Luminescence Behavior of Er^{3+} in Oxyfluoride Borosilicate Glass Ceramics Containing Ba_2LaF_7 Nanocrystals*

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Abstract: Spectroscopic properties of Er^{3+} doped transparent oxyfluoride borosilicate glass ceramics containing Ba_2LaF_7 nanocrystals are systematically investigated. The formation of Ba_2LaF_7 nanocrystals in the glass ceramics was confirmed by X-ray diffraction. According to the Judd-Ofelt theory, the intensity parameters Ω_i ($i=2,4,6$) is calculated and the decrease of Ω_2 suggests that rare earth ions are incorporated into Ba_2LaF_7 nanocrystals. Compared with the precursor glass, significantly increased upconversion luminescence is observed in the transparent glass ceramics. This is attributed to the low phonon energy of fluoride nanocrystals, when Er^{3+} is incorporated into the precipitated Ba_2LaF_7 nanocrystals. And the emission mechanism can be described as a two-photon mechanism.

Key words: Oxyfluoride glass ceramics; Er^{3+} ions; Upconversion luminescence
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0 Introduction

Rare-earth (RE) doped materials for upconversion luminescence are attractive for realizing the solid-state lasers and three-dimensional displays in addition to their application in telecommunications. The upconversion efficiency depends largely on the structure of the energy levels of RE ions and their local environments. The key technique to design upconversion luminescence materials was to situate the RE ions in low-phonon-energy environment. Recently, oxyfluoride glass ceramics have widely been investigated as host materials for active optical ions because they have not only comparatively low phonon energies due to fluorides, but also high chemical and mechanical stabilities related to oxides[1-3].

RE doped oxyfluoride nanocrystals, characterized by the low phonon energy and the large transfer coefficient between the RE ions, has been revealed to be a suitable host to achieve laser and upconversion[4-5]. However, there are few reports of upconversion luminescence of rare earth ions in oxyfluoride borosilicate glasses and glass ceramics. In this paper, an Er^{3+} doped transparency oxyfluoride borosilicate glass ceramics containing Ba_2LaF_7 nanocrystals was prepared and the change of upconversion luminescence was discussed.

1 Experiment

The precursor glass with the molar composition 59.5 SiO_2-15B_2O_3-16Na_2O-5BaF_2-4LaF_3-0.5ErF_3 was prepared. The mixed materials were melted in an alumina crucible at 1 400 ℃ for about 0.5 hour. Then the glass was quenched into a brass mold. The quenched sample was annealed at a temperature 450 ℃ for 2 h and cooled slowly to release the thermal stress associated with these glasses during the quenching process. The DTA result of the oxyfluoride borosilicate glass shows that the transition temperature was 500 ℃, and no obvious crystallization peak was observed. Four different temperatures, 560 ℃, 580 ℃, 600 ℃ and 620 ℃, were selected to carry out heat-treatment for 2 h to form transparent glass ceramics, and the fabricated samples were named as GC560, GC580, GC600 and GC620, respectively. The samples were cut and polished into 10×5×2 mm^3 size.

2 Results and discussions

The XRD patterns of Er^{3+} doped precursor glass and the sample GC620 were shown in Fig. 1. The precursor glass is completely amorphous with no obvious diffraction peaks, meanwhile the sample GC620 show intense diffraction peaks, which are easily assigned to the Ba_2LaF_7 nanocrystal(JCPDS Nos. 48-0099).

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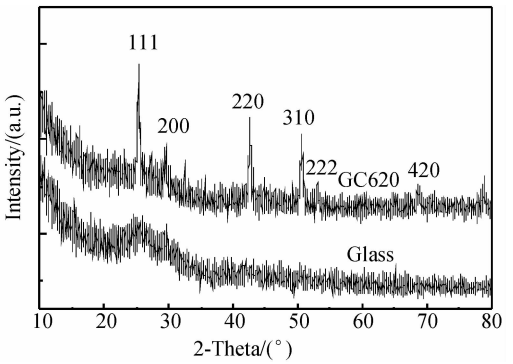

Fig. 1 XRD patterns of the parent glass and heat-treated at 620 ℃ sample

From the peak width of XRD pattern, the size of Ba_2LaF_7 nanocrystals in obtained glass ceramic was calculated to be about 20 nm by using Sherrer′s equation

$$D=K\lambda/\beta\cos\theta \quad (1)$$

Where D is the crystal size at the vertical direction of (hkl), λ is the wavelength of X-ray, θ is the angle of diffraction, β is the full-width at half maximum (FWHM) of the diffraction peak and the constant K determined by β and the instrument. Due to much smaller size of precipitated Ba_2LaF_7 nanocrystals than wavelength of visible light the Er^{3+} doped glass ceramics remain excellent transparency.

