Energy transfer in single phase Eu$^{3+}$-doped Y$_2$WO$_6$ phosphors

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Inorganic phosphors based on monoclinic Y$_2$WO$_6$ doped with Eu$^{3+}$ ions were prepared via conventional solid-state reactions at high temperature. A total of five samples were obtained with different Eu$^{3+}$ concentrations (0–9%). The purity of the as-prepared phases was checked by powder X-ray diffraction (PXRD). Through the Rietveld refinement, at low concentrations Eu$^{3+}$ ions are found to occupy preferentially the Y2 (2f) sites in the host compound. However, for higher dopant concentrations, the occupancy of the (2e) and (4g) sites becomes relevant. The excitation, emission, and time-resolved emission spectra were examined in detail. Efficient energy transfer from the (WO$_6$)$^{5-}$ groups to the Eu$^{3+}$ activators was observed. The decay curves for the Eu$^{3+}$ 5D$_0$ $\rightarrow$ 7F$_4$ transition show a non-exponential behavior that is enhanced with increasing Eu$^{3+}$ concentration. The experimental decay curves were fitted to the Inokuti–Hirayama model to gain some insight into the mechanism of the interaction between the Eu$^{3+}$ ions in these phosphors.

Inorganic phosphors typically consist of an inert host material, normally either oxides, nitrides/oxynitrides, or sulfides/oxy sulfides, doped with a small concentration of activator ions. In particular, metal oxides containing d$^0$ transition metal ions, such as VO$_x$$^{2+}$, MoO$_x$$^{2+}$, or WO$_x$$^{3-}$ have attracted much attention as host lattices in inorganic phosphors. Tungstates with different stoichiometries, such as Y$_2$WO$_6$, have been studied less extensively, probably due to their rich crystallographic variation. Depending on the synthetic method, Y$_2$WO$_6$ can crystallize in a tetragonal (S.G. P4/nmm), monoclinic (S.G. P2/c), or orthorhombic (S.G. P2$_1$ab) form. On the other hand, Borchardt identified Y$_2$WO$_6$ as a bright photoluminescent material that emitted a pale blue light under ultraviolet excitation, showing that the excited tungstate groups can effectively transfer energy to doping activator ions.

In the past few years, we have been actively involved in the preparation and characterization of new red-emitting phosphors. In this paper, Y$_2$Eu$_x$WO$_6$ red phosphors were synthesized via solid-state reactions and their photoluminescent features were studied. We have carried out a detailed analysis of the energy transfer process between the luminescent excited levels of the dopant Eu$^{3+}$ ions as a function of their concentration and the interaction between these ions and the host lattice structure. The energy transfer process is found to be well described by the Inokuti–Hirayama model.

2. Experimental

2.1. Synthesis

All Y$_2$Eu$_x$WO$_6$ samples in this study were prepared at high temperature using solid-state reactions starting from

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a thoroughly ground mixture of the corresponding oxides, Y₂O₃, Eu₂O₃, and WO₃, in stoichiometric proportions. These mixtures were placed in an alumina boat and heated at 973 K for 10 h before being cooled to below 400 K. The samples were then removed from the crucible, ground into a powder, and reheated for 10 h at 1273 K. The procedure was repeated and the sample was finally heated to 1373 K for another 10 h. Optical inspection of the products showed homogeneous powders with a white color. All of the above synthetic processes were performed under an air atmosphere.

2.2. Characterization

To verify the purity of the phases, powder X-ray diffraction (PXRD) data were collected using a Bruker D8 Advance diffractometer fitted with a graphite monochromator. The spectra were collected across the range \(10^\circ \leq 2\theta \leq 60^\circ\), using Cu Kα radiation (\(\lambda = 1.54057 \ \text{Å}\)) generated at 40 kV and 30 mA. The excitation spectra were measured using a JASCO FP-6500 spectrophotometer with a 150 W xenon lamp as the excitation source. The emission spectra were obtained by exciting the samples at 300 nm using a 400 W Oriel xenon lamp. The spectra were recorded with a system of two convex lenses that collimated and focalized the Eu³⁺ emission into an optical fiber coupled to a 0.3 m single grating spectrometer (Andor Shamrock-3031-B). The final measurement was done using a cooled CCD detector (Newton DU920 N) with a resolution of 0.7 nm and an integration time of 2 s. For the lifetime measurements, a tunable optical parameter oscillator (OPO) was used as the excitation source (10 Hz repetition rate, 8 ns pulse temporal width) and the time resolved emission was focused on the entrance slit of a monochromator (Triax 180) coupled with a photomultiplier (Hamamatsu r928). The signal was acquired and averaged by an oscilloscope (Lecroy WaveSurfer 424). All measurements were carried out at room temperature.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses were carried out on a STA 448 Jupiter F3 type simultaneous thermal analyzer (Netzsch). The samples used for TG and DSC were powders of about 69 mg in weight. The sample cells were aluminum oxides pans. The parent reagents were heated up to 1373 K at a heating rate of 5 K min⁻¹ under flowing of nitrogen atmosphere at 20 mL min⁻¹.

