Electronic Supplementary Information

Probing the structure, morphology and multifold blue absorption of a new red-emitting nanophosphor for LEDs†

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Preparation of GCZO:Eu^{3+} nanophosphor:

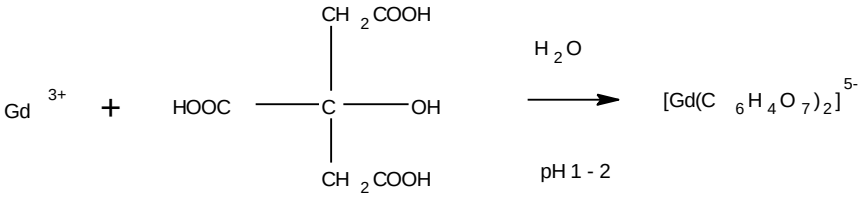
To sum up the whole in a reaction:

$$Gd_2O_3 + CaO + ZnO \rightarrow Gd_2CaZnO_5$$

For this a modified citrate-gel combustion method was employed to prepare GCZO:Eu^{3+} nanophosphor. AR grade salts from MERCK were used for the experiments. Optimal amount of precursors in the form of nitrates for the complete process were calculated using the above chemical reaction. In the experiment, the rare earth oxides of Gd and Eu were dissolved in stoichiometric amount of concentrated nitric acid to make $Gd_2(NO_3)_3$ and $Eu_2(NO_3)_3$, respectively. Then the required metal nitrates from calcium carbonate and zinc oxide were also prepared similarly and added to the above solution. According to the following equations:

$$Eu_2O_3 + 6\,HNO_3 \rightarrow 2\,Eu(NO_3)_3 + 3H_2O$$
$$Gd_2O_3 + 6\,HNO_3 \rightarrow 2\,Gd(NO_3)_3 + 3H_2O$$
$$CaO + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$$
$$ZnO + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$$

All these nitrate precursor solutions were taken together and were rigorously stirred with citric acid (metal to citric acid is 1:4 molar ratio) dissolved in water for 15 minutes. The overall pH of the solution was maintained around 1-2 in order to obtain size controlled nanophosphor particles. Citric acid acts as the monomer to form transparent complex gel from the initial solution upon drying overnight in an oven at 75^{o}C. Further the gel was taken in a quartz boat and fired in air in a pre-heated furnace at 800^{o}C for 15 minutes. Initially in the furnace the citrate complex gel transforms to a black fluffy mass nearly ten times the gel volume and starts decomposing to CO_2 and H_2O vapours, ending the decarboxylation of citric acid which occurs at temperatures above 175^{0}C. Generally Gadolinium ion with citric acid makes a soluble transparent complex $[Gd(C_6H_4O_7)_2]^{5-}$ as following:



[Gd (Hcit) $(H_2O)_2$.(H_2O)]n, Hcit = C (OH) (COO^-) $(CH_2COO^-)_2$ intermediate polymer like compounds crystallize as monoclinic, P $2_{1/n}$ linear polymers. Our sample also makes a similar complex chain but with Ca^{2+} and Zn^{2+} in the lattice. And after 15 minutes a white fluffy mass of GCZO:Eu^{3+} nanophosphor is obtained which could easily be crushed to ultra-fine powder used for further characterization. Resultant complex compound is insoluble in most polar and non polar solvents. Synthesis of size-controlled nanophosphor particles with high yield (~90%) is one of the highlights of this method.
Final by-products were the result of the following:

$$CaCO_3 \rightarrow CaO + CO_2$$
$$Gd(NO_3)_3 \rightarrow Gd^{3+} + 3\,O^- + 3\,NO_2$$

So, finally Gd^{3+} ions, 3 O^- along with CaO and ZnO result in the required lattice system. Europium concentration in the lattice was varied from 0 to 20 mol %.