5d–4f emission of Eu$^{2+}$ and electron-vibrational interaction in several alkaline earth sulfides doped with Eu$^{2+}$ and Er$^{3+}$

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A B S T R A C T

Several alkaline earth sulfides doped with Eu$^{2+}$ and Er$^{3+}$ ions have been synthesized and shown to be potential phosphors for applications in the visible spectral range. The excitation and emission spectra corresponding to the 4f–5d interconfigurational transitions of Eu$^{2+}$ were analyzed with an aim of extraction of the main parameters of the electron-vibrational interaction. The values of the Huang–Rhys factor, effective phonon energies, and zero-phonon line positions were systematically compared for all studied materials; physical trends were discussed. As a test for the validity of the obtained parameters, the Eu$^{2+}$ 5d–4f emission bands were modeled to yield good agreement with the experimental spectra.

1. Introduction

Photostimulated luminescence (PSL) is a well studied luminescence phenomena and so many phosphors have been developed over the past. In PSL the emission is due to the recombination of the electrons and hole traps which are created by the high energy radiation sources such as X rays, UV rays, cathode rays, and gamma rays. The depth of the trapping centers are usually large and are in the order of 1–2 eV. At room temperature, the probability of thermal activation of the trapping centers is extremely small and hence the PSL phosphors can serve as excellent data storage materials. The recombination process is induced by the energy supplied to the material in the form of infrared or visible radiations and this result in the emission of light from the activator. Most of the PSL phosphors are wide band gap II–VI semiconductors doped with two types of selected rare earths in divalent and trivalent states.

The applications of PSL phosphors in the Photonics industry and military area are very wide such as optical storage, PSL dosimeters, infrared sensors, image intensifiers, NIR to visible convertors, and tracking of IR sources such as vehicles and missiles [1–5]. These materials also have high quantum conversion efficiency of the order of 66% and short IR response time.

Rare earth doped alkaline earth sulfides are considered as very efficient PSL phosphors [6,7]. Over the past several reports have been published on the synthesis and characterizations of various rare earth doped Ca and Sr sulfide phosphors both in bulk and nano crystalline forms [6–9]. Especially the Eu$^{2+}$ doped SrS and CaS are considered as two of the most efficient red phosphors for LED applications [10]. It was found that the emission color can be considerably shifted by changing the nature of the alkaline earth cation as well as its composition in the crystal lattice. In this paper we report the synthesis and optical characterization of CaS, SrS, CaSrS, CaMgS doped with Eu$^{2+}$ and Er$^{3+}$. A theoretical model based on the electron–phonon interaction was used to interpret the spectral shift as a function of the cationic compositions.

2. Sample preparation and measurements

All phosphor samples were prepared by the solid state reaction technique in CO reductive atmosphere. The starting raw materials were CaCO$_3$, SrCO$_3$, (MgCO$_3$)$_2$Eu$_{20}$O$_{30}$Er$_2$O$_3$, elemental S, and LiF (Sigma Aldrich, 99.99% pure). Based on published report [11] the
rare earth dopant concentration was fixed at 0.2 mol% for the best emission intensity. Elemental S is added in excess to compensate the oxidation losses and LiF is added as a flux which is typically 10% of the total weight of the reactants. All the chemicals were mixed in an agate mortar and fired at 1100 °C for 1.25 h and the obtained sample was crushed to obtain the ceramic phosphor sample.

Powder X-ray diffraction was performed at 40 kV and 30 mA in the parallel beam configuration using a RIGAKU Ultima IV X-ray diffractometer with Cu Kα (λ = 1.5 Å). The absorption spectra were measured in the 300–1700 nm range using a spectrophotometer (Cary, Model 14R) in transmission mode by mixing the powder sample with epoxy and keeping in between glass slides. The emission spectra of the samples were recorded by exciting the sample with 980 nm band of a Ti:Sapphire laser (Spectra Physics, Model 3900S) pumped by a frequency doubled Nd:YVO4 laser (Spectra Physics Millennia). The emission from the sample was collected with a 1.25 m single grating scanning monochromator (SPEX, Model 1250 M) and detected by a photo multiplier tube (Model 1911, Horiba) for the visible.

3. Results and analysis of the electron-vibrational interaction

Figs. 1a and 1b show the XRD patterns of the CaS and SrS phosphors in comparison with the standard powder pattern. Both XRD pattern obtained are in agreement with the respective sample standard (JCPDS card no. 75-0895 for SrS, JCPDS card no. 08-0464 for CaS). The room temperature UV–VIS absorption spectrum in Fig. 2 shows two well defined peaks at 250 (Eu2+ 4f7 6g5/2 → 4f6 5d1) and 543 nm (Er3+ 4I13/2 → 4I15/2) and a very broad NIR band at 1203 nm (Er3+ 4I13/2 → 4I11/2) that extend from 800 to 1600 nm which makes this phosphor for wide excitation range upconversion applications. Upon excitation at 980 nm strong upconversion was observed in the red region and the emission spectra are shown in Figs. 3a–e for various phosphor compositions.