3. Results and discussion

Samples for a total of five different compositions were synthesized in the Y₂₋ₓEuₓWO₆ system with \(x \equiv 0, 0.02, 0.06, 0.14\) and 0.18. The powder X-ray diffraction patterns for these compounds are similar to those for the monoclinic Y₂WO₆ phase previously reported in the ICSD (Inorganic Crystal Structure Data) database and by Efremov et al., indicating that all samples crystallized isostructurally adopting the monoclinic Y₂WO₆ structure belonging to the P2\(_1\)/c space group (no. 13). In this structure there are three different crystallographic sites for the Y³⁺ ion. Two of them are eight-fold coordinated by O⁻ atoms, whereas in the third one, the lanthanide ion is seven-fold coordinated by oxygen atoms (Fig. 1). Upon doping, the trivalent europium ions are expected to occupy the yttrium sites in Y₂WO₆ : Eu³⁺ since the ionic radii of Eu³⁺, \(r = 106.6\ \text{pm (C.N.} = 8)\) and \(r = 101.0\ \text{pm (C.N.} = 7)\), are only slightly larger than those of Y³⁺, \(r = 96\ \text{pm (C.N.} = 8)\) and 101.9 pm (C.N. = 7). The values of the cell parameters, confirmed by a Le Bail refinement, for all compounds are given in Table 1, together with their standard deviations. The variation of the unit cell with the Eu³⁺ content confirms the existence of a range of solid solutions represented by the formula Y₂₋ₓEuₓWO₆ \((x \equiv 0.02, 0.06, 0.14\) and 0.18).

Rietveld refinements for the Y₂₋ₓEuₓWO₆ \((x \equiv 0.0, 0.02, 0.18)\) structures were carried out using the Jana 2006 software. The calculated patterns are consistent with the experimental data (see Fig. 2). The occupation factors, refinement parameters and refined compositions are shown in Table 2. As seen, the crystallographic volume of the samples increases with increasing Eu³⁺ content, while the lattice parameters change only slightly.

Changes in the cell parameters are correlated with the occupation of the Eu³⁺ ions in the Y³⁺ positions. One can see that at low concentrations Eu³⁺ ions occupy preferentially the Y2 (2f) sites, while the occupancy of the Y1 (2e) and Y3 (4g) sites becomes relevant as the concentration of Eu³⁺ ions increases. This trend in the occupancy of the different sites explains some of the irregularities in the variation of the unit cell parameters for the doped phases (vide supra). On the other hand, the refined compositions obtained through the Rietveld refinement are in good agreement with the TG-DSC experiments (Fig. 3) ruling out the possibility of volatilization of WO₃ during the synthesis process.

The emission spectrum of un-doped Y₂WO₆ under 300 nm UV radiation is shown in Fig. 4. As it has been previously described, tungstate based materials emit blue light (450 nm) themselves under ultraviolet radiation. The excitation spectrum of the 450 nm emission for the un-doped sample is dominated by a broad band that can be attributed to the adsorption by \((\text{WO}_4)^{6-}\) groups with a peak centered at about 300 nm (Fig. 4). The decay curve of the blue emission under pulsed laser excitation (300 nm) shown in the inset of Fig. 4 is non-exponential with an intrinsic lifetime of \(\tau = 6.65\ \mu\text{s}\).

PLE spectra of the Eu-doped samples are similar to those previously reported. They exhibit a broad band centered at
about 300 nm along with very weak f–f transitions at about 395 nm (7F0 → 5L6), 465 nm (7F0 → 5D2), and 540 nm (7F0 → 5D1). The broad, intense band consists of overlapping O2/C0–Eu3+ and O2/C0–W6+ charge transfer bands.

