Microstructure and up-conversion luminescence properties of Er³⁺ and Yb³⁺ ions co-doped oxyfluoride silicates

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Abstract

Microstructure and up-conversion luminescence properties of Er³⁺ and Yb³⁺ co-doped PbF₂–ZnF₂–SiO₂ oxyfluoride silicate were investigated. Up-conversion luminescence spectra consist of four bands centered at 408, 523, 541 and 660 nm which are similar to other Yb³⁺ and Er³⁺ co-doped up-conversion materials, but the violet emission near 408 nm accounting to 16.8% in overall intensity is much stronger than others. Another feature is that the change of the ratio of the intensity of the green to red emission is not monotonously. These phenomenon can be explained by micro dendrite crystal appeared in the as cast sample with 0.1 mol% Er³⁺. The dendrite crystal is identified to be β-PbF₂ by X-ray diffraction in which the content of rare-earth ions, Yb³⁺ and Er³⁺, is determined to be ∼7.0 mol%. The violet emission near 408 nm of the sample with the concentration of 0.1 mol% Er³⁺ decreased to 1.6% after the heat treatment because of the diminish of the dendrite.
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1. Introduction

Recently, oxyfluoride silicate attracted much attention and become to be very appropriate materials for telecommunication, amplifier, sensors, high density optical data reading/storage and all-solid-state laser [1,2]. Oxyfluoride silicates combine the good spectroscopic properties of fluoride with the excellent chemical and thermal stability of silicate. Erbium-doped oxyfluoride silicate glasses [1] exhibit the promising spectroscopic and structural properties for the applications mentioned above. Watekar et al. [2] reported the good optical properties of rare-earth doped silicate glass with the calculated Judd–Ofelt parameters (mean values: X2 = 1.97, X4 = 1.54, and X6 = 0.24) and reasonably high Abbe number of around 56. Especially, comparing with fluoride glasses, gallate glasses, and tellurite glasses, oxyfluo-

ride silicate glasses are the most chemically and mechanically stable and also are much easier to fabricate into various shapes such as rod, plate and optical fiber.

The study of the up-conversion properties of oxyfluoride silicate [3–5] is also very valuable. Comparing with other techniques, up-conversion has some characteristic of itself. One advantage is that the photoionization induced by the degradation of the hosts is reduced over direct UV excitation. In contrast to non linear techniques, up-conversion does not need either the stringent constraint of phase matching or the high excitation wavelength stability. The output wavelength is not restricted to a given harmonic [6]. But, previous research into rare-earth doped oxyfluoride silicate focused mostly on the up-conversion luminescence process and the efficiency [7–9]. However, the relationship between microstructure and the up-conversion luminescence properties of oxyfluoride silicate has rarely been reported. It is well known that not only the mechanical properties but also the physical properties are determined by its microstructures including composition, defect, crystalline status, etc. Researchers working on the structural materials paid much more attention to the study of the relationship

Table 1
Compositions of sample S1, S2 and S3, ratio of the intensity of the green to red emission (RGR) of as cast samples, percentage of violet emission of as cast (PVEC) and annealed (PVEA) samples, excitation power

Referred as	Compositions (mol%)					RGR	PVEB (%)	PVEA (%)	Excitation power (mW)
	PbF_2	ZnF_2	SiO_2	Yb_2O_3	Er_2O_3				
S1	50	17.5	30.4	2	0.1	1.300	16.8	1.6	20
S2	50	17.5	30	2	0.5	3.653	2.5	2.2	20
S3	50	17.5	29.5	2	1	2.552	2.8	2.7	20

between the microstructure and mechanical property than the researchers working on functional materials did. Oxyfluoride silicate received so much attention at present, in order to understand the luminescence mechanism thoroughly, it is important to investigate the relationship between microstructure and the up-conversion luminescence properties of oxyfluoride silicate.

In this paper, the up-conversion luminescence properties of Er^{3+} and Yb^{3+} co-doped PbF_2–ZnF_2–SiO_2 oxyfluoride silicate were investigated by combining the analysis of microstructure which was determined by SEM images and X-ray diffraction (XRD). High RE-ion concentration in the β-PbF_2 crystals was confirmed by comparing lattice constant change.

