Upconversion fluorescence Jump in PbF_2 nanocrystal doped with Er^{3+}/Yb^{3+}

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The oxyfluoride glass ceramics(GC) doped with rare earth ions(Res) have attracted great concern because of their upconversion fluorescence intensity jumping 200 times after the pioneer work by Wang and Ohwaki in 1993[1]. However, the physics mechanisms of fluorescent multiplication have not been cleared up to now. This work research the bottleneck question by the NC structure and electron cloud disorder of the Re^{3+}.

The oxyfluoride glass ceramics(GC) were prepared by conventional melting-quenching method. β-PbF_2 nanocrystals(NC) doped with Er^{3+}/Yb^{3+} were formed in the GCs. The β-PbF_2:Er^{3+}/Yb^{3+} NC were embedded in the oxide matrix. The transmission electron microscopy (TEM) and the model of the GC were shown in Fig1.
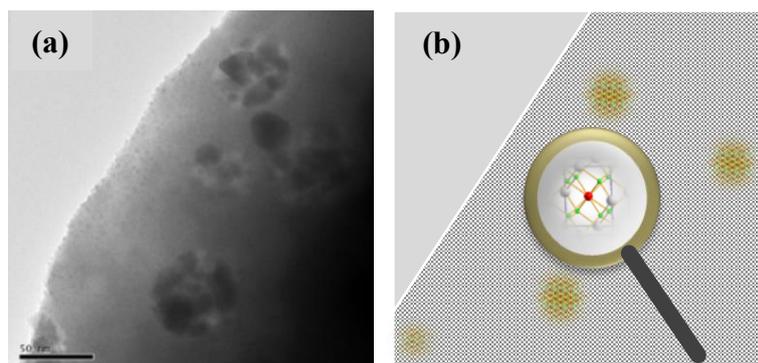
Figure 1. The TEM image(a) and mode(b) of fluoride nanocrystals embedded in oxyfluoride glass ceramics. The blace bar is 50nm in Fig1(a)

β-PbF_2 is a cubic structure crystal. Re^{3+} ions are selectively incorporated into the β-PbF_2 NCs to substitute for lead ion (Pb^{2+}) and the fluoride ion interstitial(F_i^-) mechanism is as a charge compensation mechanism in Re^{3+} doping oxyfluoride GCs. β-PbF_2 doping with Re^{3+} is called pseudo-cubic structure crystal. Based on our previous work [2,3], there exists a structure change of NCs in oxyfluoride GCs induced by different doping concentration of Re^{3+} and heat treatment temperature. In our system, on account of doping level of Re^{3+} and heat treatment temperature, NCs undergo a structure change from pseudo-cubic structure to tetragonal structure of $Pb_2Re_2F_{10}$. Crystal structure of the NCs were investigate by XRD, as showed in Figure 2, compared to standard diffraction peaks of β-PbF_2.The peak positions of NCs doped with Re^{3+} ions move towards a higher angle which indicates the shrinkage of the β-PbF_2 lattice and confirms the incorporation of Re^{3+} ions into the β-PbF_2 NCs. Besides, there existing splits of main peaks pattern, the splits reflect NCs in GCs are tetragonal structure, (as inset pattern illustrating in Figure 2).

The structure change from pseudo-cubic structure β-PbF_2:Re^{3+} to $Pb_2Re_2F_{10}$ actually is the process of the lattice shortened along the A axis and B axis while stretched along the C axis. In
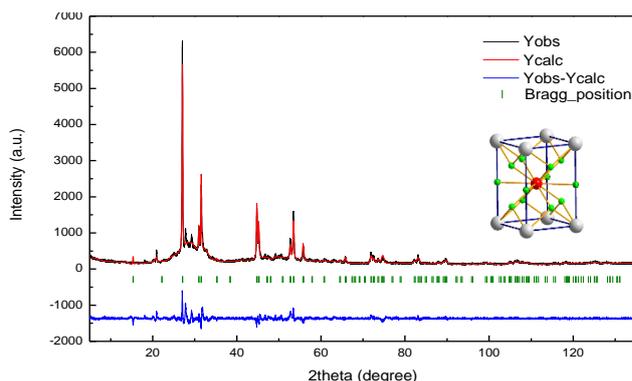
Figure 2. Rietveld analyses for the X-ray diffraction patterns. The positions of the Bragg diffractions are indicated by vertical green bars. The difference between the experimental (black line) and the calculated (red line) intensities from the model is shown by the plot in the lower part of the diagram (blue line). The insert is cell structure with composition formula $Pb_2Re_2F_{10}$.

the pseudo-cubic, the distance of interstitial fluoride ions (F^-_i) between Pb^{2+} equals the distance of F^-_i between Re^{3+}, while in the $Pb_2Re_2F_{10}$, the distance of F^-_i between Pb^{2+} is larger than the distance of F^-_i between Re^{3+}. So, the process of structure change from pseudo-cubic structure to tetragonal structure actually makes F^-_i be closer to Re^{3+} and aloof from Pb^{2+}. In order to prove our conjecture, the electron cloud of pseudo cubic structure and tetragonal structure was simulated using ab initio computer simulation methods (embodied in the Cambridge Sequential Total Energy Package module, CASTEP) respectively. The Perdew-Burke-Ernzerhof (PEB) generalized gradient approximation (GGA) as the exchange-correlation function and Ultrasoft as the pseudo-potential were chosen. This simulation result just was shown in the figure 3.In the pseudo-cubic structure, the electron cloud of F^-_i tends to be closer to the Pb^{2+} than to Yb^{3+}, while in tetragonal structure, F^-_i tends to be closer to the Yb^{3+} than to Pb^{2+}, just opposite to the situation in the pseudo-cubic structure. The distance of Re^{3+} goes to shorter. The simulation result is consistent with the theoretical models established previous in this paper.
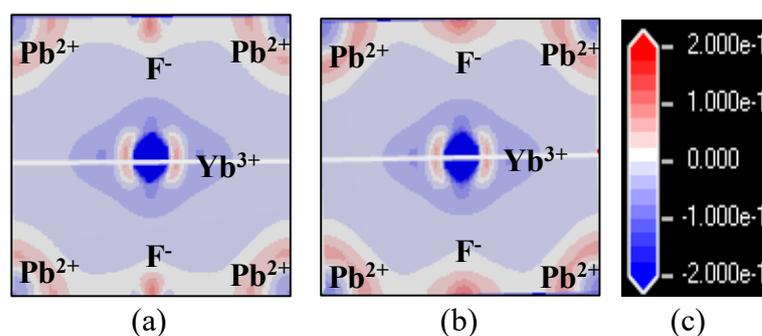
Figure 3.   The electron cloud distortion of F^-_i in pseudo-cubic(a) and tetragonal structure(b). (a)The electron cloud in (100) plane of pseudo-cubic structure. (b)The electron cloud in (100) plane of tetragonal structure. (c) The intensity standard rule.

In one word, the structure of β-PbF_2:Re^{3+} undergoes a structure change from pseudo-cubic structure to tetragonal structure $Pb_2Re_2F_{10}$ with a certain concentration. The interstitial F^- induced the cell extending and the distance of Re^{3+} shortening. The distance of Re^{3+} shorter, upconversion fluorescence intensity higher.

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