Room temperature emission spectra of the Y2xC0Eu1–xWO6 (x = 0.0, 0.02, 0.06, 0.14, and 0.18) samples are shown in Fig. 5. The intra-configurational 4f–4f transitions of the Eu3+ ions originating from the 5D0 → 7Fj (j = 0–4) transitions were identified. The most intense emission corresponds to the electric dipole 5D0 → 7F2 transition centered at approximately 610 nm. The emission spectra are also characterized by the band at about 450 nm, originating from the (WO6)6+/C0 groups of the host matrix. This emission band disappears when the concentration of the dopant ion is increased. The variation of the emission intensity at 450 nm with the dopant concentration is shown in the inset of Fig. 6. It is observed that while the intensity of the band at 450 nm decreases, that of the band at 610 nm increases for concentrations up to x = 0.14. This phenomenon implies that an energy transfer from the (WO6)6+/C0 groups to the Eu3+ ions must occur. At the same time, we observe that the PL intensity decreases when x exceeds 0.14 due to concentration quenching, related to an energy transfer between activator centers. For a good characterization of the PL behavior in this system it is therefore necessary to determine the critical distance between donors (activator) and acceptors (quenching site) that can be estimated using the equation proposed by Blasse et al.:29

\[
R_0 = 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3}
\]

where \(R_0\) = critical distance, \(V\) = the unit cell volume, \(x_c\) = the critical concentration, and \(N\) = the number of formula units in the unit cell. Using \(V = 445.2\ \text{Å}^3\), \(x_c = 0.14\), and \(N = 4\), the critical distance is found to be \(R_0 = 11.5\ \text{Å}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>Vol. (Å³)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y2WO6</td>
<td>7.578(9)</td>
<td>5.330(8)</td>
<td>11.361(18)</td>
<td>104.36(9)</td>
<td>444.6(12)</td>
<td>22 and 23</td>
</tr>
<tr>
<td>Y1.98Eu0.02WO6</td>
<td>7.578(14)</td>
<td>5.331(10)</td>
<td>11.364(2)</td>
<td>104.36(11)</td>
<td>444.8(14)</td>
<td></td>
</tr>
<tr>
<td>Y1.94Eu0.06WO6</td>
<td>7.578(8)</td>
<td>5.331(10)</td>
<td>11.365(1)</td>
<td>104.33(6)</td>
<td>444.8(12)</td>
<td></td>
</tr>
<tr>
<td>Y1.90Eu0.10WO6</td>
<td>7.579(1)</td>
<td>5.333(7)</td>
<td>11.367(1)</td>
<td>104.31(1)</td>
<td>445.2(14)</td>
<td></td>
</tr>
<tr>
<td>Y1.86Eu0.14WO6</td>
<td>7.581(15)</td>
<td>5.335(10)</td>
<td>11.372(2)</td>
<td>104.32(12)</td>
<td>445.7(16)</td>
<td></td>
</tr>
<tr>
<td>Y1.82Eu0.18WO6</td>
<td>7.581(15)</td>
<td>5.335(10)</td>
<td>11.372(2)</td>
<td>104.32(12)</td>
<td>445.7(16)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2 Rietveld refinement results for (a) Y2WO6; (b) Y1.98Eu0.02WO6 and (c) Y1.82Eu0.18WO6. The blue line shows the difference between observed and calculated data.
In order to evaluate the efficiency of the energy transfer ($\eta_{\text{ET}}$) from the host matrix to the Eu$^{3+}$ ions, we estimated the emission intensities of the matrix in the presence ($I_s$) and absence ($I_{s0}$) of the activator ion, using these values to calculate $\eta_{\text{ET}}$ using the following expression:10–12

$$\eta_{\text{ET}} = 1 - \frac{I_s}{I_{s0}}$$

The quantum efficiency of the activator ions (QE) $\eta_{\text{Eu}^{3+}}$ can be calculated using the relevant emission spectra and the following expression:

$$\eta_{\text{Eu}^{3+}} = \frac{\int I_{\text{Eu}^{3+}} \, d\lambda}{\int I_{\text{exc}} \, d\lambda} = \frac{\int I_{\text{Eu}^{3+}} \, d\lambda}{\int (I_{\text{exc}} - I_s) \, d\lambda}$$

where $I_{\text{Eu}^{3+}}$ is the emission of the Eu$^{3+}$ ion, and the remaining symbols have their usual meaning described in eqn (2) (vide supra). The calculated $\eta_{\text{ET}}$ and $\eta_{\text{Eu}^{3+}}$ values are shown in Table 3, where it is observed that the $\eta_{\text{ET}}$ values increase along with the increase in the Eu$^{3+}$ concentration, while the values of $\eta_{\text{Eu}^{3+}}$ reach a maximum when $x = 0.14$.