Influence of the lattice vibrations on the impurity ion electron states manifest itself in the shift of the emission band maximum with respect to the maximum of the corresponding absorption band. Such an interaction is more pronounced for open electron shells (like 5d shells of rare-earth ions, for example) and is considerably weaker for inner 4f shells. Quantitatively, interaction between electronic states of an impurity ion and vibrations of ligands is described by the following parameters: the Stokes shift ΔEs (the difference in energy between the absorption and emission peaks), the Huang–Rhys factor S (which is proportional to ΔEs) and effective phonon energy hν0. All these parameters can be estimated from a comparative analysis of the emission and absorption (or excitation) spectra. The following equations can be used [12]

\[ \Delta E_s = (2S - 1)h\nu_0, \]

\[ \Gamma(T) = 2.35h\nu_0 \left[ S \coth \left( \frac{h\nu_0}{2kT} \right) \right]^{1/2}. \]

where the last equation describes the full width ½ (FWHM) of the emission band determined at the absolute temperature T.

Before proceeding with applications of Eqs. (1) and (2) to the title systems, we point out here that the Eu2+ 4f7 → 4f6 5d1 (excitation) bands are very broad (Fig. 2). This is related to the crystal field splitting of the Eu2+ energy levels. In the sulfides studied in the present work the Eu2+ ions occupy the divalent cation positions, which are surrounded by six S2− ions. In the octahedral crystal field the 5d states of Eu2+ are split into the t2g (the lowest) and eg (the highest) levels [13], which can be split further due to the low-symmetry component of crystal field. Then one may expect in general five excitation bands (which can be strongly overlapping) in the excitation spectra. The emission transition will start from the lowest 5d level, according to the general shape of the photoluminescence band, which represents a practically Gaussian function with one clearly distinguished maximum and without any additional structure (Fig. 3). The general scheme (not to scale) of the 5d levels splitting with characteristic emission and absorption transitions relevant for the present discussion is shown in Fig. 4.

For each considered host the absorption band corresponding to the t2g states was decomposed into three Gaussian functions, and the position of the longest wavelength maximum was taken as the first absorption transition. Results of application of Eqs. (1) and (2) are summarized in Table 1.

The structure of the absorption spectra of the studied samples clearly reveals presence of two wide bands, which correspond to the transitions from the ground Eu2+ state to the t2g (lower in energy band) and eg (higher in energy band) states, which arise from the crystal field splitting of the 5d states of europium. Separation between the barycenters of this states is the crystal field strength parameter 10Dq.

Analysis of the 10Dq (5d states splitting) shows that it is maximum for CaS and Ca0.7Mg0.3S. With increasing of the Sr content and with gradual move to SrS, the 10Dq value is decreasing due to increasing interatomic distances (this trend can be understood by comparing the Sr–S and Ca–S distances in pure materials (3.0095 Å [14] and 2.8452 Å [15], respectively)). In addition, the longest wavelength of the Eu2+ emission corresponds to the strongest crystal field (largest 10Dq value), whereas the shortest wavelength is related to the weakest crystal field (Table 1),
Fig. 2. UV–VIS absorption spectra of $\text{Ca}_{0.7}\text{Mg}_{0.3}\text{S}$, $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{S}$, $\text{Ca}_{0.7}\text{Sr}_{0.3}\text{S}$, $\text{SrS}$ and $\text{CaS}$ doped with Eu and Er. Inset shows the typical NIR absorption profile in $\text{CaS}$: Eu$^{2+}$, Er$^{3+}$.

Fig. 3a. Fitting of the experimental emission spectrum of $\text{Ca}_{0.7}\text{Sr}_{0.3}\text{S}$: Eu$^{2+}$, Er$^{3+}$ with theoretical model. Fitting parameters are summarized in Table 1.

Fig. 3b. Fitting of the experimental emission spectrum of $\text{Ca}_{0.7}\text{Mg}_{0.3}\text{S}$: Eu$^{2+}$, Er$^{3+}$ with theoretical model. Fitting parameters are summarized in Table 1.

Fig. 3c. Fitting of the experimental emission spectrum of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{S}$: Eu$^{2+}$, Er$^{3+}$ with theoretical model. Fitting parameters are summarized in Table 1.

Fig. 3d. Fitting of the experimental emission spectrum of $\text{CaS}$: Eu$^{2+}$, Er$^{3+}$ with theoretical model. Fitting parameters are summarized in Table 1.
as can be understood from the overall splitting of the europium 5d states.

