phonon relaxation to the lowest excited states, this is an unlikely possibility unless these states somehow exhibit metastability. The reason why these states could be metastable is also not clear. The second anomaly is that the highest excited state exhibited the most efficient energy transfer and that the energy transfer process became less efficient as the excitation energy was decreased. This again cannot be explained by energy transfer theory. Also, the activator concentration dependence of the energy transfer lifetime deviated slightly from the prediction of energy transfer theory.

The failure of energy transfer theory led us to investigate the possibility of electron transport as a coupling mechanism between Cu and Ag ions in SrS : Cu,Ag. First, we would like to point out the high concentration of these ions. The samples investigated in this study have Cu and Ag concentrations between 0.1 and 0.6 at%, which correspond to activator doping between 1.8×10^{19}–1.1×10^{20} cm^{-3}. This concentration range gives a range for the inter-activator spacing of 20–40 Å. It should also be noticed that the higher excited states of these ions are located very close to the conduction band edge. The highest excitation band was observed at 4.46 eV. Considering that the band gap of SrS is 4.6 eV, the highest excited state is expected to lie within 100–200 meV below the conduction band edge. For these states, it is highly likely that the electronic wave functions extend over 20 Å and start to form extended states. This model can provide a qualitative explanation for our experimental observations. The higher excited states lie closer to the conduction band edge and therefore the actual wave functions should possess a more extended nature, exhibiting stronger overlap with the neighboring ions. The lower excited states, on the other hand, lie deeper into the band gap and therefore their wave functions should exhibit more localized nature, which is expected to cause weaker interionic coupling. The activator concentration dependence can be determined only after one has an accurate knowledge of the electronic wave functions. However, it can still be argued that the electronic transport will not depend critically on the activator concentration once the activators form extended states. Thus, the weaker concentration dependence is also considered to be consistent with this conduction model. To be more conclusive, however, it is necessary to acquire more information on the electronic structure of the higher excited states of Cu and Ag activators in the SrS host.

In summary, an investigation of a selective excitation PL and time-resolved PL properties of the SrS : Cu,Ag two-component phosphors were reported. In agreement with the previously reported PL and PLE results, a strong coupling between Cu and Ag ions was observed. However, the energy transfer process from Cu to Ag exhibited anomalous properties that cannot be explained by the standard energy transfer theory. Therefore, instead of a Dexter-type energy transfer, electron transport was proposed as a possible coupling mechanism between the Cu and Ag ions in SrS and a qualitative explanation for the experimental observations was given based on this model.

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