

Effect of nanocrystals on up-conversion luminescence of $\text{Er}^{3+}, \text{Yb}^{3+}$ co-doped glass-ceramics

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Different up-conversion luminescent spectra of Er^{3+} ions were observed in the oxyfluoride glass-ceramics. The ratio of two fluorides in the original compositions was modified in order to form different nanocrystals. The intensity of up-conversion luminescence increased sharply when the ratio of PbF_2 and CdF_2 was 40:10. The data of differential thermal analysis and X-ray diffraction were used to explain the optimization fluoride ratio. The intensity of up-conversion luminescence is not only decided by the crystallizability but also mainly related with the stoichiometric proportion of fluoride nanocrystals in the glass-ceramics.

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A new class of transparent glass-ceramics attracted much attention in the past decades^[1,2], in which the fluoride nanocrystals doped with rare earth ions were dispersed in an oxide network. The optical properties of rare earth ions in oxyfluoride glass depend on the fluoride nanocrystals, and the mechanical properties depend predominantly on the oxide host. Hence, the oxyfluoride glass-ceramics are promising materials for optical amplifiers and laser up-conversion applications^[3,4]. Wang *et al.*^[4] prepared $\text{Er}^{3+}, \text{Yb}^{3+}$ co-doped transparent oxyfluoride glass-ceramics firstly. And then many researchers^[5-7] investigated the up-conversion characteristics of Er^{3+} in glass-ceramics. Glass-ceramics showed efficient infrared-to-visible up-conversion luminescence under infrared laser excitation. As we know, the formation of fluoride nanocrystals was the main reason, which caused high efficient up-conversion luminescence.

In aluminosilicate glass, it is easy to form fluoride nanocrystals. Most of investigations focused on preparing of transparent glass-ceramics and up-conversion properties of rare earth ions under infrared laser excitation. However, the properties of nanocrystals, which are decided by the stoichiometric and treatment process, are very important to prepare high efficiency up-conversion glass-ceramics. Some groups thought the rare earth ions were doped in $\text{Cd}_x\text{Pb}_{1-x}\text{F}_2$ by measurements of fluorescence and X-ray diffraction (XRD)^[8,9]. Tikhomirov *et al.*^[10] concluded that the rare earth ions were doped in PbF_2 using transmission electron microscopy (TEM) and Raman spectroscopy. There are no publications about stoichiometric proportion of nanocrystals and related up-conversion luminescent intensities. In our experiments, the optimum ratio of PbF_2 and CdF_2 was found, which was different from the previous results^[4-7]. The up-conversion luminescence intensity of Er^{3+} doped in the oxyfluoride glass-ceramics increased 200 times compared with the oxyfluoride glass. Nevertheless, up-conversion luminescent intensity would re-increase 20 times under the optimum ratio of PbF_2 and CdF_2 in glass-ceramics. Moreover, different Pb/Cd ratios caused different intensities ratios of red and green

up-conversion luminescences.

Oxyfluoride glasses with compositions of $30\text{SiO}_2 \cdot 15\text{Al}_2\text{O}_3 \cdot (50-x)\text{PbF}_2 \cdot x\text{CdF}_2$ doped with $4\text{ErF}_3 \cdot 1\text{YbF}_3$ ($x = 0, 10, 22$, whose labels are b, c, d, respectively), which are high purity reagents (except for CdF_2), were prepared. The 10-g batches of the raw materials were melted in covered Pt crucibles at 1000 °C and in the atmosphere for 120 minutes. The melts were poured onto a steel plate and then annealed for 8 hours at the nucleation temperature (450 °C) of the oxyfluoride glass measured by differential thermal analyzers. Sample a, which was not heat-treated, has the same compositions as sample d. The samples were cut, polished and subjected to optical measure at room temperature. The size of all samples was $15 \times 15 \times 2.7$ (mm). XRD spectra were carried out using a D/Max-2500 system X-ray diffractometer that produced $\text{Cu } K_\alpha$ radiation. Scanning speed of XRD was 4 °/min. Up-conversion fluorescent spectra were measured by a spectrofluorimeter (SPEX Fluorolog-2) under the 980-nm laser excitation. The exciting power was about 67 mW.