Finally, an additional check of reliability of the obtained values of the $S$ and $h\omega$ values is the emission band modeling. In the single configurational coordinate approximation, the intensity of the emission band at energy $E$ can be approximated by the following expression:

$$I \propto \frac{e^{-S\beta}}{p!} \left( 1 + S^2 \frac{e^{-h\omega/kT}}{p+1} \right),$$

(3)

where $E_0$ is the zero-phonon line (ZPL) energy (not estimated yet and thus allowed to vary freely), and $p$ is the number of the phonons involved into the emission transition. The values of $E_0$ resulting in the best agreement between the calculated and experimental emission band shape are also given in Table 1. In Figs. 3a–e a comparison of the experimental and theoretically simulated emission spectra is shown for all compositions studied. For most of the compositions best agreement between experimental and theory can be seen which confirm the validity of the proposed model. In addition, Table 1 offers comparison of the estimated parameters of the electron-vibrational interaction obtained in the present work with those for three thiogallates crystals CaGa$_2$S$_4$, BaGa$_2$S$_4$, and SrGa$_2$S$_4$ [15,16]. In all these materials Eu$^{2+}$ ions are surrounded by the sulfur ions. As can be seen from Table 1, all effective phonon frequencies, Huang–Rhys factors and Stokes shifts are highly compatible (we note here that the effective phonon frequency in the Ca$_{0.7}$Mg$_{0.3}$S phosphor is lower than in other cases, presumably, due to some effective local modes in this particular case). We also notice that

![Fig. 3e. Fitting of the experimental emission spectrum of SrS: Eu$^{2+}$, Er$^{3+}$ with theoretical model. Fitting parameters are summarized in Table 1.](image)

![Fig. 4. Simplified diagram of the 4$f$$^7$ → 4$f^5$5d absorption and 4$f^5$5d → 4$f^7$ emission transitions of Eu$^{2+}$ in a deformed octahedral environment.](image)

<table>
<thead>
<tr>
<th>Host</th>
<th>Emission maximum (nm)</th>
<th>First absorption maximum (nm)</th>
<th>Stokes shift $\Delta E$ (cm$^{-1}$)</th>
<th>FWHM of the emission band, cm$^{-1}$</th>
<th>10Dq (cm$^{-1}$)</th>
<th>Zero-phonon line position, $E_0$ (cm$^{-1}$)</th>
<th>Huang–Rhys factor ($S$)</th>
<th>Effective phonon energy ($h\omega$)</th>
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</thead>
<tbody>
<tr>
<td>This work</td>
<td>617</td>
<td>551</td>
<td>1941</td>
<td>1709</td>
<td>16,100</td>
<td>17,040</td>
<td>4.0</td>
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</tr>
<tr>
<td>Ca$<em>{0.5}$Sr$</em>{0.5}$S</td>
<td>625</td>
<td>573</td>
<td>1452</td>
<td>1586</td>
<td>17,620</td>
<td>16,600</td>
<td>2.6</td>
<td>346</td>
</tr>
<tr>
<td>Ca$<em>{0.7}$Mg$</em>{0.3}$S</td>
<td>640</td>
<td>587</td>
<td>1411</td>
<td>1360</td>
<td>19,940</td>
<td>16,300</td>
<td>5.5</td>
<td>140</td>
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<tr>
<td>CaS</td>
<td>650</td>
<td>562</td>
<td>2410</td>
<td>1939</td>
<td>19,530</td>
<td>16,500</td>
<td>4.2</td>
<td>326</td>
</tr>
<tr>
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<td>2145</td>
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<td>14,700</td>
<td>17,600</td>
<td>5.1</td>
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<tr>
<td>Refs. [15,16]</td>
<td>504</td>
<td>424</td>
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<td>2450</td>
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<td>BaGa$_2$S$_4$</td>
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<td>1975</td>
<td>1600</td>
<td>~19,000</td>
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<td>~19,000</td>
<td>20,746</td>
<td>4.0</td>
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</table>
the zero-phonon line positions in our materials are all red-shifted if compared with those for the thiogallates.

4. Conclusions

In conclusion, for the purpose of comparison with our proposed modeling of the electron–phonon interaction model we have explored the cationic influence on the emission spectral shift in a series of alkaline earth sulfide storage phosphors doped with Eu$^{2+}$ and Er$^{3+}$. By detailed analysis of the emission and excitation spectra, we have arrived at reliable estimations of the Huang–Rhys factor, effective phonon frequencies, zero-phonon lines and crystal field splitting of the Eu$^{2+}$ 5d states in all phosphors considered. Comparison of the obtained results with those reported previously for a series of the Ba, Ca, Sr thiogallates has yielded high consistency. In addition, we have modeled the emission band shapes of the Eu$^{2+}$ 5d–4f emission, and a good agreement with the experimental emission spectra (except for the Ca$_{0.7}$Mg$_{0.3}$S case, for which the quality of the fit is worse presumably to inhomogeneous distribution of the Ca and Mg ions through the cation sites in the crystal lattice) confirms the reliability of the obtained values of the main parameters of the electron-vibrational interaction.

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