2. Experimental

The samples with compositions listed in Table 1 were prepared. The starting materials are regent grade PbF_2, ZnF_2 and SiO_2, while the rare-earth oxide Er_2O_3 and Yb_2O_3 are 4N purity. The powder was fully ground in an agate mortar by hand at least for 1 h. The sufficient fine and fully homogenous powder was introduced in a covered corundum crucible and heated in a SiC furnace at temperature 1050 °C for 20 min at an air atmosphere. The melt was cast at the room temperature on a pure copper plate. Subsequently, the up-conversion fluorescence spectra of different compositions under excitation of a 980 nm LD of as low as 20 mW were recorded with a spectrophotometer (R500). In order to analyze the heat treatment effect on the up-conversion luminescence, all the three samples S1, S2 and S3 were divided into two parts. The part one, i.e. as cast sample S1, S2 and S3, was taken SEM (JEOL 6360) images and X-ray diffraction (XRD) (D/Max-3c). Another part of S1, S2 and S3 was transferred to the annealing furnace and kept for 2.5 h at 550 °C. The up-conversion fluorescence spectra of the annealed S1, S2 and S3 were recorded in the exactly same condition as the part one. The annealed S1 was taken SEM (JEOL 6360) images and X-ray diffraction (XRD) (D/Max-3c) as well. Intensity data were calculated by integrating the emission spectra.

3. Results and discussion

3.1. The relationship between microstructure and up-conversion property

Figs. 1 and 2 show that the up-conversion luminescence spectra of as cast and annealed Er^{3+} and Yb^{3+} co-doped PbF_2–ZnF_2–SiO_2 silicate under the excitation of a 980 nm LD consist of four bands centered at 408, 523, 541 and 660 nm, respectively. All the samples emit dazzlingly bright light under as low as a 20 mW excitation. Fig. 1 shows the up-conversion fluorescence emission spectra of as cast Er^{3+} and Yb^{3+} doped PbF_2–ZnF_2–SiO_2 silicate with different Er^{3+} concentrations. In Fig. 1(a), the green emission near 523 and 541 nm is a little
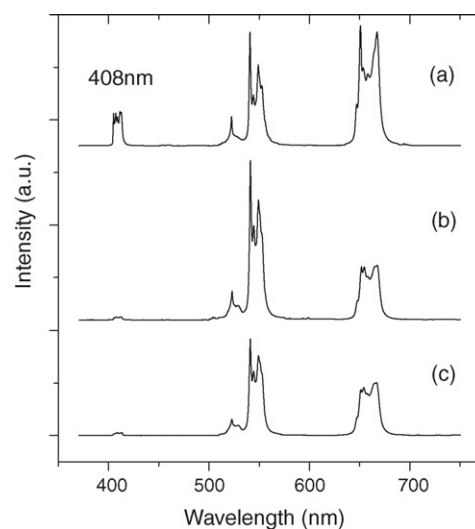

Fig. 1. Fluorescence emission spectra of Er^{3+} and Yb^{3+} co-doped $50PbF_2$–$17.5ZnF_2$–$(30.5 - x)SiO_2$–$2Yb_2O_3$–xEr_2O_3: (a) $x = 0.1$ mol%, (b) $x = 0.5$ mol%, and (c) $x = 1$ mol%.

weaker than the red emission near 660 nm. Spectra of S2 and S3 show bright green and relatively weaker red emissions which are similar with those of other glass systems [10–13]. The violet emission near 408 nm is quite strong compared to the analogous
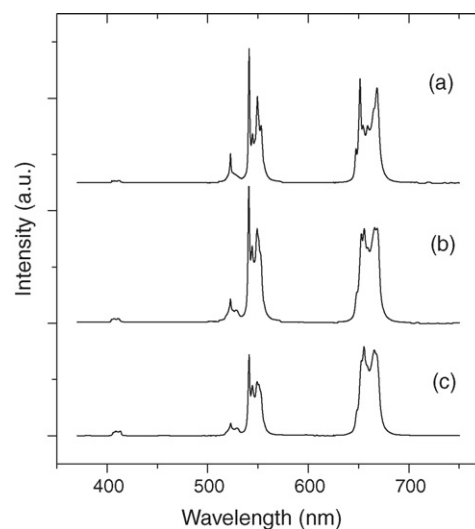

