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Nanocrystal formation and structure in oxyfluoride glass ceramics*

Yu Hua(余 华)†, Zhao Li-Juan(赵丽娟), Meng Jie(孟 婕),
Liang Qin(梁 沁), Yu Xuan-Yi(禹宣伊),
Tang Bai-Quan(唐柏权), and Xu Jing-Jun(许京军)

Photonics Research Center, College of Physical Science, Nankai University, Tianjin 300071, China
The MOE Key Laboratory of Advanced Technique & Fabrication for Weak-Light Nonlinear Photonics Materials, and Tianjin Key Laboratory of Photonics Materials & Technology for Information Science, Nankai University, Tianjin 300457, China

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The up-conversion luminescent property of the oxyfluoride glass ceramics $30SiO_2{\cdot}15Al_2O_3{\cdot}$ $(50–x)PbF_2 \cdot xCdF_2$ doped with $4ErF_3{\cdot}1YbF_3$ has been investigated. Up-conversion luminescent intensity of Er^{3+} ions increased obviously after heat-treatment due to co-doping with CdF_2. The structure model of nanocrystals $Pb_xCd_{1-x}F_2$ was determined and the effect of CdF_2 in oxyfluoride glass ceramics was explained by the analysis of x-ray diffraction data. Different nucleation temperatures of samples with different compositions were obtained by differential thermal analysis curves and the results showed the growth process of different nanocrystals in glass ceramics.

Keywords: up-conversion, glass ceramics, structure
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There has been extensive interest in rare-earth-doped transparent oxyfluoride glass ceramics. After heat-treatment, the luminescent centre Er^{3+} ions are incorporated into the nanocrystals in the oxyfluoride glass ceramics. Hence, up-conversion luminescent intensity is stronger than that before treatment due to the fact that the surrounding of the rare earth ions is fluoride rather than oxide. Fluoride nanocrystals play an important role in Er^{3+} high-efficient up-conversion luminescence. The fluoride, which has low phonon energy, can decrease the non-radiation loss of rare earth ions due to the multiphonon relaxation. After the work of Wang and Ohwaki,[1] transparent oxyfluoride glass ceramics have attracted much more interest, especially in fluoride nanocrystals.[1–9] Initially, it was believed that the nanocrystal structure was $Pb_xCd_{1-x}F_2$ by x-ray diffraction measurements, and it was assumed that the rare earth ions act as dopants in these nanocrystals.[1,2] Then, researchers used Eu^{3+} as a probe to investigate the local structure in glass ceramics.[3] The results indicated that the rare earth ions doped into the fluoride nanocrystals with low phonon energy. In recent years, researchers put forward some new viewpoints for fluoride nanocrystal structure, such as PbF_2, mixture of ErOF and PbF_2 or $Pb_8Er_6F_{32}O(F_2)$ phases.[4–7]

Almost all of the glass material compositions investigated have been $SiO_2{\cdot}Al_2O_3{\cdot}PbF_2{\cdot}CdF_2{\cdot}$ doped with rare earth ions. It is expected that PbF_2 phase is easy to form nanocrystals in the oxyfluoride glass, which are composed of Pb, F and Er or O ions. However, the existence of CdF_2 could increase up-conversion luminescence efficiency, confirmed by our experimental results. This paper attempts to characterize the real nanocrystal structure, the nanocrystal growth process and the role of CdF_2 in the oxyfluoride glass ceramics, which have not been reported before to our knowledge.

Oxyfluoride glass with compositions of $30SiO_2{\cdot}$ $15Al_2O_3 \cdot (50-x)\ PbF_2 \cdot xCdF_2$ doped with $4ErF_3{\cdot}$ $1YbF_3$ (x= 0, 10, 22, whose samples are designated B, C, D, respectively) were prepared from high purity

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†Corresponding author. E-mail address: yuhua@nankai.edu.cn

reagents (except for CdF_2). The raw materials were melted at 1000°C for 120 min in the covered Pt crucible in the atmosphere. The melts were poured onto a steel plate and then annealed for 8h at 450°C. The composition of sample A was the same as sample D, but sample A was not heat-treated. All of the obtained glass ceramics was transparent. The samples were cut, polished and subjected to optical measurement at room temperature.

The content of oxide is the same in samples B and C, but the content of fluoride is different. Figure 1 shows the relation between Er^{3+} up-conversion luminescent intensity and the composition of the oxyfluoride glass ceramics. The luminescent characteristics and the energy transfer process of the rare earth ions has been explained elsewhere.[10] The up-conversion luminescence intensity of Er^{3+} ions in sample C, which has the proper quantity of CdF_2, is higher than that of sample B which does not have CdF_2. This means that CdF_2 also plays an important role in the up-conversion luminescence and the nanocrystal structure. The behaviour of CdF_2 in the structure is not clear up to now. We think that the main nanocrystal structure is $Pb_xCd_{1-x}F_2$ in our samples. A series of measurements and calculations will be carried out in the following.

