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Highly matched spectrum needed for photosynthesis in $Ce^{3+}/Er^{3+}/Yb^{3+}$ tri-doped oxyfluoride glass ceramics

Weirong Wang [a, b], Huiping Gao [a, b], Yanli Mao [a, b, *]

[a] School of Physics and Electronics, Henan University, Kaifeng 475004, China
[b] Institute for Computational Materials Science, Henan University, Kaifeng 475004, China

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ABSTRACT

A series of oxyfluoride glass ceramics containing CaF_2 nano-crystals tri-doped with $Ce^{3+}/Er^{3+}/Yb^{3+}$ ions were prepared by high temperature melting method and subsequent heat treatment. The structural properties were examined by X-ray diffraction measurements. The absorption, excitation, and emission spectra of the glass ceramics were investigated. Difference in erbium emission spectra between glass and glass ceramics had been studied. The emission bands originating from the $^4F_{9/2}$ state of Er^{3+} were enhanced when the CaF_2 nano-crystal created. By down-converting the ultraviolet wavelength region (280~400 nm) light and up-converting the near-infrared wavelength region (900~1100 nm) light, the glass ceramics can also emit strong reddish orange emission. The emission spectra consisting of bluish violet (400~500 nm) and reddish orange (640~680 nm) bands match well with the action spectrum of photosynthesis and absorption spectra of chlorophylls. Our materials will be favored to promote the development of glass greenhouses for green plant.

1. Introduction

Green Plant can seek out sunlight for photosynthesis, which helps sustain almost all life on earth. Currently, increases in yield potential will rely in large part on improved photosynthesis [1–4]. Solar radiation incident onto the earth's surface has wavelengths ranging from about 200 nm for ultraviolet radiation to about 2500 nm for infrared radiation. For the green plant, they are on the preference of absorbing more reddish orange and bluish violet lights than any other wavelengths. Longer wavelengths are not absorbed by chlorophylls and other photosynthetic antenna pigments, while shorter wavelengths are even harmful to the plant. An ability to use UV and near-infrared (NIR) radiation would greatly improve the efficiency of photosynthesis.

To promote the growth of the green plants, the plastic greenhouses are generally used when the temperature is low. However, the poor transparency of the plastic hinders the photosynthesis of the green plants [5,6]. Moreover, the plastic films can cause white pollution which is a serious pollution all around the world. To solve this problem, the glass greenhouses with good light transmittance, thermal retardation, and long service life, have been given deep concern [5,6]. For the host materials, the glass ceramics are more promising because they not only have the merits of the glass, but also contain nano-size crystallite phases that can improve the optical properties without loss of transparency. Notably, glass materials have better stability against UV irradiation which can favor the growth of green plant. Rare earth doped transparent glass ceramics has been investigated widely because of their wonderful luminous traits in the UV, visible and NIR wavelength regions [7–17]. Oxyfluoride glass ceramics, which contain fluoride nano-crystals inside the glass matrices, have particular properties. Fluoride nano-crystals in the glass matrices provide the low phonon energy environment for optically active ions, and the glass matrices, which are close to the oxide glasses, guarantee the good chemical and mechanical properties of these composite materials [13,18]. Among fluorides, the CaF_2 crystal is an important optical material with high solubility of both sensitizer and activator rare earth ions, and is highly transparent in the near UV to middle infrared range.

In this paper, we report on the preparation of the $Ce^{3+}/Er^{3+}/Yb^{3+}$ tri-doped oxyfluoride glass ceramics. Remarkably, it is found that the samples are transparent in the visible wavelength region and also have a good absorption in the light of UV and NIR wavelength regions. With the excitation of UV and NIR lights, the strong red orange light has been obtained. The useful bluish violet light can also be attainable.

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* Corresponding author. School of Physics and Electronics, Henan University, Kaifeng 475004, China.
E-mail address: ylmao@henu.edu.cn (Y. Mao).

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2. Experiment section

The samples were prepared by high temperature melting method and subsequent heat treatment with the following composition in a mole percentage: $50SiO_2-20Al_2O_3-20CaF_2-10NaF-xCeF_3-yErF_3-zYbF_3$. The doped CeF_3 and YbF_3 content were fixed to $x = 0.1\%$ and $z = 5\%$, while the ErF_3 content was $y = 0.1\%, 0.3\%, 0.6\%, 0.9\%$ respectively. The corresponding samples were named P1, P2, P3, P4, respectively. For each batch, about 10 g raw materials were fully mixed and then heated in a covered corundum crucible at 1350 °C for 2 h to achieve a homogeneous melt, then the melt was cast into a copper mold to process quenching. The resulted glasses were kept at 300 °C for 120 min in an annealing furnace to relinquish inner stress. They were called AG glasses. Then the glasses were heated at 600 °C for 8 h to form glass ceramics (named GC) through crystallization. The crystallization phase and the mean size of crystallites were examined by X-ray diffraction (XRD) using Philips X Pert Pro X-ray diffractometer with CuKa. The absorption spectra were recorded by a UV–Vis–NIR spectrometer (CARY5000) and the photoluminescence and excitation spectra were measured by a Tau-3 fluorescence spectrophotometer (Jobin Yvon-Inc, France). Luminescence decay curves were measured with a FLS980E spectrometer (Edinburgh Instruments Ltd., UK).

