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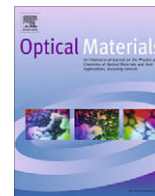**178** PUBLICATIONS **1,815** CITATIONS

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Vacuum ultraviolet and visible spectra of Eu^{3+} in Y_2O_2S and Eu_2O_2S

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ABSTRACT

The vacuum ultraviolet excitation spectrum and visible luminescence spectra of Y_2O_2S:Eu^{3+} (10 at.%) and Eu_2O_2S are reported and assigned. Excitation bands peaking at 312 nm (3.97 eV) and 244 nm (5.08 eV) are assigned to S-3p and O-2p to Eu^{3+} charge transfer absorptions. The bands peaking at 175 nm (7.08 eV) and 224 nm (5.54 eV) are due to absorption from the valence band dominated by O-2p orbitals to the different Y-4d conduction bands. The absorptions from the valence band dominated by S-3p orbitals to the conduction bands are weaker.

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1. Introduction

Yttrium oxysulfide doped with europium ions was recommended in 1968 as an efficient red phosphor for color television [1]. The visible $4f^6$–$4f^6$ emission, excitation [2] and absorption spectra [3] have been studied in detail. More recent interest has focused upon the performance of phosphors excited in the vacuum ultraviolet (VUV) region [4] as well as quantum confinement effects in these nanocrystals [5–7]. We are unaware of studies of europium-doped oxysulfides using synchrotron radiation. In the present study the VUV spectra of neat Eu_2O_2S and Y_2O_2S:Eu^{3+} have been recorded and assigned.

2. Experimental

The preparation of Eu_2O_2S and Y_2O_2S:Eu^{3+} (10 at.%) by the H_2S gas and flux methods has previously been described [3]. The X-ray diffraction patterns of powders taken by a Siemens D500 X-ray diffractometer matched the library files. Powders were sealed in glass ampoules until spectroscopic use. Emission and excitation spectra were recorded at a resolution of 0.3–1.3 nm at room temperature using the photoluminescence end station coupled to the high flux BL03A synchrotron radiation beam line at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan [8].

3. Results and discussion

The purity of the samples prepared can be assessed from their luminescence spectra. Fig. 1 shows the emission spectra of Eu_2O_2S and Y_2O_2S:Eu^{3+} (10 at.%) excited by synchrotron radiation at 243 nm and 320 nm, respectively. For Eu_2O_2S the spectrum recorded using 180 nm was similar, but weaker; whereas for Y_2O_2S:Eu^{3+} the spectra recorded using 250 nm and 180 nm excitation wavelengths were also similar. The relevant electronic transitions from ^5D_J multiplets are marked in the figure and are in agreement with previous studies [2]. The major interest herein concerns the excitation spectra of the emission, shown in Fig. 2. The spectrum of Eu_2O_2S is similar to, but two orders of magnitude weaker than that of Y_2O_2S:Eu^{3+}. This demonstrates the concentration quenching of Eu^{3+} emission. Several features are observed in the excitation between 160 and 340 nm which require explanation.

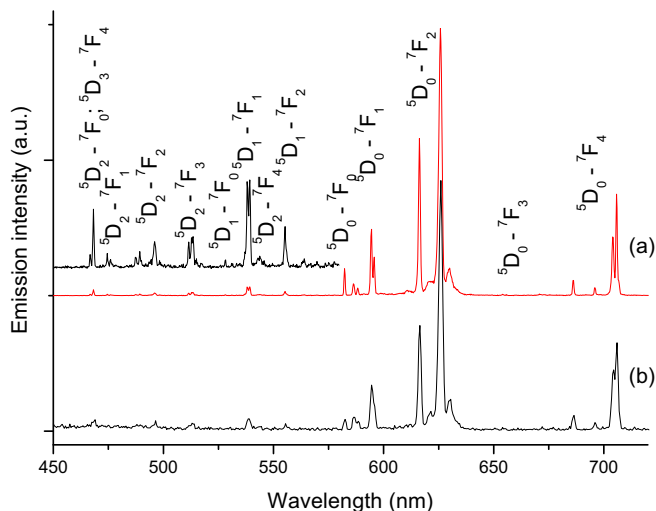**Fig. 1.** Room temperature emission spectra of Eu^{3+} in oxysulfides: (a) 320 nm excited spectrum of $Y_2O_2S:Eu^{3+}$ (resolution 0.63 nm) with the ordinate for the short wavelength region (<580 nm) expanded; (b) 243 nm excited spectrum of Eu_2O_2S (resolution 1.3 nm).

