Low temperature sensitivity of upconversion emission in $\text{Y}_2\text{O}_3:\text{Yb,Tm}$ and $\text{Y}_2\text{O}_3:\text{Yb,Ho}$ powders

V. Lojpur¹, M. Nikolic², M. Medic², L. Mancic¹, O. Milosevic¹, M.D. Dramicanin²

¹Institute of Technical Sciences of SASA K.Mihailova 35/IV, Belgrade, Serbia
²Vinča Institute of Nuclear Science, University of Belgrade, P.O. Box 522, Belgrade, Serbia

Introduction

Phosphors are materials composed of a transparent host and an activator, typically a small quantity of a transition metal or rare earth ion. After absorbing a specific form of energy, these materials emit light in the ultraviolet (UV), visible (VIS) or infrared (IR) spectral regions. Rare earth (RE)³⁺ ion doped materials have been widely used as fluorescent and light-emitting diodes (LED), biological labels, lasers and components in a variety of display technologies. Because the absorption and emission properties of phosphors change with temperature, they could find applications in optical temperature sensing devices. Phosphor thermometry represents an optical technique for surface temperature measurements that is based on the time and temperature dependence of phosphorescence intensity. The fluorescent intensity ratio (FIR) is the foremost technique used to reduce the influence of measurement conditions and improve the sensitivity of the measurement. This simple, non-contact and precise method is applicable over a wide temperature range (from 10 K to 3000 K) and involves the comparison of intensities of two emission lines or areas in photoluminescent spectra. Herein, we discuss the structural and optical characterization of $\text{Y}_2\text{O}_3:\text{Yb,Tm}$ and $\text{Y}_2\text{O}_3:\text{Yb,Ho}$ powders synthesized using the spray pyrolysis method. We also examine their emission properties in the temperature range of 10 K to 300 K to explore for the first time the possibility of utilizing these materials in low temperature sensing applications.

Results and discussion

The powders obtained via spray pyrolysis exhibit a cubic crystal structure, e.g. Ip-7, that corresponds to the $\text{Y}_2\text{O}_3:\text{Yb,Tm}$ compound (PDF 87-2368). Fig. 2a provides the X-ray diffraction pattern of $\text{Y}_2\text{O}_3:\text{Yb,Tm, Ho}$ annealed at 1100 °C for 2 h. The typical morphology of particles synthesized using the spray pyrolysis method is shown in Fig. 2b. The resulting particles are spherical, sub-micron in size and un-agglomerated. A closer inspection reveals that the particles are composed of smaller primary subunits, which give rise to a grainy surface appearance. Significant particle porosity is also observed.

Materials and methods

Yttrium oxide powders doped with either of $\text{Yb}^{3+}, \text{Tm}^{3+}$ or $\text{Yb}^{3+}:\text{Ho}^{3+}$ were synthesized via spray pyrolysis. The precursor solutions were composed of $\text{Y(NO}_3)_3\cdot5\text{H}_2\text{O}, \text{Yb(NO}_3)_3\cdot5\text{H}_2\text{O}, \text{Tm}_2\text{O}_3$ and $\text{Ho}_2\text{O}_3$, in appropriate stoichiometric ratios for generating the following compositions: $\text{Y}_2\text{O}_3\cdot\text{Yb}_2\text{O}_3\cdot\text{Tm}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\cdot\text{Yb}_2\text{O}_3\cdot\text{Ho}_2\text{O}_3$. The nitrate salts were dissolved in distilled water, whereas the oxides were dissolved in hot nitric acid. The resulting precursors (containing either of $\text{Ho}^{3+}$ or $\text{Yb}^{3+}$ or $\text{Tm}^{3+}$) were atomized at 1.7 MHz using an ultrasonic (spherical) generator (Prufi Sonica-Pjema, Serbia) and then injected into a heated quartz tube by air flow (1.6 dm³/min). Aerosol atomization was performed at 900 °C. The droplet/particle residence time in the reactor was 21 s. The resulting powders were collected at the end of a quartz tube and thermally treated at 1100 °C for 24 h.

The up-conversion emission spectra of $\text{Y}_2\text{O}_3:\text{Yb,Tm}$ and $\text{Y}_2\text{O}_3:\text{Yb,Ho}$ were obtained using 978 nm laser excitation in the range of 10 K to 300 K. As shown in Fig. 3, three emission bands are observed for $\text{Tm}^{3+}$: a blue emission band (450-500 nm), a weak red emission band (600-680 nm) and a near infrared emission band (785-840 nm). The emission intensities of the red bands increase with decreasing temperature, whereas the blue and near infrared bands do not exhibit any obvious trends with varying temperature. As shown in Fig. 4, two emission peaks are observed for $\text{Ho}^{3+}$: a strong green emission peak centred at 550 nm and weak near infrared peak at 755 nm. Both emissions exhibit the same trends with increasing temperature, wherein the intensity significantly increases with decreasing temperature.

Table 1. Fitting results of the experimentally obtained FIRs in $\text{Y}_2\text{O}_3:\text{Yb,Tm}$ and $\text{Y}_2\text{O}_3:\text{Yb,Ho}$ powders annealed at 1100 °C for 24 h

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Ho³⁺</th>
<th>Yb³⁺, Tm³⁺</th>
<th>Yb³⁺, Ho³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>0.65</td>
<td>0.17</td>
<td>0.20</td>
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<tr>
<td>178</td>
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<td>0.20</td>
</tr>
<tr>
<td>300</td>
<td>0.68</td>
<td>0.17</td>
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</tbody>
</table>

Table 2. Fitting results of the experimentally obtained FIRs in $\text{Y}_2\text{O}_3:\text{Yb,Ho}$ powders annealed at 1100 °C for 24 h

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Thermalization process occurs between the Stark components of the excited levels, the emitted intensities are proportional to the population of each energy level, as shown in Fig. 5.

Conclusion

Yttrium oxide powders doped with either $\text{Yb}^{3+}, \text{Tm}^{3+}$ or $\text{Yb}^{3+}:\text{Ho}^{3+}$ were synthesized via the spray pyrolysis method. Spherical, sub-micron, un-agglomerated porous particles, composed of smaller primary subunits, exhibit a significant temperature sensitivity of up-conversion emission. In the case of $\text{Y}_2\text{O}_3\cdot\text{Tm}^{3+}$, the temperature dependence of the emission intensity ratios of excited states with a large energy difference is due to the thermalization between the Stark components in the excited states. In the case of $\text{Y}_2\text{O}_3\cdot\text{Yb}^{3+},\text{Ho}^{3+}$, emissions occur from adjacent excited states to two lower states, so the temperature dependence of the emission intensity ratio is a consequence of the thermalization between adjacent excited states. The observed temperature sensitivity of both systems is significant enough for thermometry applications in the range of 10 to 300 K.

Literature

F. Vetrone, J. C. Boyer, J. A. Capobianco, A. Speghini, M. Bettinelli, Significance of $\text{Yb}^{3+}$ concentration on the up-conversion mechanisms in codoped $\text{Y}_2\text{O}_3\cdot\text{Er}^{3+}$ nanocrystals, J. Appl. Phys. 96 (2004) 661-667.

Acknowledgement

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