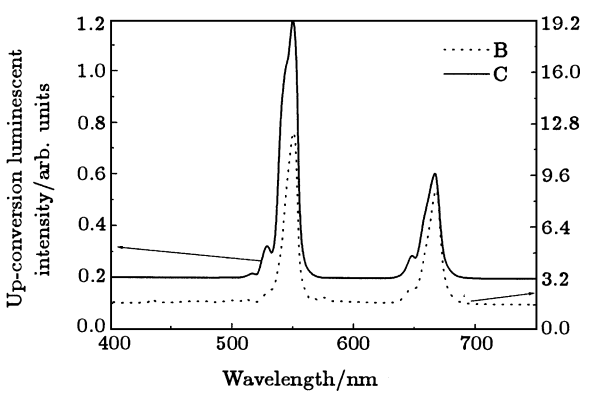


Fig.1. The spectra of the up-conversion luminescence in the sample excited by 980nm laser. The compositions of sample B and C are respectively $30SiO_2{\cdot}15Al_2O_3{\cdot}50PbF_2$ and $30SiO_2{\cdot}15Al_2O_3{\cdot}40PbF_2{\cdot}10CdF_2$ doped with the same rare earth ions.

In the patterns of x-ray diffraction(XRD), the marked difference from envelope curve to sharp peaks indicates the formation of nanocrystals in glass after heat-treatment, as shown in Fig.2. Since samples A, B, C and D all are prepared at 1000°C before heat-treatment, the four samples are in glass state, whose XRD patterns are of the shape of envelope curve as shown in curve *a* in Fig.2. After heat-treatment, sharp

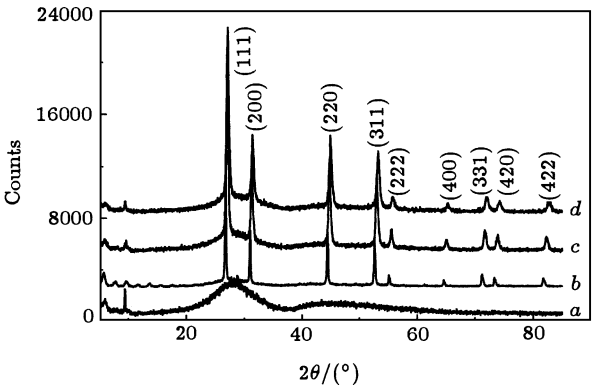


Fig.2. XRD patterns of the glass (curve *a*) and the nanocrystal glass ceramics with different compositions of $(50-x)PbF_2 \cdot xCdF_2$. Curve *b* for x=0, curve *c* for x=10, curve *d* for x=22.

XRD peaks in the curves *b*, *c*, and *d* indicate that the samples have changed into glass ceramics. In other words, nanocrystals have formed in the glass ceramics. The diffraction patterns are of a typical face-centred-cubic (fcc) array compatible with β-PbF_2 structure after heat treatment of samples B, C and D. The full width at half maximum (FWHM) of XRD lines gradually broadens with increasing CdF_2. But the XRD lines do not change much, still corresponding to a face-centred-cubic (fcc) structure. The size of the fluoride nanocrystals can be calculated by using Sherrer's equation:

$$D = \frac{K\lambda}{\beta \cos\theta}, \tag{1}$$

where K is the crystallite shape constant, β is the FWHM of the XRD peak, θ is the Bragg angle and λ is the x-ray wavelength. The sizes of the nanocrystals are 40, 23, 20 nm in samples B, C and D, respectively. That is to say, the size of nanocrystals decreases with increasing content of CdF_2. However, they keep the same fcc array of β-PbF_2 structure, as shown in Fig.3(a). The corresponding nanocrystals model is displayed in Fig.3(c). $Pb_xCd_{1-x}F_2$ structure is also fcc structure like PbF_2 (Fig.3(b)). But the lattice constant decreases because of small Cd ions occupying the position of Pb ions. The lattice constant of the fcc crystal can be calculated by the peak positions of x-ray diffraction and the indices of crystallographic plane according to Eq.(2):

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

where a is the lattice constant and h, k, l is the indices of the crystallographic plane. The lattice constants a are 0.577, 0.573 and 0.570nm for samples B, C and

D, respectively. By the same preparation method under the measurement condition, we consider that the decreasing lattice constant is due to the increasing amount of CdF_2 in samples B, C and D. The atomic radius of Cd (0.097nm) is smaller than that of Pb (0.1290nm). In the formation process of nanocrystals, the smaller Cd ions replace the larger Pb ions in β-PbF_2 nanocrystals, leading to lattice constant decreasing and nanocrystals $Pb_xCd_{1-x}F_2$ deforming. It is interesting that the lattice constant varies irregularly. Compared with sample B, the lattice constant a of sample C decreases by 0.004nm due to the fact that the fluoride contains 20% CdF_2 in the glass ceramics. The CdF_2 percentage content in sample D increases 24% compared with sample C, so the lattice constant a of sample D should decrease greater than 0.004nm by theoretical analysis. But the actual change is 0.003nm, which is even less than the theoretically predicted value. This interesting result may be related to CdF_2 also.

