

Photoluminescence of $Y_2O_2S:REE$ and $Gd_2O_2S:REE$ phosphors under 257 nm excitation

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Introduction

The present investigations into the visible emissions of rare earth doped Y_2O_2S and Gd_2O_2S phosphors under ultraviolet (257 nm) excitation were undertaken in order to examine the mechanisms of their emission processes. This makes possible a comparison with the corresponding visible upconversion emissions that are obtained from these phosphors when they are excited with red and near infrared light.

The motivation for these studies is to develop new, improved photoluminescent phosphors for lighting applications that can be excited in the near ultraviolet region. The current studies use an excitation wavelength of 257 nm as this comes in the same region as the mercury emission line at 253.7 nm that is commonly used to excite phosphors in fluorescent lights. Our ultimate aim is to obtain quantum cutting in oxide and oxysulfide lattices which are doped with two different rare earth ions, whereby more than one visible photon is emitted for each ultraviolet photon that is absorbed.

Experimental

The urea homogeneous precipitation method was used to prepare spherical $Y_2O_3:REE$ hydroxycarbonate sub-micrometre phosphor precursor powders. Stock solutions of yttrium nitrate and REE nitrate were prepared from the respective oxides and nitric acid. Following the addition of urea the mixture was heated to boiling and this was maintained for two hours after precipitation had begun. The precipitated rare earth hydroxy carbonate was filtered, washed with distilled water and air dried. The rare earth hydroxyl carbonate was then mixed with 3/2 mole equivalents of sodium carbonate and 2 mole equivalents of sulfur. A mixture of yttrium oxide, 1.5 mole equivalents of sodium carbonate and 2 mole equivalents of sulfur was ground together and added loose powder to the crucible in order to exclude as much air as possible. The crucible was covered and fired in a muffle furnace at a temperature of 900°C for 1 hour. After firing and cooling, the loose mixture at the top of the crucible was discarded and the tightly packed mixture was boiled with distilled water to remove flux and other impurities. The $Y_2O_2S:REE$ samples were then fired in a tube furnace at 1100°C under argon. $Gd_2O_2S:REE$ samples were similarly prepared using Gd_2O_3 precursor instead of Y_2O_3 .

The resultant phosphors were excited with 257 nm laser light provided by an intracavity frequency-doubled argon ion laser (Coherent Ltd.) which is a loan pool laser (CWL3) from the Central Laser Facility. Emission spectra were collected with a Spex 1877 Triplemate Raman spectrometer equipped with a Peltier-cooled open electrode CCD detector (Wright instruments).

Results and Discussion

Photoluminescence spectra of $Y_2O_2S:REE$ and $Gd_2O_2S:REE$ have been obtained under 257 nm excitation. The lattices of the rare-earth oxysulfides and Y_2O_2S are hexagonal (belonging to the D_{3d} factor group), and the primitive unit cell contains one molecule of REE_2O_2S ^{1,2}. Under 257 nm excitation, the energy of the incident photons is too low to excite the Y_2O_2S lattice and consequently the trivalent rare earth cation is excited directly.

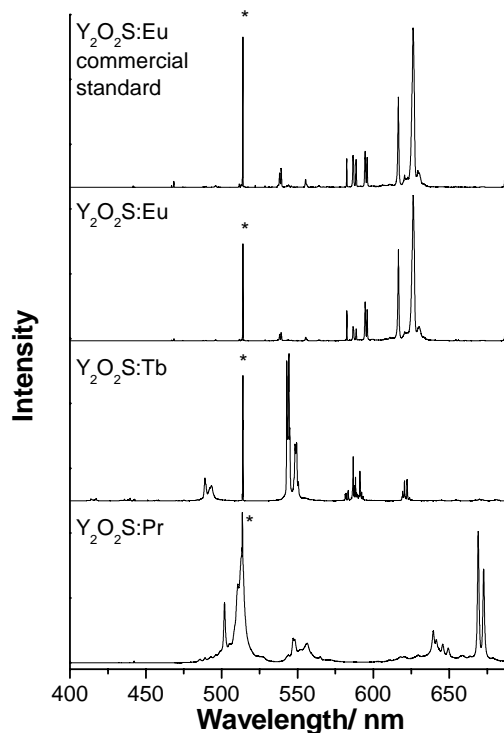


Figure 1. Photoluminescence spectra of $Y_2O_2S:REE$ under 257 nm excitation.

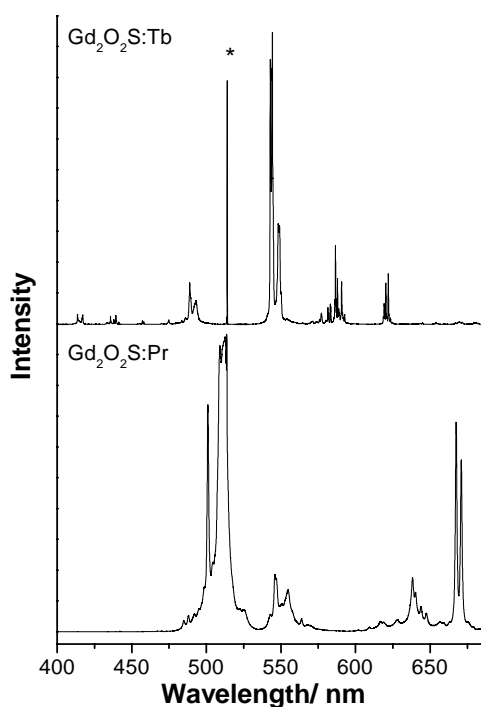


Figure 2. Photoluminescence spectra of $Gd_2O_2S:REE$ under 257 nm excitation.