Figure 1 shows the up-conversion spectra of Er^{3+} ions in the glass (sample a) and glass-ceramics (samples b, c, d) with different nanocrystals. The intensity of up-conversion luminescence of Er^{3+} ions in the glass-ceramics increases about two orders of magnitude than those in the glass under the same measuring condition. The radiation peaks are located at 550 and 665 nm, corresponding to the $^2S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of Er^{3+} ions, respectively. The strongest radiation peak is located at 550 nm. The different nanocrystal structure influences the up-conversion luminescent intensity and the intensity ratio of 550- and 665-nm emissions. In the process of the up-conversion luminescence of Er^{3+} ions, green up-conversion luminescence is caused from the excited state absorption, while red up-conversion luminescence could result from the three-photon absorption^[11]. The electrons located at the ground state absorb three infrared photons and transit to $^4G_{11/2}$ and $^2H_{9/2}$ levels under the excitation of 980-nm laser. And then the energy of

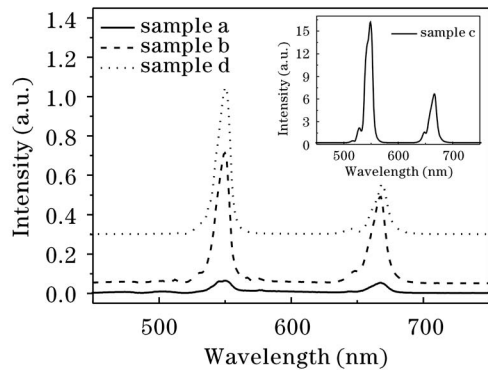


Fig. 1. Up-conversion luminescent spectra of Er³⁺ ions in the glass-ceramics with different compositions of (50 - x)PbF₂ · xCdF₂ for (sample b) x = 0, (c) x = 10, (a and d) x = 22.

the excited electrons are distributed to ⁴F_{9/2} level of Er³⁺ ions and ²F_{5/2} level of Yb³⁺ ions by the cross relaxation process. The red up-conversion luminescence of Er³⁺ ions is caused by the ⁴F_{9/2} → ⁴I_{15/2} transition. This energy cross relaxation could happen in the situation that the rare earth ions exist in the fluoride nanocrystals with the low phonon energy. In the compositions of 30SiO₂·15Al₂O₃ · (50 - x)PbF₂ · xCdF₂·4ErF₃·1YbF₃ (x = 0, 10, 22), the crystal symmetry is the highest when the value of x is 0 (nanocrystals are pure PbF₂). The energy loss in the cross relaxation becomes smaller with decreasing x from 22, 10 to 0. Relative intensity of red up-conversion luminescence produced by energy transfer enhances more in comparison with green up-conversion luminescence with intensity ratios of 0.54, 0.76, 0.96, respectively. When x is not equal to 0, a part of Pb position is replaced by Cd ions. Crystal symmetry is broken and the phonon energy of the crystallites is changed. The efficiency of the cross relaxation would decrease due to the fact that the phonon energies are different in the PbF₂ and Cd_xPb_{1-x}F₂ nanocrystals, which would lead to decrease in relative intensity of red up-conversion luminescence. The symmetry of the crystal field could be changed by co-doping Cd.

In the oxyfluoride glasses, PbF₂ and CdF₂ are used to form nanocrystals. Luminescent mechanisms of rare earth ions in oxyfluoride glasses are generally researched. However, it is important to seek the optimization ratio of PbF₂ and CdF₂ for practical application. The intensity of up-conversion luminescence enhances about 200 times in glass-ceramics than that in glass, as shown in Fig. 1. The obvious difference is attributed to the nanocrystals embedded in glass host. In order to gain nanocrystal information, the XRD of the oxyfluoride glass (sample a) and glass-ceramics (samples b, c, and d) were measured. In the XRD patterns, the marked differences from envelope curve to sharp peaks indicate the formation of nanocrystals in glass (Fig. 2). The diffraction patterns show a typical face-centered-cubic (fcc) array compatible with β-PbF₂ structure after heat treatment for the samples b, c, and d. The full-width at half-maximum (FWHM) of XRD gradually broadens with increasing content of CdF₂. But the patterns of XRD curves do not change, which are still corresponding to a fcc structure. It indicates that fluoride nanocrystal structures deform gradually with the increase of CdF₂ content. We believe

