Rare earth doped sulfides as colour conversion phosphors: an overview and new candidates

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Solid state lighting using light emitting diodes (LEDs) can be considered as the preferred lighting method of the near future, due to their long lifetime and high efficiency. To generate white light, the emission from a near-UV or blue LED is partially converted by one or more phosphors. The need for white LEDs (with high efficiency, good colour rendering and appropriate colour temperature) requires further research into host-dopant combinations of the phosphors. The main requirements are a good overlap of the phosphor's excitation bands with the emission of the LEDs, high conversion efficiency, a high thermal quenching temperature and chemical stability. Several host compositions have been put forward in the past decade besides the currently often used YAG:Ce^{3+}, namely nitrides, oxynitrides, silicates,… and also sulfides.

In this report, the large class of sulfide materials is revisited and reviewed, including simple sulfides (e.g. (Ca,Sr)S:Eu, orange-red emission), thiogallates (e.g. $SrGa_2S_4$:Eu, green), thioaluminates (e.g. $CaAl_2S_4$:Eu, green) and the thiosilicates. For these materials, the possible use as LED conversion phosphor is evaluated regarding the abovementioned requirements, with special emphasis on the thermal quenching behaviour. Especially the (almost forgotten) thiosilicates are discussed in more detail [1,2]. Depending on the host composition (M_2SiS_4, with M = Mg, Ca, Sr or Ba) and the rare earth dopant (Ce^{3+} or Eu^{2+}), the emission colour can be changed from deep blue (Ba_2SiS_4:Ce) to red (Ca_2SiS_4:Eu), with a reasonably high thermal quenching temperature $T_{0.5}$ of 470K for the latter.

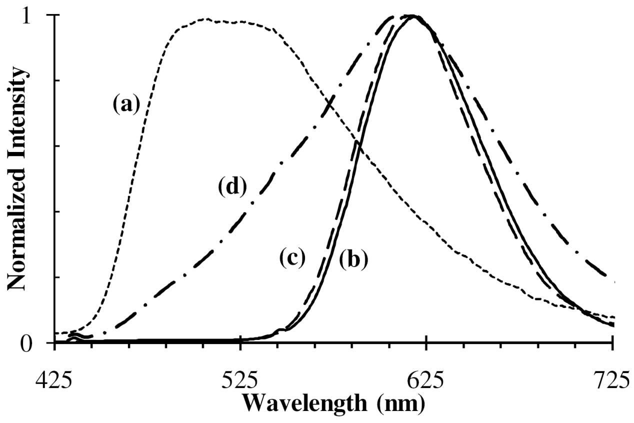

Fig. 1. Photoluminescence emission spectra of (a) SrS:Ce^{3+}, (b) SrS:Eu^{2+},Ce^{3+} and (c) SrS:Eu^{2+} particles. (d) SrS:Eu^{2+}|SrS:Ce^{3+} core|shell particles.

As a new approach in white light generation, we report on the use of micron-sized SrS:Eu^{2+}|SrS:Ce^{3+} core|shell particles grown by a solvothermal method [3], where both rare earth ions are physically separated. This is reflected in a broad emission spectrum (Fig. 1), comprising both the blue-green emission from SrS:Ce^{3+} and the orange emission from SrS:Eu^{2+}, which is not the case if the Ce^{3+} and Eu^{2+} ions are simultaneously doped into the lattice, due to energy transfer from Ce^{3+} to Eu^{2+}. Using SEM-CL (cathodoluminescence in a scanning electron microscope) it is proven that each core|shell particle indeed shows a broad emission band, with small colour variations between particles .

The main disadvantage of several sulfide materials is their limited stability, i.e. most sulfides degrade upon contact with moist air. Approaches to improve the stability are discussed, including incorporation in a matrix or encapsulation at the single phosphor particle level [4].

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[2] A.B. Parmentier, P.F. Smet, F. Bertram, J. Christen, D. Poelman, J. Phys. D: Appl. Phys., in press (2010)

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