Fig. 2. Fluorescence emission spectra of annealed Er^{3+} and Yb^{3+} co-doped $50PbF_2$–$17.5ZnF_2$–$(30.5 - x)SiO_2$–$2Yb_2O_3$–xEr_2O_3: (a) $x = 0.1$ mol%, (b) $x = 0.5$ mol%, and (c) $x = 1$ mol%.

up-conversion materials reported in the literature. The percentage of the intensity of violet emission is 16.8% which is even much higher than that of the Er^{3+} and Yb^{3+} co-doped ZBLAN [14]. It can be seen that the green light in Fig. 1(b) and (c) is stronger than in Fig. 1(a), but the red light is weaker than in Fig. 1(a) and the violet emissions are much weaker than that in Fig. 1(a). Fig. 2 shows the up-conversion fluorescence emission spectra of annealed Er^{3+} and Yb^{3+} co-doped PbF_2–ZnF_2–SiO_2 silicate with different Er^{3+} concentrations under a 980 nm excitation. Comparing the spectra of as cast with that of annealed S1, S2 and S3, the largest change is the variation of the violet emission of S1. The percentage of violet emission of S1 decreased from 16.8% before annealing to 1.6% after annealing. Another feature of the up-conversion luminescence is that the variation of spectra is not regular when the Er^{3+} concentration changed from 0.1 to 1 mol%. The ratio of the intensity of the green to red emission increased when the concentration of Er^{3+} ion changed from 0.1 to 0.5 mol%, but, decreased while the concentration of Er^{3+} ion changed from 0.5 to 1 mol%. This phenomenon is not in agreement with many reported results [15,16] which change with RE-ions concentration monotonously. In order to explain the unusual phenomenon, it is necessary to observe microstructures and analyze the relationship between the microstructure and the up-conversion luminescence properties of Er^{3+} and Yb^{3+} co-doped PbF_2–ZnF_2–SiO_2 silicate.

