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Influence of local phonon energy on quantum efficiency of Tb^{3+}-Yb^{3+} co-doped glass ceramics containing fluoride nanocrystals

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Abstract: The Tb^{3+} single-doped and Tb^{3+}-Yb^{3+} co-doped glass ceramics with the precipitation of CaF_2, CaF_2-SrF_2 solid state solution and SrF_2 nanocrystals were designed and prepared by taking different amounts of CaF_2 and SrF_2 as the starting fluorides to investigate the influence of the crystalline phase on the total quantum efficiency. The formation of the fluoride nanocrystals and the incorporation of the doped rare earth ions into the fluoride nanocrystals were proved by the XRD measurement. The energy transfer from Tb^{3+} to Yb^{3+} was studied by the steady and time resolved spectra. The total internal quantum efficiencies were calculated based on the measured Tb^{3+} lifetime, which was about 10.5% improved in the SrF_2 nanocrystals precipitated glass ceramics compared with that in the CaF_2 nanocrystals precipitated glass ceramics mainly due to the lower phonon energy environment. Meanwhile, the total external quantum efficiencies were evaluated with the integrating sphere measurement system, which were 18.6%, 19.3% and 24.4%, respectively, for the CaF_2, CaF_2-SrF_2 and SrF_2 nanocrystals precipitated glass ceramics. Additionally, obvious difference between the calculated total internal quantum efficiency and the measured total external quantum efficiency was also discussed.

Keywords: glass ceramics; crystalline phase; rare earths; down conversion luminescence; quantum efficiency

Rare earth (RE) ions doped luminescent materials have been widely developed as white light emitting diodes, solid-state lasers, optical amplifiers, and long lasting phosphors, etc. Recently, they have also been explored as spectral conversion materials to improve the photovoltaic conversion efficiency of crystal silicon solar cell[1]. As the mismatch of incident solar photon energy to the band gap of silicon semiconductor is one of the major reasons that are responsible for the energy loss during the photovoltaic conversion process, the RE doped spectral conversion materials that can convert one incident high-energy photon into two low-energy photons around 1000 nm (corresponding to the highest spectral response of the crystal silicon) may have potential application for the improvement of photovoltaic conversion efficiency by putting them in the front surface of the silicon solar cells[2,3].

By now, the researches on how to use the RE ions to realize this spectral conversion have been widely carried out and Yb^{3+} has been inevitably selected as the luminescent center as its $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition gives off a broadband emission around 1000 nm. Various energy sensitizers for Yb^{3+} have been explored, such as the f-f transition RE ions of Tb^{3+}, Pr^{3+}, Tm^{3+}, Ho^{3+} and Er^{3+} [4–9], the f-d transition RE ions of Ce^{3+}, Eu^{2+} and Yb^{2+} [10–12], Cr^{3+} [13], Bi^{3+} [14] and ZnO semiconductor[15]. Among them, the cooperative energy transfer efficiency by taking Pr^{3+}, Tm^{3+} and Tb^{3+} as sensitizers for Yb^{3+} has been systematically compared in different hosts, such as the $GdAl_3(BO_3)_4$ powder and CaF_2 nanocrystals precipitated glass ceramics, to investigate the most efficient spectral conversion condition[16,17]. Besides optimizing the combination of RE ions and the doping concentration, the improvement of quantum efficiency can also be achieved by choosing matrix with low phonon energy as the doping host, such as the glass ceramics with the precipitation of LaF_3 nanocrystals, the $NaYF_4$ powder, the YF_3 crystal, etc.[6–8]. It is true that the local crystal field with low phonon energy can promote the radiative emission and the cooperative energy transfer between the RE ions and therefore obtain high quantum efficiencies, however, how much the local phonon energy will influence the quantum efficiency was rarely reported. In addition, there may be other possibilities that could influence the quantum efficiency, such as differences in donor-acceptor inter-ionic distances, non-uniform dopant distribution, etc. In this research, the widely reported Tb^{3+}-Yb^{3+} couple was taken as an example to generally study the influence of crystalline phases on the quantum efficiency in the CaF_2, CaF_2-SrF_2 solid state solution and SrF_2 nanocrystals precipitated glass ceramics. The total internal quantum efficiencies of the Tb^{3+}-Yb^{3+} couples were calculated

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from Tb^{3+} lifetime under the excitation of Tb^{3+}:$^5D_4$ energy level. Meanwhile, the total external quantum efficiency were also evaluated by using an integrating sphere measurement system and further compared with the expected internal quantum efficiency.

1 Experimental

The $0.3TbF_3$ single-doped and $0.3TbF_3$-$3.0YbF_3$ co-doped as-made glasses with the composition of $45SiO_2$-$23Al_2O_3$-$(32–x)CaF_2$-$x SrF_2$ (x=0, 16, 32) were prepared by the conventional melt quenching method. The raw materials of SiO_2, CaF_2, SrF_2, Al_2O_3, TbF_3, and YbF_3 were mixed homogenously according to the composition ratio and melted at 1400 ºC for 45 min in a covered corundum crucible in air. The melts were poured onto a cold stainless steel plate and then pressed by another plate. The glass ceramics were obtained by heat treatment of the as-made glasses at 630 ºC for 2 h. The X-ray diffraction measurements were carried out using a Rigaku D/MAX-RA diffractometer with Cu Kα as the incident radiation source. The Photoluminescence (PL) and photoluminescence-excitation (PLE) spectra and the fluorescence decay curves were recorded with a FLS920 fluorescence spectrophotometer. The external quantum yield was evaluated by using the integrating sphere measurement system (Labsphere) with 488 nm Ar^+ laser as the excitation source.

