Preparation and up-conversion luminescence properties of Er\(^{3+}-\)Yb\(^{3+}\) co-doped CaO–WO\(_3–\)SiO\(_2–\)B\(_2\)O\(_3–\)NaF glass ceramics

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Er\(^{3+}-\)Yb\(^{3+}\) co-doped CaO–WO\(_3–\)SiO\(_2–\)B\(_2\)O\(_3–\)NaF glass ceramics containing CaWO\(_4\) crystals were prepared by the melt-quench and crystallization method. The luminescence effect of the glass ceramic sample which was maintained for 70 min at 750°C exhibited the highest emission peak intensity in this work. As the crystallization time increased, the amount and the size of crystals increased and the crystal shape transformed from sphere to irregular polyhedron. Green and red up-conversion light appeared and the crystal materials with scheelite structure have attracted increasing interest, because of their electrical and especially its optical properties which are necessary for applications as a scintillator. In this paper, the luminescence properties of CaWO\(_4\) crystals in the precursor oxyfluoride glass are studied.

In recent years, a lot of attention has been concentrated on the synthesis, properties and application of tungstate.\(^1\) The calcium tungstate crystal is a good materials for laser matrix with excellent physical and luminescent stability.\(^2\) The Eu\(^{3+}\) doped CaWO\(_4\) phosphor powder prepared by high temperature solid phase synthesis method was reported by Feng Liang.\(^3\) Who concentrated on study about energy transmission between [WO\(_4\)]\(^2–\) ions and Eu\(^{3+}\) ions. Ho\(^{3+}/\)Yb\(^{3+}/\)Tm\(^{3+}\) doped CaWO\(_4\) crystal prepared by cochiralski method was reported by Yanling Xu.\(^4\) Tungstate glass prepared by melting method was reported by Yong Wang.\(^5\) Tungstate glasses and tungstate powder have been researched widely in the past few decades but the tungstate glass ceramic is seldom reported.\(^5\)\(^–\)\(^14\)

With the development of laser technology and laser material, the materials which possess high potential for up-conversion luminescence application has become one of the hot topics in the study. Er\(^{3+}\) has been widely studied as its abundant and uniform distributed energy levels.\(^5\)\(^–\)\(^14\) Liu F investigated the infrared luminescence of transparent glass ceramic containing Er\(^{3+}:\)NaYF\(_4\) nanocrystals.\(^17\) Vicente D Rodriguez investigated up-conversion and laser properties of Er\(^{3+}:\)Yb\(^{3+}\) co-doped nano-structured glass-ceramics.\(^18\) In this paper, transparent glass ceramics containing CaWO\(_4\) crystal were prepared by melt-quench and crystallization method. The up-conversion properties of Er\(^{3+}-\)Yb\(^{3+}\) doped CaO–WO\(_3–\)SiO\(_2–\)B\(_2\)O\(_3–\)NaF glass ceramics were investigated and the energy transition in up-conversion process was discussed.

1. Introduction

Glass ceramics not only possess excellent mechanical strength and chemical stability, but also remain highly transparent after doping high concentration of rare earth ions. Because of the low phonon energy of fluorite oxide glass, it can be used as an ideal up-conversion luminescent material. In recent years, the CaWO\(_4\) crystal materials with scheelite structure have attracted increasing interest, because of their electrical and especially its optical properties which are necessary for applications as a scintillator. In this paper, the luminescence properties of CaWO\(_4\) crystals in the precursor oxyfluoride glass are studied.

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NIR spectrophotometer. Fluorescence spectra measurement range of 400–700 nm on bulk samples using high resolution laser spectroscopy with the model of F9000 produced by British BIO-RAID company.

3. Results and discussion

Figure 1 shows the DSC curve of precursor glass. An unobvious endothermic peak at 597°C was observed, which indicates the occurrence of glass transition. There were two obvious endothermic peaks at 697 and 890°C, corresponding to the crystallization peaks process. An melting phenomenon occurred when the temperature rose to 960°C. The heat treatment system of glass ceramics are shown in Table 1.

The XRD patterns of the glass ceramic samples heat-treated under different conditions are shown in Fig. 2. It demonstrated that all the diffraction peaks of samples (a)–(e) could be readily indexed to tetragonal phase CaWO₄ according to the PDF standard card No. 41-1431. Figure 3 shows the crystal structure of CaWO₄. Each calcium ion is surrounded by eight oxygen ions, which resulted in the distortion of original tetrahedral. Ca²⁺ ions can be easily substituted by rare earth ions because they existed in the tetrahedral voids. It is known that a = b = 5.576 Å, c = 11.397 Å through the XRD figure of the sample (c). The change of structure illustrates that the rare earth ions enter the crystal. After smoothing and fitting of the diffraction patterns, the degree of crystallinity of the glass ceramics samples were obtained (a): 20.14%, (b): 42.57%, (c): 62.35%, (d): 76.82%, (e): 84.31%, (f): 86.27%, respectively. With the extension of heat treatment time or rising of temperature, the intensity of diffraction peaks of samples was increased gradually, meaning that the crystalline degree of them was increased.