Fig. 3 shows the SEM images of as cast S1, S2 and S3. In Fig. 3(a), two different phases were observed obviously and just one phase in Fig. 3(b) and (c). Patterns of X-ray diffraction (XRD) in Fig. 4 show that the sample in Fig. 3(a) is composed of dendrite crystal and amorphous phase while the samples in Fig. 3(b) and (c) are just composed of amorphous phase. The size of the white dendrite distributed in the grey host is about 1 μm in diameter. From the XRD pattern in Fig. 4(a), it can be identified that the dendrite is β-PbF_2. The content of RE ions in the β-PbF_2 can be determined by lattice parameter change as proposed by Beggiora et al. [17]. Comparing the calculated lattice parameter ($a = 0.589$ nm) of RE ions modified β-PbF_2 with that ($a = 0.594$ nm) of pure β-PbF_2, high concentration (∼7 mol%) of RE-ions in the β-PbF_2 crystals was determined if the difference of diameter between Er^{3+} and Yb^{3+} ions is ignored. It is verified that the dendrite is a RE rich phase and therefore would play an important role in the up-conversion luminescence. Fig. 5 presents a SEM image of annealed S1 and Fig. 6 shows the X-ray diffraction plot of annealed S1. It can be seen that the dendrite diminished after annealing accompanied by diminish of the violet emission. It accounts for that the violet emission is caused by dendrite. It is reasonably assumed that the dendrite is responsible for not only the violet emission but also the red emission because the red emission in as cast S1 is much stronger than that of the annealed one. The irregular change of the red and green
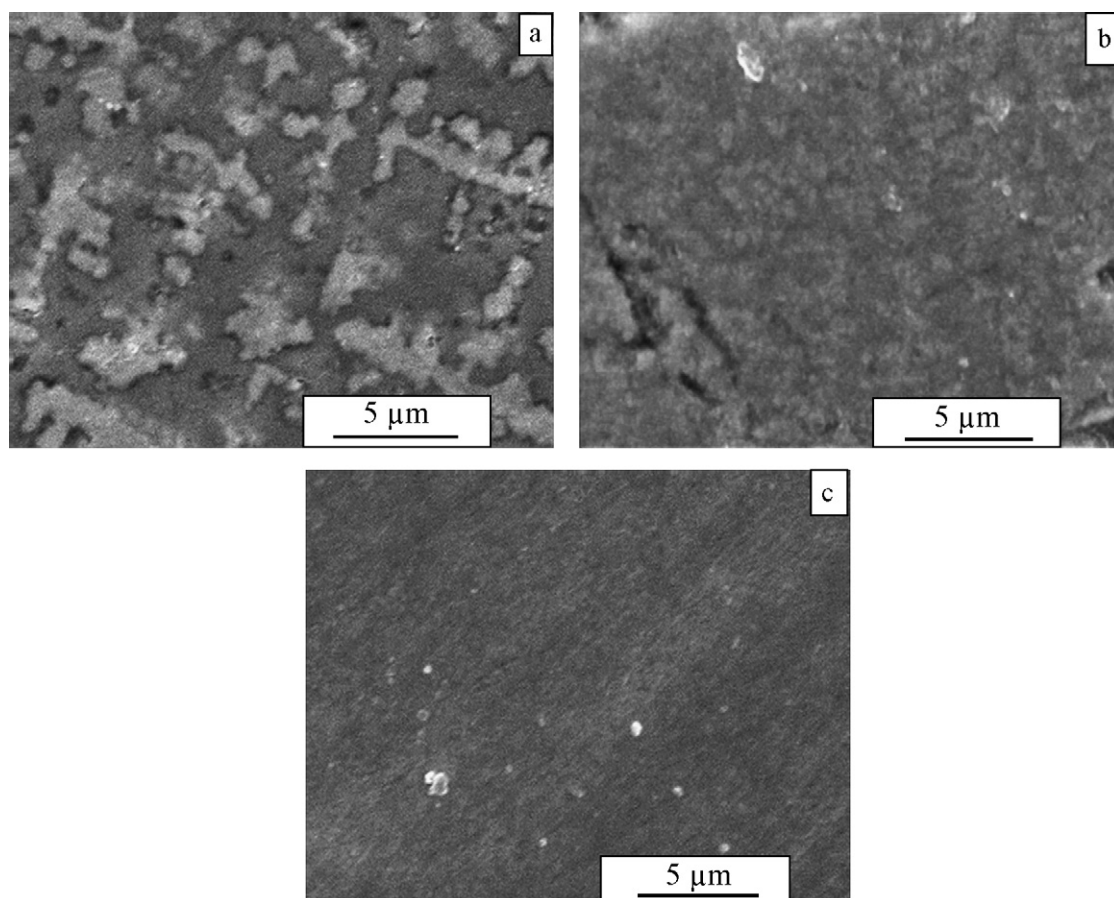

