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Infrared-to-visible upconversion of rare-earth doped glass ceramics containing CaF_2 crystals

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Abstract

Oxy-fluoride glass ceramics containing CaF_2 crystals doped with YbF_3–LnF_3 (Ln = Er, Tm) were prepared by heat-treatment from SiO_2–Al_2O_3–CaO–CaF_2 glasses. The upconversion emission spectra of Er^{3+} and Tm^{3+} ions in the visible range were measured by 970 nm pumping. In the spectrum of the Er doped sample, 540 nm upconversion band due to the $^4S_{3/2}$–$^4I_{15/2}$ and 660 nm band due to the $^4F_{9/2}$–$^4I_{15/2}$ were observed. In the Tm doped sample, a blue upconversion emission band due to the $^1G_4$–$^3H_6$ was observed at 480 nm as well as an 800 nm band. The intensity of these upconversion emissions were very weak in the corresponding as-made glasses. These results indicate that rare-earth ions are incorporated in the CaF_2 crystal phases after crystallization and the energy transfer efficiency from Yb^{3+} to Er^{3+} or Tm^{3+} are dramatically improved.

Keywords: Upconversion; Optical properties; Yb^{3+}; Er^{3+}; Tm^{3+}; Energy transfer

1. Introduction

For the candidate materials of the optical devices such as a laser, phosphors and optical amplifier, rare-earth doped oxide or fluoride glass and glass ceramics have been used. Fluoride glasses and crystals are highly transparent materials, from the near-UV to the middle IR, with excellent rare-earth ion solubility and low phonon energy, making them excellent candidates as laser host materials [1]. On the other hand, the silicate glasses have higher phonon energy and limited rare-earth solubility. However, fluoride glasses have less favourable chemical, thermal and mechanical properties, compared to oxide glasses, and thus, are hard to prepare and to handle. In fact, most oxide glasses have better chemical and mechanical stabilities and are easily fabricated into rods and optical fiber than fluoride glasses [2]. To combine advantages of both glasses, oxy-fluoride glass ceramics that has fluoride crystal phase in oxide glass matrix, were suggested. In 1993, Wang and Ohwaki [3] reported a transparent oxy-fluoride glass ceramics based on $Pb_xCd_{1-x}F_2$ crystal phase containing Er^{3+} and Yb^{3+} ions, which is dispersed in a continuous aluminosilicate glass matrix. This glass ceramic material was shown to combine advantages of rare-earth doped fluoride crystals with the ease of forming and handling of conventional oxide glasses. With an excitation wavelength of 970 nm, the measured upconversion emission intensity of Er^{3+} in the glass ceramics was 100 times higher than that of the precursor oxy-fluoride glass. However, the lead and cadmium in this oxy-fluoride glass ceramic material are designated as specified toxic substances by the Restriction Hazardous Substance (RoHS) in 2006. Therefore, an alternative material of PbF_2 and CdF_2 is needed for the environmental issue. In this study, we selected CaF_2 for an alternative material of PbF_2, fabricated rare-earth (Er, Tm) doped oxy-fluoride glass ceramics containing CaF_2 crystal and investigated the optical properties of Er^{3+} and Tm^{3+} in the oxy-fluoride glass ceramics.

2. Experimental procedure

Oxy-fluoride glasses in the system $45SiO_2$–$20Al_2O_3$–10CaO–$22CaF_2$–$2YbF_3$–$1ErF_3$ (–$20CaF_2$–$5YbF_3$–0.05-TmF_3) were prepared by melting method; 20 g batches in

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a platinum crucible were melted at 1300 °C for 1 h. The glass transition temperature (T_g = 620 °C) and the onset of crystallization temperature (T_x = 702 °C) were measured by the differential thermal analysis (DTA) measurement (Rigaku TG-DTA TG8120). Glass ceramics containing CaF_2 were prepared by heat-treatment at 700–750 °C for 4 h. The crystal phases, which were precipitated in the oxide glass matrix, were detected by the X-ray diffraction (XRD) measurement (Rigaku RINT1400). The upconversion emission of Er^{3+} and Tm^{3+} in the visible range of oxy-fluoride glass and glass ceramics were measured with the InGaAs laser diode (SDL-6362-PI) for 970 nm pumping, the monochromator (Nikon G-250) controlled with computer and the photo-multiplier.