These results are in good agreement with those reported by Z. Zhao et al. where the optimal concentration of Eu$^{3+}$ in the Y$_2$WO$_6$ matrix is found to be $x = 0.13$ (ref. 33) and with those reported by Li. et al., where $x = 0.09$.16 The behavior found for the Y$_2$WO$_6$ matrix is quite different from that found for the KLa(WO$_4$)$_2$ matrix, for example, where the critical concentration is reached when the Eu$^{3+}$ concentration is about 40% at.34

As shown in Fig. 6, room temperature emission decay curves upon excitation at 300 nm were measured for the Eu$^{3+}$ doped samples with different concentrations of the rare-earth ion. Our studies are focused mainly in the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition, because the broad emission band of the matrix overlaps the emission corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition at 610 nm. The decay curves for the Eu$^{3+}$ $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition emission show a non-exponential behavior that is enhanced with increasing Eu$^{3+}$ concentration. The non-exponential character of the decay curves can be explained by taking into account the fact that at intermediate doping concentrations the Eu$^{3+}$ and the Y$^{3+}$ ions are randomly distributed in the Y$^{3+}$ sites in Y$_2$WO$_6$.35 According to Collins et al.36 there are three different regimes of donor decay: (i) no diffusion, where the energy transfer occurs between

### Table 2: Cell parameters, occupation factors, refined parameters and refined compositions for Y$_{2-x}$Eu$_x$WO$_6$ ($x = 0.0, 0.02, 0.18$). Atomic positions are referenced in ref. 22 and 23.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Y$_2$WO$_6$</th>
<th>Eu$<em>{0.02}$Y$</em>{1.98}$WO$_6$</th>
<th>Eu$<em>{0.18}$Y$</em>{1.82}$WO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a/\text{Å}$</td>
<td>7.578(12)</td>
<td>7.578(14)</td>
<td>7.581(15)</td>
</tr>
<tr>
<td>$b/\text{Å}$</td>
<td>5.330(8)</td>
<td>5.331(10)</td>
<td>5.335(10)</td>
</tr>
<tr>
<td>$c/\text{Å}$</td>
<td>11.361(18)</td>
<td>11.364(21)</td>
<td>11.372(20)</td>
</tr>
<tr>
<td>$\beta(\degree)$</td>
<td>104.36(9)</td>
<td>104.36(11)</td>
<td>104.32(12)</td>
</tr>
<tr>
<td>$V/\text{Å}^3$</td>
<td>444.6(12)</td>
<td>444.8(14)</td>
<td>445.7(16)</td>
</tr>
<tr>
<td>Site occupancy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y1/Eu1 (2e)</td>
<td>1.00(4)</td>
<td>1.00(3)/0.00(3)</td>
<td>0.83(7)/0.17(7)</td>
</tr>
<tr>
<td>Y2/Eu2 (2f)</td>
<td>1.00(5)</td>
<td>0.95(7)/0.05(7)</td>
<td>0.86(7)/0.14(7)</td>
</tr>
<tr>
<td>Y3/Eu3 (4g)</td>
<td>1.00(3)</td>
<td>0.98(5)/0.02(5)</td>
<td>0.90(5)/0.10(5)</td>
</tr>
<tr>
<td>$R_p(%)$</td>
<td>13.51</td>
<td>13.87</td>
<td>12.77</td>
</tr>
<tr>
<td>$R_w(%)$</td>
<td>20.41</td>
<td>20.89</td>
<td>20.13</td>
</tr>
<tr>
<td>$R_F(%)$</td>
<td>5.89</td>
<td>7.03</td>
<td>6.57</td>
</tr>
<tr>
<td>Refined composition</td>
<td>Y$_{2,00(5)}$WO$_6$</td>
<td>Eu$<em>{0.04(3)}$Y$</em>{1.96(3)}$WO$_6$</td>
<td>Eu$<em>{0.25(9)}$Y$</em>{1.75(9)}$WO$_6$</td>
</tr>
</tbody>
</table>

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**Fig. 3** TG-DSC analysis of the heating cycles in the synthesis process of the doped samples.

