Luminescent Heterometallic Europium(III)-Lutetium(III) Metal-Organic Frameworks

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Synthesis

$$(2x)\text{EuCl}_3+(2-2x)\text{LuCl}_3+3\text{Na}_2(1,4\text{-}bdc)=\text{Eu}_x\text{Lu}_{1-x}(1,4\text{-}bdc)_3↓+6\text{NaCl}$$

XRD

100-180 °C: dehydration

$$\text{Eu}_x\text{Lu}_{1-x}(1,4\text{-}bdc)_3\cdot n\text{H}_2\text{O} \rightarrow \text{Eu}_x\text{Lu}_{1-x}(1,4\text{-}bdc)_3 + n\text{H}_2\text{O}$$

TGA

Acknowledgements

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Luminescent properties $\lambda_{\text{ex}}=280$ nm

5$^D_0$ excited state lifetimes and luminescence quantum yields

<table>
<thead>
<tr>
<th>$x_{\text{Eu}}$, (%)</th>
<th>$\tau_1$, ms</th>
<th>$\tau_2$, ms</th>
<th>$\Phi$, %</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>0.390</td>
<td>10±1</td>
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</tr>
<tr>
<td>60</td>
<td>0.435</td>
<td>11±1</td>
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</tr>
<tr>
<td>10</td>
<td>0.449</td>
<td>12±1</td>
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<td>6</td>
<td>0.459</td>
<td>16±1</td>
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<tr>
<td>4</td>
<td>0.392</td>
<td>22±1</td>
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<tr>
<td>2</td>
<td>0.367</td>
<td>22±1</td>
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Conclusions

1. At Eu$^{3+}$ concentration 1-20 at. %, heterometallic europium(III)-lutetium(III) terephthalates are formed as a mixture of (Eu$_x$Lu$_{1-x}$)$_2$bdc and (Eu$_x$Lu$_{1-x}$)$_2$bdc·4H$_2$O crystalline phases. At higher Eu concentrations, a single crystalline phase is formed, (Eu$_x$Lu$_{1-x}$)$_2$bdc·4H$_2$O.
2. All the synthesized samples containing Eu$^{3+}$ demonstrate bright red emission corresponding to $^5D_0\rightarrow^7F_j$ ($j=0-4$) transitions of Eu$^{3+}$ ion ($\lambda_{\text{ex}}=280$ nm).
3. Eu$^{3+}$ ion unevenly distributed between Ln$_3$bdc and Ln$_3$bdc·4H$_2$O phases: Ln$_3$bdc·4H$_2$O crystalline phase is enriched by Eu$^{3+}$ ions.
4. In Eu$_x$bdc·4H$_2$O, the local symmetry of Eu$^{3+}$ ion is pseudo-C$_3$. In (Eu$_x$Lu$_{1-x}$)$_2$bdc·4H$_2$O, the increase of Lu$^{3+}$ ions ratio leads to the Eu$^{3+}$ local symmetry distortion to C$_3$ or lower point group (symmetry). The local symmetry of Eu$^{3+}$ is proposed to be C$_3$ in anhydrous (Eu$_x$Lu$_{1-x}$)$_2$bdc.
5. $^5D_0$ excited state lifetimes are 4 - 4.8 times larger for Eu$^{3+}$ in Ln$_3$bdc crystalline phase than in Ln$_3$bdc·4H$_2$O due to the absence of luminescence quenching of Eu$^{3+}$ by coordinated water molecules.
6. The luminescence quantum yields of terephthalate ions decrease with the increase of europium concentration from 2 to 100 at. % Eu$^{3+}$ upon excitation into $S_1$ (4π*) singlet electronic excited state.