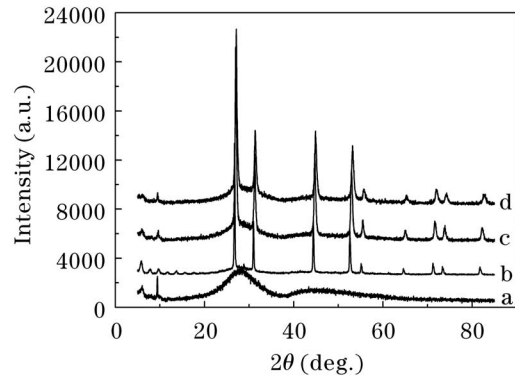


Fig. 2. XRD spectra of the glass (a) and the glass-ceramics with different compositions of (50 - x)PbF₂ · xCdF₂ for (b) x = 0, (c) x = 10, (d) x = 22.

that Cd ions would replace the position of Pb ions and lead to the deformation of nanocrystal structures. Kukkonen *et al.*^[8] proved that Er³⁺ preferentially partitions to the PbF₂ phase and not to a complex Pb_xCd_{1-x}F₂ by high-resolution TEM and energy dispersive spectra. Comparing with fluoride, the content of Er ions is very small. So, the main reason of the deformation of nanocrystals structure is from the different cation in fluoride, the structure of nanocrystals is Pb_xCd_{1-x}F₂. At the same time, in order to explain the reasons of nanocrystal formation, the differential thermal analysis (DTA) curves were measured, as shown in Fig. 3. The results show us the transition temperature and the nucleation temperature of samples. When Pb/Cd ratio of the oxyfluoride glass-ceramics is 28:22, the transition temperature and nucleation temperature are 420 and 445 °C respectively, while for samples with only CdF₂ nanocrystals they are 430 and 485 °C respectively. It indicates that the nucleation temperature of the glass-ceramics with CdF₂ is higher than that of the glass-ceramics with PbF₂/CdF₂. The existence of CdF₂ increases the nucleation temperature of fluoride nanocrystals. Interestingly, neither absorption peaks of PbF₂ nor the peaks of CdF₂ appear in the DTA curves. It implies that there is one nanocrystal phase formed in the oxyfluoride glasses, which is a complex Pb_xCd_{1-x}F₂. We believe that PbF₂ phase could be formed easily due to the low nucleation temperature. However, the existences of Cd make nanocrystals be formed difficultly, decrease the Er³⁺ solubility, and further influence the luminescent intensity.

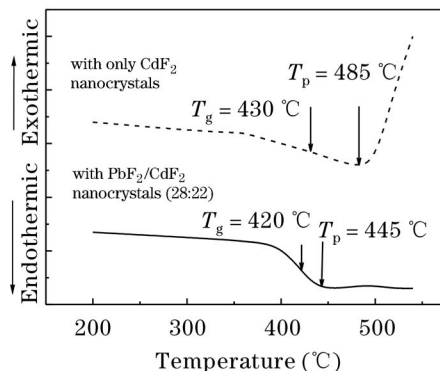


Fig. 3. DTA curves of the samples.

The TEM measurement indicated the shape of nanocrystals like spheroidal particles^[9,10]. So, the nanocrystal size of fluoride can be estimated by Scherrer's equation

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where K is the crystallite shape constant, β is the FWHM of the peak in XRD spectra, θ is Bragg angle, and λ is X-ray wavelength. The nanocrystal sizes are about 40, 23, 20 nm in samples b, c, and d, respectively. According to the estimated results, it is more difficult to form $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$ phase with increasing Cd content. After heat treatment, the transmission of sample b was poor due to the good tendency towards devitrification. The low nucleation temperature of PbF_2 makes sample b easy to form nanocrystals^[6].