**Fig. 4** Emission ($\lambda_{\text{exc}} = 300 \text{ nm}$) and excitation spectra ($\lambda_{\text{em}} = 450 \text{ nm}$) of Y$_2$WO$_6$. The inset shows the decay curve of the emission band of the un-doped host structure.
donor and acceptor with little or no diffusion among donors; (ii) diffusion limited decay, where there is significant diffusion among donors before donor-acceptor energy transfer occurs; and (iii) fast diffusion, during which the diffusion among donors is so fast that the excited atom rapidly comes close enough to an acceptor to allow for a donor-acceptor energy transfer. The non-exponential behavior of the decay curves reveals that the energy transfer process occurs with little or no diffusion among the donors. Hence we use the Inokuti–Hirayama model in order to analyze the decay curves. In this model, it is assumed that the activator ions are randomly distributed in the host structure. The Inokuti–Hirayama equation can be formulated as follows:

\[ I_t = I_0 \exp \left( -\frac{t}{C_0^3/s} \right) \]

where \( s \) is the intrinsic lifetime of a single ion (0.85 ms in our case, obtained from the sample with the lowest Eu\(^{3+}\) concentration), \( C \) is the acceptor concentration, \( C_0 \) the critical concentration of acceptors, \( \Gamma \left( 1 - \frac{3}{s} \right) \) the gamma function, and \( s \) a parameter that depends on the type of interaction (for dipole–dipole interactions \( s = 6 \)). The critical concentration \( C_0 \) is defined as: \( C_0 = 3/(4\pi R_0^3) \), where \( R_0 \) is the critical transfer distance, which is defined as the distance between donor and acceptor at which the probability of energy transfer per unit time is equal to the probability of decay of the donor per unit time. Assuming a dipole–dipole character for the interaction between donor and acceptor ions, the energy transfer parameter \( Q \) is given by:

\[ Q = \frac{4\pi}{3} \Gamma \left( 1 - \frac{3}{s} \right) C(R_0)^3 \]

where for a dipole–dipole interaction \( \Gamma \left( 1 - \frac{3}{s} \right) = \Gamma \left( \frac{1}{2} \right) = \sqrt{\pi} = 1.77 \). The energy transfer parameter \( Q \) can also be described as follows:

\[ Q = \frac{4\pi}{3} \Gamma \left( 1 - \frac{3}{s} \right) C(C_{DA}\tau)^{3/2} \]

where \( C_{DA} \) is the donor–acceptor energy transfer parameter. By combining eqn (5) and (6), \( C_{DA} \) can be defined as:
rearranging the equation, we get the following expression:

\[
C_{DA} = \frac{(R_0)^6}{\tau}
\]  

(7)

The unit ‘number of ions per cm\(^3\)’ is used to describe the concentration of both donor and acceptors ions and the intrinsic lifetime of a single ion, \(\tau = 0.85\) ms, was obtained from the sample with the lowest concentration of Eu\(^{3+}\) (vide supra). By replacing \((R_0)^3\) in eqn (5) by the expression \(R_0^3 = 3/(4\pi C_0)\) and rearranging the equation, we get the following expression:

\[
\frac{C}{C_0} = \frac{R_0^3}{(4\pi C_3)}
\]  

(8)

from which we can estimate \(R_0\), the critical distance, determining the slope of the \(C/C_0\) vs. \((4\pi C)/3\) plot by a simple linear fitting. The data points and the fitted line are shown in Fig. 7 from where \(R_0 = 2.48\) Å and \(C_0 = 1.57 \times 10^{22}\) ions per cm\(^3\). The value of \(R_0\) is of the same order of magnitude as, but not comparable to, that obtained from Blasse’s equation (11.5 Å).

The measured decay curves are quite well described by the Inokuti–Hirayama model assuming a dipole–dipole interaction. All results indicate that Eu\(^{3+}\) ions are localized randomly in the structure ruling out the possibility of cluster formation.

4. Conclusions

We prepared Y\(_2\)WO\(_6\) based phosphors doped with different concentrations of Eu\(^{3+}\) via a classic solid-state reaction at high temperature. The luminescent properties of the resultant compounds were investigated. The excitation spectrum is dominated by a broad band consisting of the overlapping O\(^{2-}\)–Eu\(^{3+}\) and O\(^{2-}\)–WO\(_6^{6+}\) charge transfer bands, as well as three bands corresponding to the excitations of electrons from the Eu\(^{3+}\) ground state to different excited 4f levels. The emission spectra have a characteristic peak caused by the electric dipole \(^{5}D_0 \rightarrow ^{7}F_2\) transition centered at 610 nm. An emission band centered at about 450 nm originating from the (WO\(_6\))\(^{6-}\) groups of the host structure is also observed. Moreover, it is found that while the intensity of the band at 450 nm decreases, that of the band at 610 nm increases for dopant concentrations up to \(x = 0.14\) implying the presence of an energy transfer from the host to the Eu\(^{3+}\) ions.

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References