Fig. 3. SEM images of Er^{3+} and Yb^{3+} co-doped oxyfluoride silicate: (a) with 0.1 mol% Er^{3+}, (b) with 0.5 mol% Er^{3+}, and (c) with 1 mol% Er^{3+}.
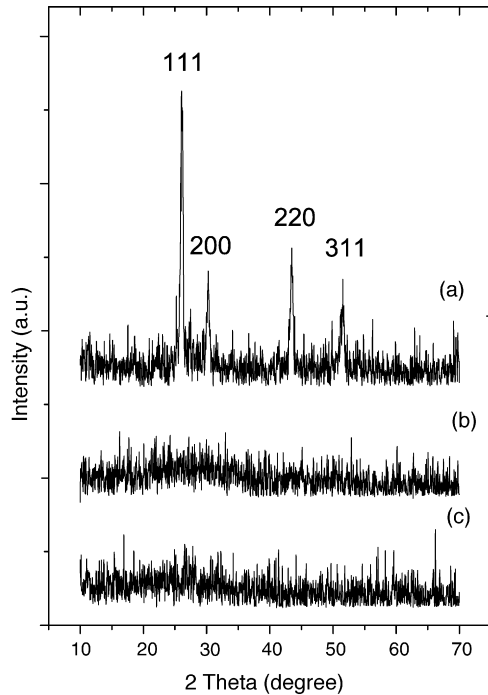
Fig. 4. X-ray diffractions of Er^{3+} and Yb^{3+} co-doped oxyfluoride silicate: (a) with 0.1 mol% Er^{3+}, (b) with 0.5 mol% Er^{3+}, and (c) with 1 mol% Er^{3+}.
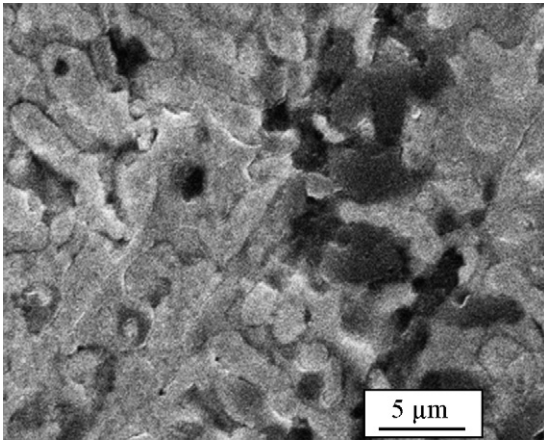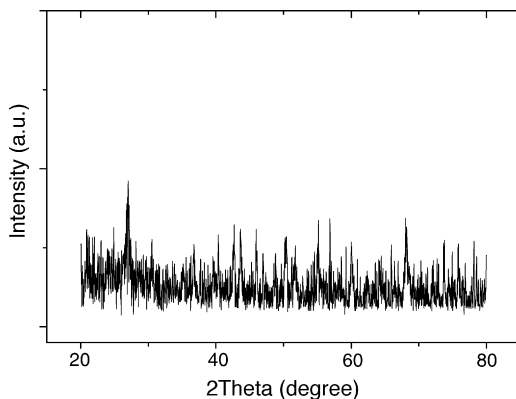

Fig. 5. SEM image of annealed S1.

Fig. 6. X-ray diffraction of annealed S1.

emission with the variation of Er^{3+} content is also attributed to the dendrite change.

3.2. Possible up-conversion mechanism

Although we did not measure log–log plots of the up-conversion luminescence intensity as a function of the excitation intensity to determine the slopes for each band, a plenty of experiments reported in the literatures [18–24] verified that there are two photons participating in the up-conversion process for the green and red emissions, while the violet emission involves three photons because the energy of two photons is not enough to excite the violet emission.

According to the energy matching and two or three photon processes dependent on the excitation power, possible mechanism for the up-conversion emission is based on the simplified energy level diagrams of Er^{3+} and Yb^{3+} ions presented in Fig. 7.

3.2.1. Excitation mechanism

In the first step of excitation, a pump photon at 980 nm provokes the excitation of the Yb^{3+} sensitizer from the $^2F_{7/2}$ ground state to the $^2F_{5/2}$ excited state. The excited Yb^{3+} ion transfers its energy to a neighbor Er^{3+} ion for the $^4I_{15/2}$–$^4I_{11/2}$ transition of Er^{3+} ion. From the long-lived $^4I_{11/2}$ level, the exited Er^{3+} ion absorbs a pump photon undergoing a transition to the $^4F_{7/2}$ level. The Er^{3+} ion populated in the $^4F_{7/2}$ level will decay nonradiatively to $^4S_{3/2}$ level by the phonon relaxation, and then absorbs a third pump photon to an upper level $^4G_{11/2}$ level.