The absorption spectra of Er^{3+} doped oxyfluoride borosilicate glass and glass ceramics in the range from 350 to 1 700 nm are shown in Fig. 2. The absorption peaks, corresponding to the transitions from the ground state $^4I_{15/2}$ to the excited states, are marked in the figure. The Judd-Ofelt theory[6-7] is often used to calculate the spectroscopic parameters, which has been successfully applied to calculate $4f$ and $5d$ transition intensities of rare earth ions in various host materials. And the intensity parameters Ω_i (i= 2, 4, 6) can be just derived from the absorption spectra and their values indicate the variation of the Er^{3+} environment from glass to glass ceramics.

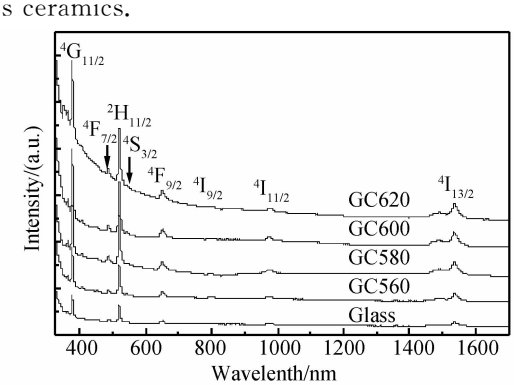

Fig. 2 Absorption spectra of Er^{3+} ions in the glass and glass ceramics

With the increase of crystallization temperature, Ω_2 decrease gradually, shown in Fig. 3, which indicated that the matrix field of Er^{3+} is more ionic in the glass ceramics. This is probably owing to the precipitation of Ba_2LaF_7 nanocrystals. During the nucleation and growth process of Ba_2LaF_7 nanocrystals, Er^{3+} ions act as crystal nucleus. Thus the Er^{3+} ions might enter into the Ba_2LaF_7 nanocrystal phase, and the La^{3+} ions were partially substituted by Er^{3+} ions. Therefore, the decrease of Ω_2 suggests that Er^{3+} had been incorporated into Ba_2LaF_7 nanocrystals after crystallization[8-10].

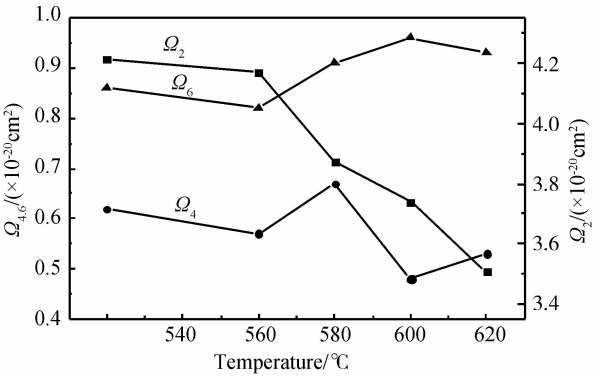

Fig. 3 The change of parameters Ω_i (i=2,4,6) with the increase of crystallization temperature

Fig. 4 shows the upconversion spectra (excited at 980 nm) of Er^{3+} ions in precursor glass and glass ceramics in the wavelength range of 400～700 nm. The emission bands can be assigned to $^2H_{11/2}\rightarrow{}^4I_{15/2}$ (520 nm), $^4S_{3/2}\rightarrow{}^4I_{15/2}$ (540 nm), and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ (656 nm) transitions, respectively. It can hardly be observed upconversion emission in the glass. However, significant upconversion luminescence of Er^{3+} can be observed in the glass ceramics and the emission bands corresponding to the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transitions are split into two peaks.

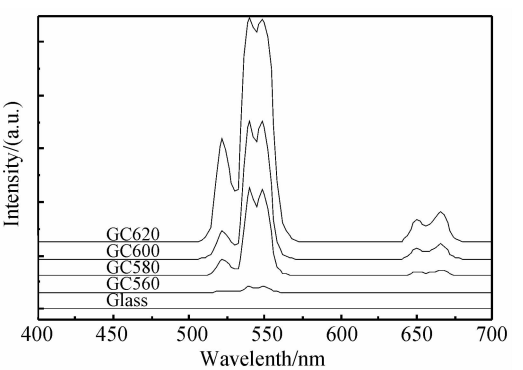

Fig. 4 Upconwersion luminescence of Er^{3+} ions in the glass and glass ceramics

It is well known that upconversion luminescence of Er^{3+} ions is usually baffled by the multiphonon relaxation. According to Miyakawa-

Dexter theory[11], the multiphonon relaxation probability (W_{MP}) depends primarily upon the energy gap between two successive levels (ΔE) and the phonon energy of host matrix($h\omega$).

$$W_{MP}=W_o\exp(-\alpha\Delta E/h\omega) \quad (2)$$

Where the constants W_o and α are determined by host matrix. The smaller the phonon energy of host matrix is, the lower the multiphonon relaxation probability is. The maximum phonon energy in Ba_2LaF_7 is about 270 cm^{-1}, which is much lower than that of oxides (the energy of Si-O and B-O vibration is 1 100 and 1 400 cm^{-1}, respectively)[12]. So much stronger upconversion luminescence is expected in Er^{3+} doped oxyfluoride glass ceramics containing Ba_2LaF_7 nanocrystals.

