Line Spectrum Emission of Eu-Activated ZnS

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It is shown that a ZnS:Eu phosphor with line emission spectrum can be prepared without coactivator introduction, contrary to previous results. The broad-band emission established in ZnS:Eu, Li is ascribed to the formation of Eu^{2+} centres due to the removal of lattice stress by lithium incorporation.

Key words: Zinc sulphide, luminescence spectrum, europium line emission, phosphor preparation.

According to the experimental data reported in [1–5] the activation of ZnS with Eu in the absence of coactivators leads to the formation of centres with broad-band luminescence. In [1] three elementary bands are obtained by resolving in the emission spectrum. The ZnS:Eu single crystals studied in [2, 3] show bands with spectral positions similar to those found in [1]. It is concluded from investigations on EPR, luminescence polarization, and dependence of emission on plastic deformation that different kinds of divalent europium centres are formed. Moreover, a band emission is observed in ZnS:Eu on argon laser excitation [4] and in samples prepared by thermal treatment of Eu doped ZnO in H_2S [5]. It is also reported that Eu-doped ZnS does not exhibit luminescence [6–8]. Line emission of Eu^{3+} has been established only in the electroluminescence spectrum of ZnS:Eu-layers obtained by coevaporation of ZnS and EuF_3, i.e. using F^- as coactivator [9]. Our investigations show that ZnS:Eu phosphors with 4f-4f-emission may be prepared without introduction of F^- or other coactivators.

Luminescent grade ZnS precipitated with H_2S from $ZnSO_4$ solution was deoxydated by heating in H_2S for 1 hour at 500 °C, $5 \cdot 10^{-3} - 1 \cdot 10^{-2}$ mole% $Eu(NO_3)_3$ was added and activation by thermal treatment was carried out for 30 min. at 1100 °C in H_2S flow; after the firing the samples were rapidly cooled to room temperature.

The spectrum of the phosphor obtained is presented by curve 1 in Figure 1. The narrow bands at 2.10 and 2.27 eV have half-widths of about 0.020 and 0.040 eV, respectively, and are thus much narrower than those found for ZnS:Eu phosphors in the above mentioned papers (0.194, 0.240 and 0.140 eV for the elementary bands established in [1] and 0.210 eV for the band 18 300 cm^{-1} in [4]). Furthermore, taking into account the broadening due to the low resolution of the spectral apparatus used in our measurements (the spectral band width of the monochromator is about 0.017 eV), it is reasonable to assume that line emission of trivalent Eu-centres takes place. The peak positions and relative band intensities differ partly from those presented in [9]. The strongest line in our spectrum ($E = 2.27$ eV) is almost absent in [9] and the 2.10 eV (592 nm) line is much stronger than the band at 587.5 nm registered by those authors. Instead of the most intensive band in [1] at 611 nm we obtain only a deformation of the emission curve. This can be understood as caused by differences in the activator surrounding.

Using the data for level energies of Eu^{3+} in the cubic crystals of $Cs_2NaEuCl_6$ [10] the line assignment presented in Table 1 could be proposed.

The problem of the preparation conditions which are responsible for the incorporation of Eu in different centres and valence states in the ZnS:Eu phosphors described in [1–5] and in the present paper is to be solved by further experiments; it is possible that the cooling rate plays an important role.

When Li is introduced in ZnS together with Eu, a strong increase of the emission intensity by more than one order of magnitude is observed and the structure of the luminescence spectrum vanishes (Fig. 1, curve 2). This effect of Li is surprising since in the presence of alkali metal cations a stabilization of the trivalent state of Eu and hence a line luminescence spectrum is to be expected. However, the assumption that the

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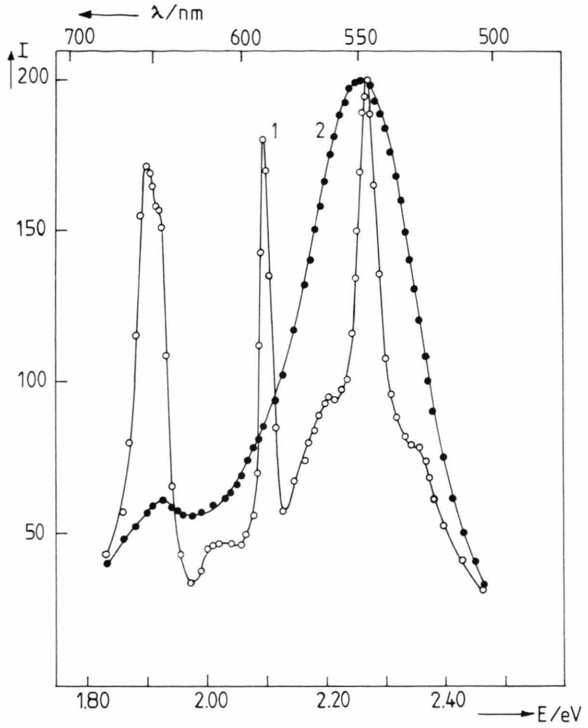

Fig. 1. Luminescence spectra of ZnS:Eu (curve 1) and ZnS:Eu, Li (curve 2) at room temperature (Eu: $1 \cdot 10^{-2}$ mol%, Li: $4 \cdot 10^{-2}$ mol%).