3.2.2. Emission mechanism

The energy phonon of the dendrite (β-PbF_2) is about $260\,cm^{-1}$ which is much lower than that ($1000\,cm^{-1}$) of silicate [25–27]. In the dendrite, the relatively lower phonon energy promoted energy transfer (ET) from Yb^{3+} ($^2F_{5/2}$) to Er^{3+} ($^4I_{11/2}$). Then, the $^4F_{9/2}$–$^4I_{15/2}$ transition of Er^{3+} ion has been considerably accelerated due to an increase of the ET processes [28].
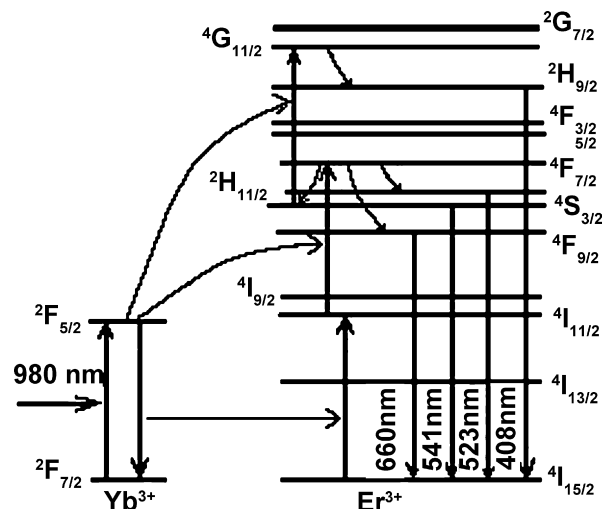

Fig. 7. Simplified energy level diagrams of Yb^{3+} and Er^{3+} and possible up-conversion mechanism of Er^{3+} and Yb^{3+} co-doped oxyfluoride silicate.

Whereas, the $^4S_{3/2}/^2H_{11/2}-^4I_{15/2}$ transitions have been weakened. Therefore, the strong red emissions occur in the dendrite. Such a result is also reported in Yb^{3+} and Er^{3+} ions co-doped Y_2O_3 glass [28]. Though the red emission is weaker than the green emission in the glass host, the total intensity of fluorescence emissions from as cast S1 is stronger than that from the as cast S2 and S3. But, S2 with 0.5 mol% Er^{3+} concentration contains only a single glass phase. The higher phonon energy relatively to S1 weakens the ET process from Yb^{3+} ($^2F_{5/2}$) to Er^{3+} ($^4I_{11/2}$) which would decrease the population of $^4F_{7/2}$ level. The green emission from the $^4S_{3/2}/^2H_{11/2}-^4I_{15/2}$ transitions was weakened slightly, and the red emission from the $^4F_{9/2}-^4I_{15/2}$ transition was weakened greatly. Higher concentration of Er^{3+} ions in S2 promoted the energy transfer up-conversion (ETU) process so that the population of the $^4F_{7/2}$ levels was increased. The $^4F_{7/2}$ state decays nonradiatively to the $^4S_{3/2}$, $^2H_{11/2}$ and $^4F_{9/2}$ levels. If a competition among the $^4S_{3/2}$, $^2H_{11/2}$ and $^4F_{9/2}$ levels was assumed, comparing different emission bands, the $^4S_{3/2}$ level has the privilege over the $^2H_{11/2}$ and $^4F_{9/2}$ levels for which the $^4S_{3/2}-^4I_{15/2}$ transition being promoted the most over the $^2H_{11/2}/^4F_{9/2}-^4I_{15/2}$ transitions are ascribed. Therefore, the fluorescence emission of S2 is comprised of intense green and weaker red emissions. As the concentration of Er^{3+} ion increases further to 1.0 mol%, the total emission intensity decreases because of concentration quench starting to occur.

The Er^{3+} ion populated in the $^4G_{11/2}$ state will decay nonradiatively to a lower level, $^2H_{9/2}$, and then transit to the ground state to emit violet light.

4. Conclusion

Up-conversion luminescence properties of Er^{3+} and Yb^{3+} co-doped $PbF_2–ZnF_2–SiO_2$ oxyfluoride silicate were investigated. The great variation of the ratio of the intensity of the green to red emission was observed when the Er^{3+} concentration increased from 0.1 to 0.5 mol%. The intensity of violet emission near 408 nm of the sample with the concentration of 0.1 mol% Er^{3+} equals 16.8% in overall intensity which decreased to 1.6% after the heat treatment. Microstructure analysis revealed that the dendrite is beneficiary to the red and violet emissions more than the green emission. Comparing the calculated lattice parameter ($a = 0.589$ nm) of RE ions modified β-PbF_2 with that ($a = 0.594$ nm) of pure β-PbF_2, high concentration (∼7 mol%) of RE-ions in the β-PbF_2 crystals was determined which implied that the influence of the up-conversion emission in the β-PbF_2 is significant on the overall emission spectra.

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