Under excitation at wavelengths less than 200 nm the host Y_2O_2S lattice is excited (band gap energy, $E_g \approx 5$ eV) with subsequent energy transfer from the host crystal to the activator³.

The nature of the valence changes on the rare earth ion activators depends on whether they capture electrons or holes. Eu^{3+} acts as an electron trap in Y_2O_2S , whereas Pr^{3+} and Tb^{3+} act as hole traps when the host lattice is initially excited.

The activator ions subsequently capture an opposite charge, thereby raising them to excited $4f$ levels³. In Y_2O_2S , radiative decay from the excited $4f$ levels to the $4f$ ground state gives rise to green and red emissions from Pr^{3+} , a predominantly green emission from Tb^{3+} and a predominantly red emission from Eu^{3+} (see Figure 1). The line at 514 nm, denoted by an asterisk in Figures 1 and 2 is due to the 257 nm laser line in second order.

In the Y_2O_2S host lattice the radiative decay times until 1/10 of the initial intensity are 6.7 μ s, 2.7 ms and 0.86 ms for Pr^{3+} , Tb^{3+} and Eu^{3+} , respectively⁴. The radiative decay time of Pr^{3+} in Y_2O_2S is the shortest lifetime observed for a $4f \rightarrow 4f$ electronic transition, almost certainly reflecting its spin allowed character.

Figure 2 shows the photoluminescence spectra obtained from $Gd_2O_2S:Pr$ and $Gd_2O_2S:Tb$. The close similarity of the photoluminescence spectra obtained from Pr^{3+} and Tb^{3+} ions in Y_2O_2S and Gd_2O_2S lattices is indicative of similar site symmetries and emission mechanisms in the two lattices.

$Gd_2O_2S:Pr$ and $Gd_2O_2S:Tb$ are used as X-ray phosphors due to their strong X-ray absorption, emission efficiency, short emission decay time and chemical stability.

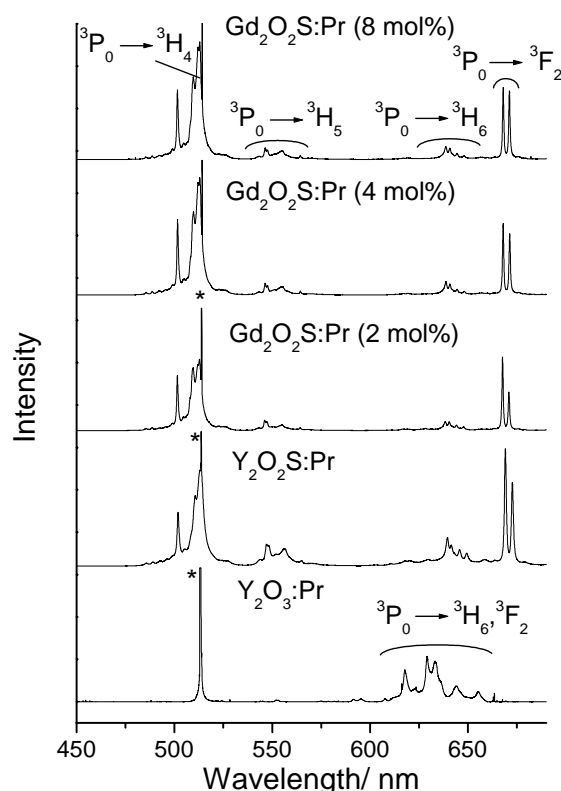


Figure 3. Photoluminescence spectra of $Y_2O_3:Pr$ (2 mol%), $Y_2O_2S:Pr$ (2 mol%), $Gd_2O_2S:Pr$ (2 mol%), $Gd_2O_2S:Pr$ (4 mol%), and $Gd_2O_2S:Pr$ (8 mol%) under 257 nm excitation.

The photoluminescence spectrum of $Y_2O_3:Pr$ is compared with those of $Y_2O_2S:Pr$ and $Gd_2O_2S:Pr$ in Figure 3. The spectrum of $Y_2O_3:Pr$ contains a number of emission lines around 630 nm which are assigned to the $^3P_0 \rightarrow ^3H_6$ and $^3P_0 \rightarrow ^3F_2$ transitions. In the Y_2O_2S and Gd_2O_2S lattices, the Pr^{3+} ion also gives red emissions due to the $^3P_0 \rightarrow ^3H_6$ and $^3P_0 \rightarrow ^3F_2$ transitions (see Figure 3). In contrast to $Y_2O_3:Pr$, however, green emissions due to the $^3P_0 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3H_5$ transitions are observed in the Y_2O_2S and Gd_2O_2S lattices.

Conclusions

Photoluminescence spectra obtained from $Y_2O_2S:REE$ and $Gd_2O_2S:REE$ ($REE = Pr^{3+}, Tb^{3+}$) under 257 nm excitation show close similarities because the REE ion has the same site symmetry in the Y_2O_2S and Gd_2O_2S lattices. However, the photoluminescence spectra of the X-ray phosphors, $Y_2O_2S:Pr$ and $Gd_2O_2S:Pr$, differ markedly from the spectrum of $Y_2O_3:Pr$, as the former show prominent green emissions due to the $^3P_0 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3H_5$ transitions.

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