2 Results and discussion

Fig. 1 shows the XRD patterns of the Tb^{3+} single-doped and Tb^{3+}-Yb^{3+} co-doped glass ceramics, in which the starting fluorides for the as-made glasses are CaF_2, CaF_2-SrF_2 and SrF_2, respectively.

It can be clearly observed that for the CaF_2 or SrF_2 single included as-made glasses, the cubic CaF_2 and SrF_2 were formed inside the glass matrix after the heat treatment. While for the CaF_2 and SrF_2 both included as-made glass, neither the CaF_2 nor the SrF_2 crystals were independently precipitated, instead, the CaF_2-SrF_2 solid state solution was formed. Since the CaF_2 and SrF_2 crystals are both cubic with similar lattice parameter, the formation of CaF_2-SrF_2 solid state solution during the heat treatment process is easy to understand. From the XRD patterns it can be estimated that the sizes for the precipitated crystals are all in nano scale around 20 nm. It can also be observed from Fig. 1 that there is an obvious large angle shift of the diffraction peak when comparing the XRD patterns for the $0.3Tb^{3+}$-$3.0Yb^{3+}$ co-doped and the $0.3Tb^{3+}$ single-doped glass ceramics with the precipitation of CaF_2, CaF_2-SrF_2 solid state solution and SrF_2 nanocrystals, respectively. The shift of the diffraction peak indicates the incorporation of the Yb^{3+} ions into the precipitated fluoride crystals. According to previous studies, most of the Tb^{3+} and the Yb^{3+} ions were incorporated into the precipitated fluoride crystals and thus led to the distortion of the crystal lattice due to the mismatches in ironic radii and valence states[18–21]. Besides, the incorporation of rare earth ions into the crystalline phase was also proved by using EDS characterization[20,22,23]. As the Tb^{3+} concentration is quite low in this experiment, the shift of the diffraction peak position is not obvious in those single-doped glass ceramics. In addition, it is clearly observed that the shift in the SrF_2 nanocrystals precipitated glass ceramics is the largest one among the three groups. This can be attributed to the larger mismatch of the ironic radius between Yb^{3+} ions and Sr^{2+} ions compared with that between Yb^{3+} and Ca^{2+}. Or another possibility is that more Yb^{3+} ions can be incorporated into the SrF_2 lattice due to the higher solubility.

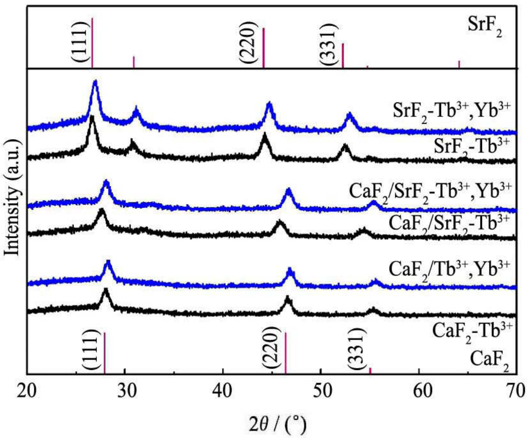

Fig. 1 XRD patterns of the Tb^{3+} single-doped (black solid lines) and Tb^{3+}-Yb^{3+} co-doped (blue solid lines) glass ceramics, in which the starting fluorides for the as-made glasses are CaF_2, CaF_2-SrF_2 and SrF_2, respectively (The XRD patterns for SrF_2 (PDF#06-0262) and CaF_2 (PDF#65-0535) are also shown for comparing)

The longitudinal optical phonon energy for CaF_2 and SrF_2 are 466 and 366 cm^{-1}, respectively, and for the CaF_2-SrF_2 solid state solution, the phonon energy is in between[24]. In this case, the influence of the local phonon energy on the total quantum efficiencies of Tb^{3+} and Yb^{3+} can be compared in those glass ceramics. In this study, low concentrations of Tb^{3+} and Yb^{3+} were doped to avoid the possibility of concentration quenching brought by the local accumulation of RE ions inside the precipitated crystal phase after the heat treatment.

The PLE and PL spectra of the Tb^{3+} single-doped and Tb^{3+}-Yb^{3+} co-doped glass ceramics with various precipitations are shown in Fig. 2. From the PLE spectra on the left side it is observed that the excitation band corresponding to Tb^{3+} 547 nm emission is situated at 484 nm, which is due to Tb^{3+}:$^7F_6 \rightarrow {}^5D_4$ absorption, as shown in Fig. 3. The PLE spectra of Yb^{3+} NIR emissions at 980 nm were also recorded, which are in good agreement with Tb^{3+}:$^7F_6 \rightarrow {}^5D_4$ absorption in all the three co-doped glass ceramics, indicating the performance of energy