3. Results and discussion

Fig. 1 shows the XRD pattern of Tm^{3+} doped glass and glass ceramics heat-treated at 750 °C. All the diffraction peaks were assigned to those of cubic CaF_2 crystal. The lattice constant calculated from the peak in Fig. 1 was 5.473 Å, larger than that of pure CaF_2 (5.462 Å, JCPDS Card No. 35-0816). The CaF_2 crystal phases containing Yb^{3+} or Ln^{3+} ions are considered to precipitate in both systems by heat-treatment at 750 °C for 4 h because the CaF_2–LnF_3 system has compositional range of solid solutions in the phase diagram and the lattice constant is lager than pure CaF_2. Fig. 2 shows the heat-treatment temperature dependence of upconversion spectra in visible region of Er^{3+} doped and Tm^{3+} doped glass and glass ceramics. The upconversion emission of Er^{3+} at 540 nm ($^4S_{3/2}$–$^4I_{15/2}$: green) and 660 nm ($^4F_{9/2}$–$^4I_{15/2}$: red) were observed in glass ceramic samples. These upconversion emission bands were very weak in the corresponding as-made glasses. The emission intensity of 660 nm was larger than that of 540 nm in all the Er doped samples. Generally, the sensitization of Er^{3+} with Yb^{3+} is favourable for infrared to green and red upconversion [3–5]. It is concluded that the Er^{3+} and Yb^{3+} ions are incorporated into the CaF_2 crystal phases by heat-treatment. From these results, the energy transfer in the Yb^{3+}–Er^{3+} can occur efficiently because the distance between Yb^{3+} and Er^{3+} ions decreased after crystallization. Typical upconversion mechanisms in the Yb^{3+}–Er^{3+} and Yb^{3+}–Tm^{3+} co-doped system are shown in Fig. 3. The Yb^{3+} ion was excited to the $^2F_{5/2}$ level by pumping laser. Two-step excitation to the $^4I_{11/2}$ and the $^4F_{7/2}$ levels in Er^{3+} comes from the energy transfer from Yb^{3+}. Fig. 4 shows temperature dependence of the integrated intensity of Er^{3+}: 540, 660 nm and Tm: 480, 650 nm and 800 nm emissions. The 660 nm integrated intensity of Er^{3+} increased more drastically than the 540 nm with increasing heat-treatment temperature. In many studies, a variety of the upconversion emission of Er^{3+} and Tm^{3+} were reported [6–10]. In this case, the reason why the red (660 nm) upconversion of Er^{3+} increased was considered. By incorporation of Er^{3+} ions into the CaF_2 crystal phases, the energy transfer among the neighbour Er^{3+} ions from $^4S_{3/2}$–$^4F_{9/2}$ to $^4I_{9/2}$–$^4F_{9/2}$ occurred efficiently (shown in Fig. 3). Increasing in the concentration of Er^{3+} ions in CaF_2 crystal phases probably caused this. Therefore, it can be considered that the ratio of population at the $^4F_{9/2}$ level (the initial level of 660 nm) increased.

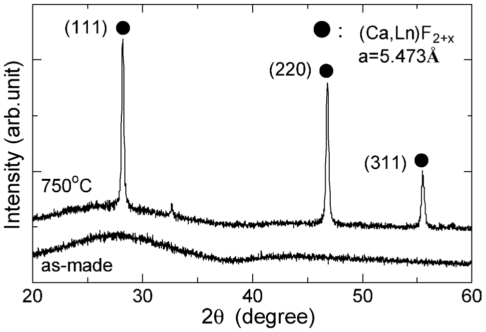

Fig. 1. XRD pattern of Tm doped as-made glass and glass ceramics heat-treated at 750 °C for 4 h.