The lattice constant of the fcc crystal can be calculated by the peak positions of XRD and indices of crystallographic plane according to

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2), \quad (2)$$

where a is the lattice constant and h, k, l are the indices of crystallographic plane. The lattice constants a corresponding to samples b, c, and d are 0.577, 0.573, and 0.570 nm, respectively. Under the same preparation method and measurement condition, the reason of the decreasing lattice constant is the increasing quantity of CdF_2 in the samples. The atomic radius of Cd (0.097 nm) is smaller than that of Pb (0.129 nm). In the forming process of the nanocrystals, the smaller Cd ions occupy the position of the larger Pb ions in $\beta\text{-PbF}_2$ nanocrystals, which lead the lattice constant to be decreased and the nanocrystals $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$ to be formed.

Under the same measuring condition, the intensities of the up-conversion luminescence are different in the samples with different Pb/Cd ratios. As shown in Fig. 1, the intensity of up-conversion luminescence is maximum when the ratio of PbF_2 and CdF_2 is 40:10. This ratio differs from the compositions (28:22) that former researchers used^[4-7]. Nanocrystal structures of sample b is pure PbF_2 , which has no deformation. The sample b has the highest crystallization ratio due to the low nucleation temperature of PbF_2 . But the up-conversion luminescent intensity of sample b is not maximum, which indicates that crystallization ratio is not the main factor to influence the up-conversion luminescent intensity. At the same time, the nanocrystal symmetry is the best in sample b, which is not the main factor to influence the up-conversion luminescence of Er^{3+} . The degree of distortion of the nanocrystal structure reaches maximum when the ratio of PbF_2 and CdF_2 is 28:22 (sample d). Large distortion of nanocrystals structure influences Er^{3+} up-conversion luminescence directly. The intensity of up-conversion luminescence is not maximum when ratio of PbF_2 and CdF_2 is 28:22. When mixing CdF_2 in PbF_2 to form nanocrystals, the up-conversion luminescent intensity for sample c with the Pb/Cd ratio of 40:10 is the strongest. Cd ions could replace the position of Pb in PbF_2 and form $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$ nanocrystals. The optimal content of Cd ions modifies the pure PbF_2 crystal field and then outputs the strongest up-conversion luminescence.

Nanocrystal sizes and crystallization ratio of sample c approach to those of sample d, but the intensity of up-conversion luminescence is different. The different nucleation temperature of fluoride nanocrystals leads to different crystallizability. The luminescent intensity is not only decided by the crystallizability but also mainly related with the stoichiometric proportion of the nanocrystals in glass-ceramics. According to the experimental results, the intensity of up-conversion luminescence would reach maximum when the ratio of PbF_2 and CdF_2 is 40:10. The intensity of up-conversion luminescence of sample c was about 20 times stronger than any other samples prepared under the same condition. The effect of nanophase size on the up-conversion luminescence is proceeding.

In summary, the glass-ceramics with the composition of $30\text{SiO}_2 \cdot 15\text{Al}_2\text{O}_3 \cdot (50-x)\text{PbF}_2 \cdot x\text{CdF}_2 \cdot 4\text{ErF}_3 \cdot 1\text{YbF}_3$ ($x = 0, 10, 22$) were prepared. The crystallizability of the glass-ceramics doped with Er^{3+} and Yb^{3+} ions is best when $x = 0$. The relative intensity of the red luminescence of Er^{3+} ions in the glass-ceramics increases with decreasing of Cd content. The intensity of the up-conversion fluorescence could be decided mainly by the stoichiometric proportion of the nanocrystals. The suitable content of CdF_2 could modify crystal lattice field of the nanocrystals in the glass-ceramics. The optimization ratio of PbF_2 and CdF_2 is found to be 40:10 in the oxyfluoride glasses. Under the optimization ratio, the intensity of up-conversion luminescence increases 20 times than former reported compositions of PbF_2 and CdF_2 in glass-ceramics^[4-7].

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