Figure 4 shows the SEM images of glass-ceramics samples (a)–(f). As shown in Fig. 4, the crystalline phase of the sample (a) appeared but the radius was small, as the amount of crystal was small. With the increase of heat treatment time, the crystal content in samples (b)–(d) increased gradually and the size of particles became larger. The fact that some irregular shape crystals appeared in sample (d). With the increase of heat-treatment temperature, a large amount of crystals was observed in sample (e), and agglomeration phenomenon was obviously seen in sample (f). As a conclusion, the effect of heat treatment temperature on the growth of crystal was significant.

Figure 5 shows the transmittance spectra of glass and glass ceramics under different heat treatment in the range of 300–1100 nm. The transmittance of glass ceramics decrease gradually with the increase of heat treatment time. It can be explained by the fact that, with the increase of crystallization, the space around crystal decreased and the light scattering, diffraction and loss increased.

Figure 6 shows the up-conversion fluorescence spectra of glass and glass ceramics. As shown in Fig. 6, two spectra bands appeared under light excitation at 980 nm, which correspond to green light spectra at 517–557 nm and red light spectra at 648–670 nm, respectively. Two strong green light bands at 525 and 545 nm correspond to $^{2}H_{11/2}\rightarrow^{4}I_{15/2}$ and $^{2}S_{3/2}\rightarrow^{4}I_{15/2}$ transitions of Er³⁺ ion. The strong red light bands at 655 nm correspond to...
With the increase of heat treatment time, the intensity of emission peaks increased and then decreased. The glass ceramics which were heated at 750°C for 70 min had homogeneous crystal distribution and highest fluorescence intensity. The following relationship exists between emission intensity $I_{num}$ and the pumping power $I_{ex}$: $I_{num} \leq (I_{ex})^n$, where $n$ is the number of IR photons absorbed per visible photon emitted. Therefore, a plot of pumping power ($I_{ex}$) versus excitation power ($I_{num}$) should yield a straight line with the slope $n$. Changing the pump power, the different intensity of the glass ceramic samples on the up-conversion spectrum can be obtained. Figure 7 shows the relationship between the emission intensity of glass ceramic and the pumping power. The slope of green emission peaks at 525 and 545 nm are 2.0998 and 1.9629, respectively, and the slope of red emission peak at 655 nm is 1.9545, which indicates that the up-conversion luminescence is related to two-photon absorption process. The possible up-conversion mechanism is shown in Fig. 8. With the increase of pumping power, the luminescence intensity of peaks at 525 nm is higher than that at 655 nm due to the slope of green and red light are all deviated from the integer 2 which demonstrate the existence of cross-
relaxation and the energy transfer.\textsuperscript{21,22) Table 2 shows the composition of the glass ceramics samples with different Yb\textsubscript{2}O\textsubscript{3} doping concentrations. The glass ceramic is obtained after the precursor glass maintained 70 min at 750°C. Figure 9 shows the up-conversion luminescence spectra of glass ceramics with different content of Yb\textsubscript{2}O\textsubscript{3}. With the increase of Yb\textsubscript{2}O\textsubscript{3}, the fluorescence intensity of the sample is increased and then decreases. The strongest fluorescence intensity of glass ceramics appears when the content of Er\textsubscript{2}O\textsubscript{3}:Yb\textsubscript{2}O\textsubscript{3} was 1:9. It can be explained by the fact that the amount of Yb\textsuperscript{3+} entering the CaWO\textsubscript{4} crystal increased and the sensitization efficiency from Yb\textsuperscript{3+} to Er\textsuperscript{3+} increased with the increase of the content of Yb\textsubscript{2}O\textsubscript{3}. On the basis of the ratio, concentration quenching took place and the up-luminescence intensity decreased. When the content of Yb\textsubscript{2}O\textsubscript{3} was increased farther, the increase of the luminescence intensity of red and green light was different. As shown in Fig. 10, with the increase of Yb\textsubscript{2}O\textsubscript{3} content, the red and green light was both increase first and then decrease. The red light decreased more rapidly than the green light.
Figure 11 shows EDS spectrum of glass ceramic sample (c).3.

4. Conclusions

The Er\(^{3+}\)–Yb\(^{3+}\) co-doped glass ceramics in CaO–WO\(_3\)–SiO\(_2\)–B\(_2\)O\(_3\)–NaF system are prepared by the melt and crystallization method and the main crystal phase is CaWO\(_4\). The best heat treatment in this study was identified as maintaining the glass for 70 min at 750°C via the XRD pattern, transmittance spectra and the fluorescence spectra. When excited at 980 nm, the glass ceramics appeared strong green and red light. The up-conversion mechanism of Er\(^{3+}\)–Yb\(^{3+}\) doped glass-ceramics were discussed. The two-photon process of red and green light are confirmed through logarithmic relationship between excitation power and fluorescence intensity.

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