Fig. 5 shows luminescence decay curves of the $^4S_{3/2}$ state of Er^{3+} in the precursor glass and GC-620 by monitoring the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ emission of Er^{3+}. The decay curve of the precursor glass can be fitted to a single-exponential function, yielding the lifetime of 47.88±0.54 μs. The decay curve of the GC-620 sample was fitted to a double-exponential function, yielding the average lifetime of 119.90±16.34 μs. The results clearly show that the lifetimes of $^4S_{3/2}$ state in glass ceramic is longer than that in precursor glass. It indicated that Er^{3+} had been incorporated into fluoride nanocrystals precipitation in the glass host[6,13].

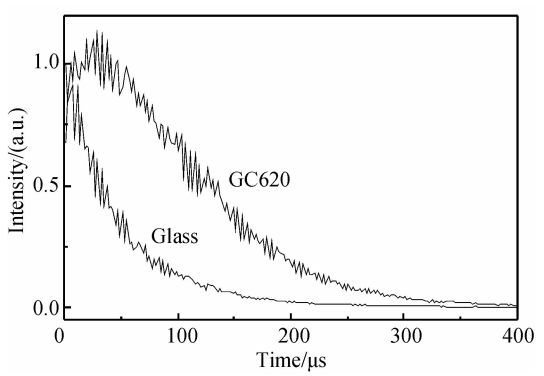

Fig. 5　Luminescence decay curves of the $^4S_{3/2}$ state of Er^{3+} in the precursor glass and GC-620

In the upconversion processes, there is the following relation between the emission intensity I_{em} and the infrared (IR) excitation intensity I_{ex}

$$I_{em}\propto(I_{ex})^n \quad (3)$$

Where n is the number of IR photons absorbed per visible photon emitted. Therefore, a plot of $\log(I_{em})$ versus $\log(I_{ex})$ should yield a straight line with the slope n. In Fig. 6 the slopes of 520 nm, 540 nm and 656 nm emission are 1.968, 1.861 and 1.768, respectively. These results indicated that the green and red emission mechanism can be described as a two-photon mechanism.

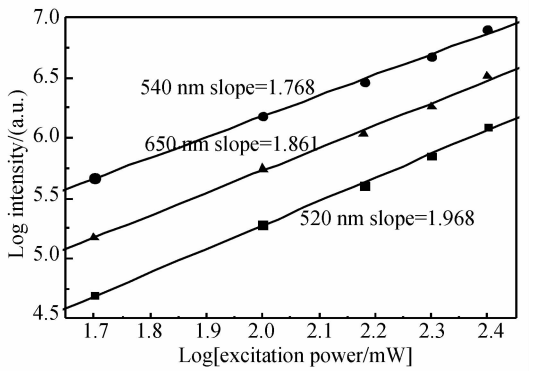

Fig. 6　Log-log plot of emission intensity as the function of excitation power

3 Conclusions

In summary, the Er^{3+} doped transparent oxyfluoride glass ceramics containing Ba_2LaF_7 nanocrystals was affirmed by XRD results were prepared. The upconversion emission of Er^{3+} ions in the glass ceramics can be observed to be much stronger than that in the glass. And the transition mechanism of the green and red emission can be ascribed to two-photon absorption process. Due to its high transparency and strong uponversion luminescence, the novel Er^{3+} doped oxyfluoride borosilicate glass ceramics containing Ba_2LaF_7 nanocrystals may be used as a potential material to improve the efficiency of solar cell, solid laser and color displays.

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Er^{3+}掺杂含 Ba_2LaF_7 纳米晶氧氟硼硅酸盐玻璃陶瓷发光性能的研究

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摘 要：制备了含有 Ba_2LaF_7 纳米晶的 Er^{3+} 掺杂氧氟硼硅盐玻璃陶瓷，并对其光谱特性进行了研究. 根据 X 射线粉末衍射结果可确认制备出 Ba_2LaF_7 纳米晶. 根据吸收曲线计算了相应的 Judd-Ofelt 参数，Ω_2 随着热处理温度的升高而减小，证明 Er^{3+} 离子进入到 Ba_2LaF_7 纳米晶中. 由于 Ba_2LaF_7 纳米晶的低声子能量，在玻璃陶瓷中观察到强烈的红光和绿光上转换发光，其上转换发光机理可以归为双光子过程.

关键词：玻璃陶瓷；Er^{3+} 离子；上转换发光

ZHENG Fei is currently working toward his M. S. degree, and his research interests focus on rear earth luminescence and glass ceramic.

勘 误

09 年 8 期 2019 页标题中“Troperties”应改为“Properties”；2126 页基金应为：国家重点高技术研究发展计划项目（2007AA12Z150、2009AA12Z108）和浙江省重大科技专项（2008C16018）；2127 页第七行“到的”应改为“得”；2129 页致谢部分删去；2141 页式(18)中“－”、“＋”均应改为“±”；2142 页图 5(g)应为：