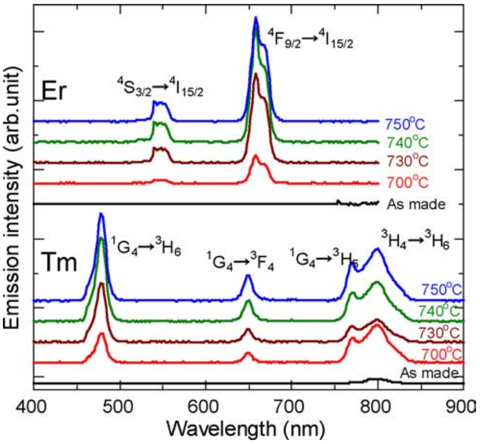

Fig. 2. Upconversion spectra of Er doped and Tm doped oxy-fluoride glass and glass ceramics heat-treated at 700–750 °C for 4 h. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

In Fig. 2, the upconversion spectra of Tm^{3+} at 480 nm ($^1G_4$–$^3H_6$: blue), 650 nm ($^1G_4$–$^3F_4$: red) and 800 nm ($^3H_4$–$^3H_6$) are shown. As shown in Fig. 3, Tm^{3+} ions can

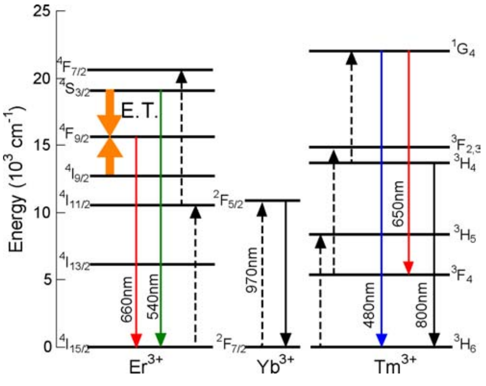

Fig. 3. Energy level diagram of Er^{3+}, Yb^{3+} and Tm^{3+} ions and upconversion mechanism. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

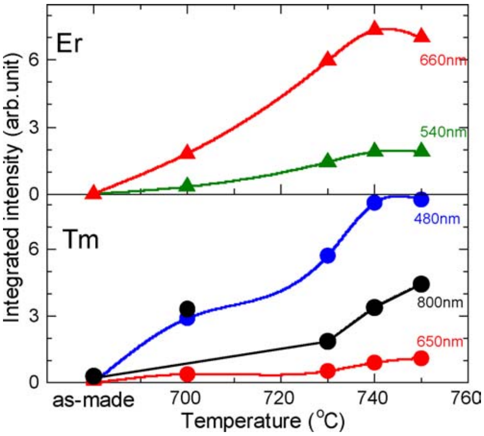

Fig. 4. Temperature dependence of integrated intensity of the emission band in Er doped and Tm doped glass and glass ceramics. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

be usually excited to the $^1G_4$ level with three-step by the energy transfer from Yb^{3+} [11]. The emission intensity of 480 nm was stronger than that of 800 nm for the samples heat-treated at above 730 °C, while the ratio was inverted for the 700 °C and as-made glass. As shown in Fig. 4, the integrated intensity of Tm^{3+} increased with increasing heat-treatment temperature. Because Yb^{3+} and Tm^{3+} ions were incorporated into CaF_2 crystal phases and the distance between these ions decreased, the energy transfer in these ions (Fig. 3.) occurred efficiently. In addition, the lower phonon energy of CaF_2 crystal phase is considered to be better for upconversion fluorescence. Generally, it is known that the phonon energy of Si–O is 1000 cm^{-1} and that of Ca–F is 400 cm^{-1}. The lower phonon energy of the matrix reduces the non-radiative decay rate [12]. Therefore, the CaF_2 crystal is favourable for the upconversion efficiency of Er^{3+} and Tm^{3+} ions.

4. Conclusion

Oxy-fluoride glass ceramics containing CaF_2 crystal were fabricated and the upconversion emission spectra of Er^{3+} and Tm^{3+} were investigated. By heat-treatment between 700 and 750 °C, the upconversion emission intensity of Er^{3+} and Tm^{3+} increased, while the intensity of these upconversion emissions were very weak in the corresponding as-made glasses. These results indicate that rare-earth ions are incorporated in the CaF_2 crystal phases after crystallization and the energy transfer efficiency from Yb^{3+} to Er^{3+} or Tm^{3+} was dramatically improved. The improved efficiency and the change of relative intensity ratio of 540 nm/660 nm bands in the Er-samples indicates that the average distance between Ln^{3+} ions are much shortened and the local phonon energy was decreased leading to higher upconversion efficiency. We conclude that both Ln^{3+} ions are condensed in the precipitated CaF_2 crystals leading to much lower multi-phonon decay loss of the excited levels of active ions.

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