White light emission materials based on simultaneous Tb^{3+}, Eu^{3+} and Dy^{3+} doping in $CaWO_4$ single-phased

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Tungstates activated by trivalent rare earth ions (RE^{3+}) can be used for many optical devices [1]. Over the last decades, the solid-state lighting sources based on phosphor converted white light-emitting diodes (pc-WLEDs) has improved to overtake fluorescent lighting types because of many advantages such as high ecofriendliness, brightness, low power consumption and fast response time [2]. Here we report preparation and spectroscopic properties of the single phase new highly luminescent white emitting of the $Tb^{3+}/Eu^{3+}/Dy^{3+}$ triply-doped $CaWO_4$ material. The $CaWO_4$:xTb^{3+},xEu^{3+},xDy^{3+}(x mol% of the Ca^{2+} amount) materials were prepared by fast coprecipitation method at room temperature with stoichiometry aqueous solutions of Na_2WO_4, $CaCl_2$ and $RECl_3$ (RE^{3+}: Tb, Eu and Dy). The XPD measurements revealed the $CaWO_4$:RE^{3+} particles belong to the tetragonal scheelite phase with $I4_1/a$ (#88) space group.

The emission spectra exhibit only narrow emission bands arising from the doping Tb^{3+}, Dy^{3+} and Eu^{3+} ions. These emission bands are assigned to the 4f transitions from the $^4F_{9/2}$ (Dy^{3+}), $^5D_4$ (Tb^{3+}) and $^5D_0$ (Eu^{3+}) emitting states to their energy levels corresponding to (in nm): 702 $^5D_0 \rightarrow {}^7F_4$($Eu^{3+}$), 655 $^5D_0 \rightarrow {}^7F_3$($Eu^{3+}$), 615 $^5D_0 \rightarrow {}^7F_2$($Eu^{3+}$), 592 $^5D_0 \rightarrow {}^7F_1$($Eu^{3+}$), 575 $^4F_{9/2} \rightarrow {}^6H_{13/2}$($Dy^{3+}$), 544 $^5D_4 \rightarrow {}^7F_5$($Tb^{3+}$), 488 $^5D_4 \rightarrow {}^7F_6$($Tb^{3+}$), 478 $^4F_{9/2} \rightarrow {}^6H_{15/2}$($Dy^{3+}$) (Fig. left). The presence of the emission bands assigned to the doping Dy^{3+}, Tb^{3+} and Eu^{3+} ions suggests clear evidence of non-radiative energy transfer from $^4F_{9/2}$ (Dy^{3+})$\rightarrow {}^5D_4$ (Tb^{3+})$\rightarrow {}^5D_0$ (Eu^{3+}) emitter states (Fig. center). The white light emission was mainly reached for 5.0 mol% RE^{3+} with x: 0.333; y: 0.352 CIE (*Commission Internationale l'Éclairage*) coordinates (Fig. right).

These phosphors could be suitable as triply-doped white light emitters with only single-phased for solid state lighting applications. Since warm white light is preferred for reading, while cold white light is preferred for public lighting the tunability of this single-phase emitting phosphor exhibit promising applications for solid-state lighting.

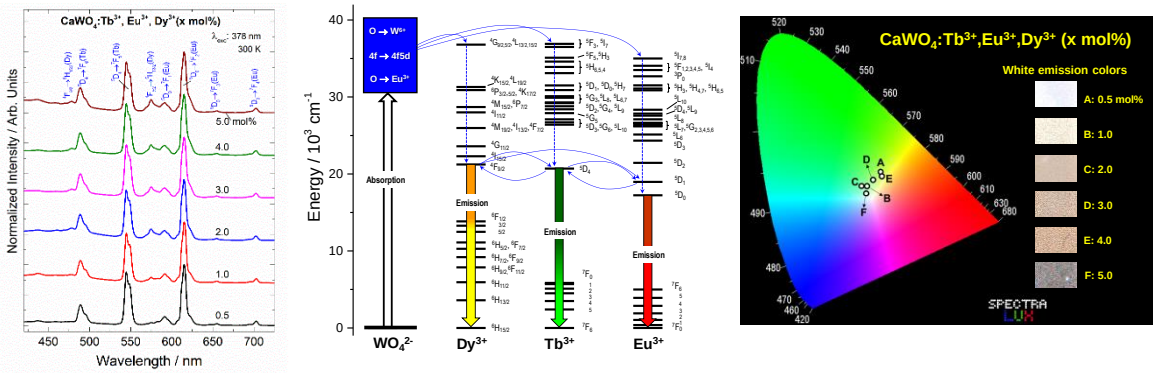

Fig. The emission spectra (left); partial energy level diagram exhibiting the transitions involved in the energy transfers (curve arrows), non-radiative decays (dashed arrows) $WO_4^{2-} \rightarrow RE^{3+}$, as well as their simultaneous emission (middle); CIE chromatic diagram showing the coordinates for the $CaWO_4$:xEu^{3+},xTb^{3+},xDy^{3+}; x: 0.5 – 5.0 mol%) materials under excitation at 378 nm.

References

1. H.P. Barbosa, J. Kai, I.G.N. Silva, L.C.V. Rodrigues, M.C.F.C. Felinto, J. Hölsä, O.L. Malta, H.F. Brito, J. Lumin. 170 (2016) 736–742.
2. J. Hye Oh, S. Ji Yang, Y. Rag Do, Light Sci. Appl. 3 (2014) e141.