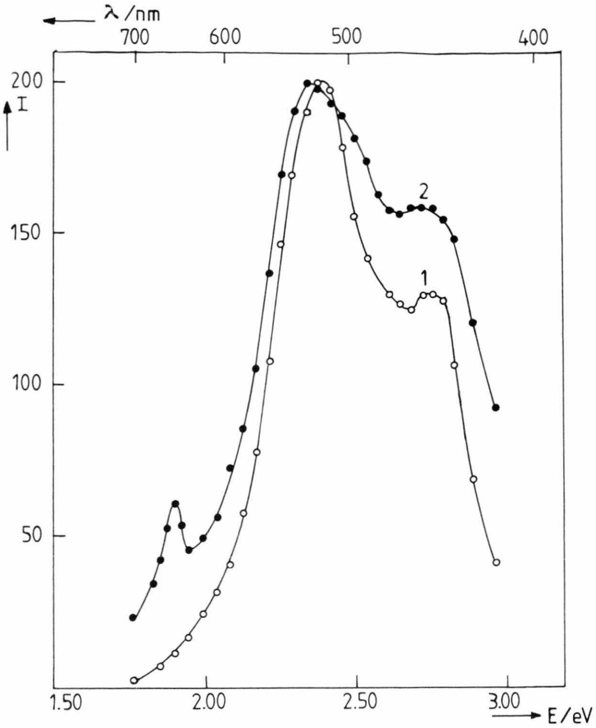

Fig. 2. Luminescence spectra of ZnS:Cu (curve 1) and ZnS:Eu, Cu (curve 2) at room temperature (Eu: $2 \cdot 10^{-2}$ mol%, Cu: $2 \cdot 10^{-2}$ mol%).

Table 1.

Energies of the ZnS:Eu lines (or line groups) E/eV (λ_{max}/nm)		Electron transition
2.33	(532)	${}^5D_0 \to {}^7F_0$
2.27	(546)	${}^5D_1 \to {}^7F_1$ or ${}^5D_1 \to {}^7F_2$
2.21	(560)	${}^5D_1 \to {}^7F_2$
2.10	(592)	${}^5D_0 \to {}^7F_1$
2.05–2.02	(605–615)	${}^5D_0 \to {}^7F_2$
1.92	(645)	${}^5D_0 \to {}^7F_3$
1.90	(652)	${}^5D_0 \to {}^7F_3$

broad bands in curve 2 arise as a result of superposition of narrow bands or lines due to different kinds of non-associated $\mathrm{Eu}_{\mathrm{Zn}}^{\cdot}$ and/or associated $\mathrm{Eu}_{\mathrm{Zn}}^{\cdot} - \mathrm{Li}_{\mathrm{Zn}}'$ centres does not seem acceptable. The spectral position of the shortwave band in ZnS:Eu, Li (2.26 eV) is equal and its half-width (0.250 eV) is close to those measured in [1].

An explanation of our findings could be given taking into consideration the activator, coactivator and host lattice cation radii. In the absence of Li^+ the incorporation of divalent europium ions according to

$$\mathrm{EuS} \rightarrow \mathrm{Eu}_{\mathrm{Zn}}^{\times} + \mathrm{S}_{\mathrm{S}}^{\times} \tag{1}$$

could be less advantageous than that of Eu^{3+} (though the f^7 configuration is preferred) because the radius of Eu^{2+} (1.19 Å) is greater than that of Zn^{2+} (0.83 Å) by about 40% and therefore a considerable lattice deformation should occur. The radius of Eu^{3+} is smaller (1.01 Å), the generated zinc vacancies for charge compensation,

$$\mathrm{Eu}_2\mathrm{S}_3 \rightarrow 2\,\mathrm{Eu}_{\mathrm{Zn}}^{\cdot} + 3\,\mathrm{S}_{\mathrm{S}}^{\times} + \mathrm{V}_{\mathrm{Zn}}'', \tag{2}$$

also contribute to the removal of the lattice stress due to replacement of Zn^{2+} by Eu^{3+}, and the sulfurizing atmosphere (H_2S) favours the higher valence state of Eu. For these reasons Eu is incorporated mainly as Eu^{3+}. When Li^+ ions, having a radius of only 0.68 Å, are present, the lattice deformation is reduced and at least part of Eu is incorporated in divalent state ($\mathrm{Eu}_2\mathrm{S}_3 + \mathrm{Li}_2\mathrm{S} \rightarrow 2\,\mathrm{Eu}_{\mathrm{Zn}}^{\cdot} + 2\,\mathrm{Li}_{\mathrm{Zn}}' + 4\,\mathrm{S}_{\mathrm{S}}^{\times} \rightarrow \mathrm{Eu}_{\mathrm{Zn}}^{\times} + \mathrm{Li}_{\mathrm{Zn}}' + \mathrm{Li}_{\mathrm{i}}^{\cdot} + 4\,\mathrm{S}_{\mathrm{S}}^{\times}$).

It is worth noting that for other lanthanide-activators (Ln) the use of Li as coactivator leads to opposite results [11]: the broad-band emission of ZnS:Ln (which is assumed to be due to $\mathrm{Ln}-\mathrm{V}_{\mathrm{Zn}}$-centres) is transformed into line emission. Experimental data about luminescence of ZnS:Eu, Li are not given in [11] or in other papers.

The effect of Cu as coactivator is drastically different. The luminescence is about 10 times weaker than that of ZnS:Eu, Li, the copper bands at 450 and 520 nm predominate in the emission spectrum, and one separate Eu band only at 653 nm arises (Fig. 2, curve 2). Probably, Cu-Eu associated centres are build-up, in which a weak Cu → Eu energy transfer and mainly non-radiative electron transitions in the activator ions occur.

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