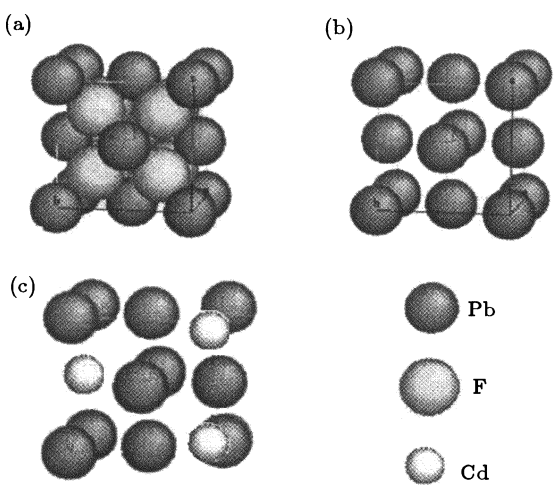


Fig.3. Schematic of fluoride nanocrystal structure, (a) the β-PbF_2 structure, (b) its cation sublattice and (c) $Pb_xCd_{1-x}F_2$ structure.

In order to clarify these interesting results, differential thermal analyses (DTA) are shown in Fig.4. Nucleation temperature of samples in which PbF_2/CdF_2 ratio in the oxyfluoride glass ceramics are 28:22 (sample D), is 445°C, while the nucleation temperature of the sample with only CdF_2 in glass ceramics is 485°C. This indicates that the fluoride nanocrystals would become difficult to be formed when CdF_2 exists in the glass. It is noteworthy that only one DTA peak occurred in the sample with a certain PbF_2/CdF_2 ratio in the glass rather than two DTA peaks corresponding to the thermal absorption peaks of PbF_2 and CdF_2, implying that only one kind of fluoride nanocrystal phase formed in the oxyfluoride glass. We think that this fluoride nanocrystal phase is $Pb_xCd_{1-x}F_2$ phase. In the formation process of fluoride nanocrystals, the $Pb_xCd_{1-x}F_2$ phase becomes difficult to form when it is doped with CdF_2 due to the higher nucleation temperature. So the size of nanocrystals becomes smaller and smaller in the sequence from sample B to sample D. Although the content of CdF_2 in fluoride (sample D) increases more than 20% compared with sample C, less Cd ions replace Pb ions and the decrease of the lattice constant a would be 0.003nm due to the higher nucleation temperature of CdF_2. It is worth noting that the x-ray diffraction pattern of sample D does not change, which implies that the nanocrystal structure is also kept to be $Pb_xCd_{1-x}F_2$ despite the high content of CdF_2 in sample D.

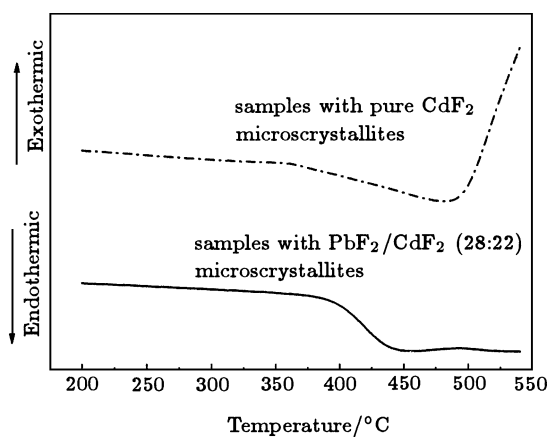


Fig.4. DTA curves of samples with different nanocrystal compositions.

Kawamoto *et al*[3] have measured DTA curve of the $50SiO_2$–$50PbF_2$–$xErF_3$ glass. The nucleation temperature of the glass with only PbF_2 is 310°C, which is lower than that of the glass with some of PbF_2/CdF_2 or the glass with pure CdF_2. At the same heat-treatment temperature, PbF_2 nanocrystals are the first to form, and then the Cd ions replace the Pb ions. This is why some authors believed that the rare earth ions were doped in the PbF_2 phase. Kukkonen *et al*[5] used energy dispersive spectroscopy (EDS) to prove that the nanocrystals structure is β-PbF_2 rather than $Pb_xCd_{1-x}F_2$. However, the Cd peak in EDS was absent, which may be caused by very short treatment time they used although the treatment temperature reached 600°C.

In conclusion, $Pb_xCd_{1-x}F_2$ nanocrystals phase could be formed in the glass ceramics. Cd ions may replace the Pb ions to form $Pb_xCd_{1-x}F_2$ nanocrystals, and $Pb_xCd_{1-x}F_2$ structure keeps a fcc structure.

The rare earth ions doped in $Pb_xCd_{1-x}F_2$ nanocrystals could greatly enhance the up-conversion luminescence. High nucleation temperature of CdF_2 makes $Pb_xCd_{1-x}F_2$ nanocrystals difficult to nucleate.

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