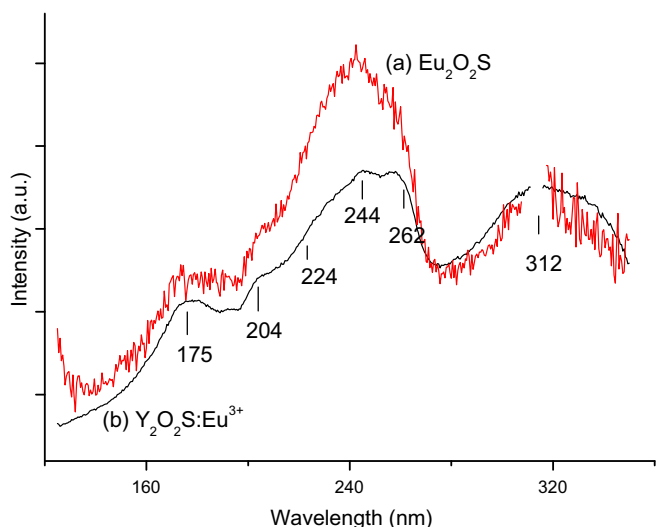**Fig. 2.** Room temperature excitation spectra of Eu^{3+} in oxysulfides: (a) monitoring 626 nm emission of Eu_2O_2S (the spectrum monitoring 706 nm emission is similar); (b) monitoring 626 nm emission of $Y_2O_2S:Eu^{3+}$ (10 at.%) (spectra monitoring the 616.5 nm and 706 nm emissions are similar). Band positions are marked in nm.

Under the tight bonding approximation, the lowest conduction band (CB) for Y_2O_2S is dominant with Y-4d orbitals, and S-3p and O-2p orbitals form the highest overlapped valence bands (VBs). The schematic diagram for the energy structure is given in Fig. 3. *Ab initio* calculations for Y_2O_2S [9] and La_2O_2S [10] confirmed this scheme, although the partial density-of-states for S-3p, O-2p and Y-4d show considerable mixing of these orbitals in the highest valence and lowest conduction bands. The calculations [9,10] gave a splitting of about 1.2 eV between the peak for S-3p bands (with considerable mixing of O-2p) and the O-2p peak closest to the S-3p one. For Y_2O_2S [9], the lowest CB is confirmed Y-4d dominant, and there is a gap of about 1.4 eV between the first peak and the remaining part of the band.

There can be two charge transfer bands: the lower energy one from S-3p and the higher energy one from O-2p, to Eu^{3+} to make Eu^{2+}. The VB to CB absorptions may also appear as two bands. Since the excitation of f–f emission of Eu^{3+} due to charge transfer (CT)
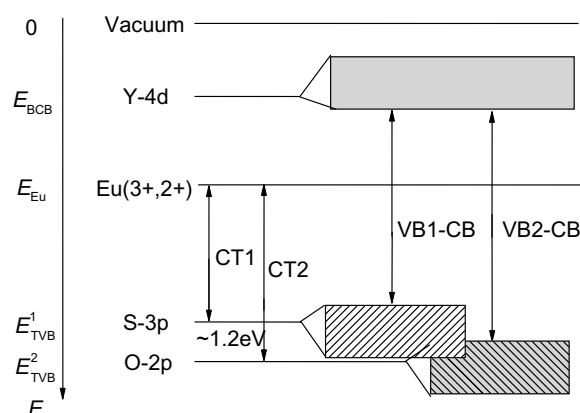

Fig. 3. Schematic diagram for the energy levels of $Y_2O_2S:Eu^{3+}$. (E_{BCB}) is the bottom of the CB relative to the vacuum, i.e., the energy released when a free electron is captured to the bottom of the CB; E^1_{TVB} and E^2_{TVB} are the energies to create a hole at the VBs composed of mainly S-3p and O-2p orbitals, respectively, under the tight bonding approximation; E_{Eu} is defined as the bonding energy for Eu^{3+} and a free electron to form Eu^{2+}. *Ab initio* calculations indicate the separation between the S-3p and O-2p VB peaks of interest is about 1.2 eV, and the splitting of the Y-4d band relevant to the excitation spectrum is about 1.4 eV.

absorption is much stronger than from the interband absorption, the excitation bands peaking at 312 nm (3.97 eV) and 244 nm (5.08 eV) are assigned to S-3p and O-2p to Eu^{3+} CT absorptions. The former is comparable to other reported experimental CT transitions in $Y_2O_2S:Eu^{3+}$ [6] and $La_2O_2S:Eu^{3+}$ [5] within the width of the band [11], and the latter is comparable with the CT transition in $Y_2O_3:Eu^{3+}$ [12] and other hosts with a Eu–O bond [11]. The energy difference between the O-2p and S-3p VBs from this assignment is then about 1.1 eV, which is very close to the *ab initio* result of around 1.2 eV. The bands peaking at 175 nm (7.08 eV) and 224 nm (5.54 eV) are assigned to absorption from the VB dominated by O-2p orbitals to different peaks in the Y-4d CB. The splitting of ~1.5 eV is comparable to the calculated separation of about 1.4 eV. The absorptions from the VB dominated by S-3p orbitals to the CBs are thus estimated to peak at 6 eV and 4.5 eV and are assigned to weaker features at 204 nm (6.08 eV) and 262 nm (4.7 eV). The peaks for interband (S-3p or O-2p VBs to Y-4d CB) absorption are at higher energy than the energy gap between the involved bands, which is common for insulators.

4. Conclusions

The Eu^{3+} ion doped at 10% into Y_2O_2S exhibits emission more intense by two orders of magnitude than neat Eu_2O_2S. Features in the excitation spectra have been assigned and an explanatory diagram is given in Fig. 3. The peaks in the excitation spectra can be related to *ab initio* calculations reasonably well considering the widths of measured peaks and the intrinsic drawbacks in predicting band gaps of density-functional methods.

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