3. Results and discussion

Herein, we focus exclusively on the red-orange emission which is the main absorption band for photosynthesis, as chlorophylls absorb more reddish orange light than other wavelengths when photosynthesis occurs. Fig. 1(a) shows the absorption spectra of the $Ce^{3+}/Er^{3+}/Yb^{3+}$ tri-doped glass ceramics. As is shown in Fig. 1(a), the absorption peak at 378 nm, 488 nm, 520 nm and 650 nm should be assigned to $^4I_{15/2}$ to $^4G_{11/2}$, $^4F_{7/2}$, $^2H_{11/2}$ and $^4F_{9/2}$ transitions of Er^{3+}. For further clarity, the absorption in the 350~1100 nm wavelength region is magnified 4 folds (inserted in Fig. 1(a)). The absorption in the UV (280~350 nm) and NIR wavelength band (900~1100 nm) should be owing to 4f→5d of Ce^{3+} and $^2F_{7/2} \rightarrow {}^2F_{5/2}$ of Yb^{3+} respectively. Besides, the samples are of highly transparency in the visible range so the visible light can pass through easily. Fig. 1(b) describes the AM1.5 reference solar spectral irradiance [19] together with the excitation spectrum of the $Ce^{3+}/Er^{3+}/Yb^{3+}$ tri-doped oxyfluoride glass ceramics. The radiation in the 200~280 nm wavelength region (also called the solar blind region) of solar spectrum could hardly reach the surface of the earth because nearly all of them are absorbed by ozonosphere existing in in the upper atmosphere. Thus, all the samples have been measured in the 280~400 nm wavelength region. The monitor wavelengths are at 668 nm. The shapes and positions of the spectra for the all samples are the same, except for the peak intensities. The wide excitation band of the 280~350 nm should be due to the 4f→5d transition of the Ce^{3+} ion. The intense excitation band of 355~400 nm (peaks at 365 nm and 380 nm) should be ascribed to the $^4I_{15/2} \rightarrow {}^4G_{9/2}$ and $^4I_{15/2} \rightarrow {}^4G_{11/2}$ transitions of Er^{3+} ions. Thus, the reddish orange light can be excited by the whole UV (280~400 nm) region.

Under the 380 nm excitation, the results of the emission spectra are attractive, when we make a comparison between the AG glass and GC of P3 sample. As is shown in Fig. 2, three main emission bands of the AG glass and GC can be observed; they have maxima at 520, 545, and 668 nm, which should be ascribed to the Er^{3+} radiative transitions from the excited state $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ to the ground state $^4I_{15/2}$, respectively. Notably, the shape as well as the peak position of the GC sample resembles that of the AG glass sample. However, the strongest emission of the GC sample shifts to the reddish orange wavelength, compared to the strongest green emission of the AG one. With further observation, the reddish orange emission intensity of the GC sample is about 27 times larger than that of the AG sample, while the green emission intensity remains about the same. We speculate the creation of CaF_2 nanocrystal should be responsible for this obvious difference. The transform of the XRD patterns (shown in the inset of Fig. 2) of the glass and glass-ceramics sample validate the formation of CaF_2 nano-crystal. The typical amorphous structure of the glass sample changes to the intense characteristic diffraction CaF_2 peaks. According to Fig. 2, intense characteristic diffraction peaks are attributed to CaF_2 crystal (JCPDS No. 87-0971). The displayed peaks correspond to <h k l> values of (1 1 1), (2 2 0), (3 1 1), (4 0 0) and (3 3 1). The XRD pattern is found to match exactly with those reported in the literature [20,21]. Furthermore, with the doping of Yb^{3+}, the diffraction peak intensity of CaF_2 crystal is increased, and compared with the glass-ceramic without Yb^{3+}, it shows the clear diffraction peak at 2θ angles of 32.8° in (200) crystal face [22,23], which could be ascribed to the precipitation of $Ca_{0.8}Yb_{0.2}F_{2.2}$ crystal [22]. So, it indicates that the rare earth ions have incorporated into calcium

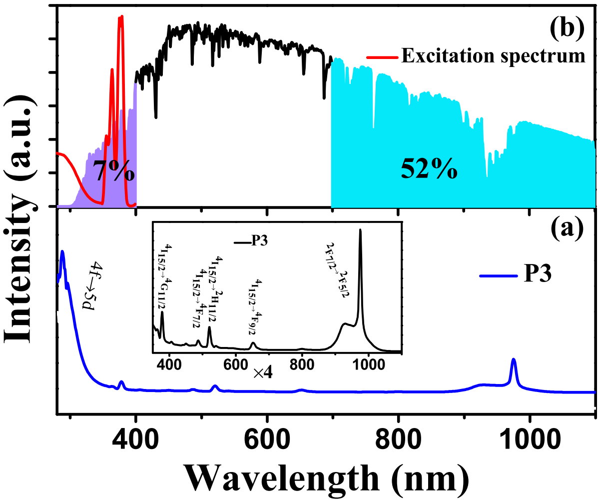

Fig. 1. The absorption spectra of the $Ce^{3+}/Er^{3+}/Yb^{3+}$ tri-doped glass ceramics (a). AM 1.5G spectrum in the 280~1100 nm wavelength region and the excitation spectrum of the P3 sample monitoring at 668 nm (b).

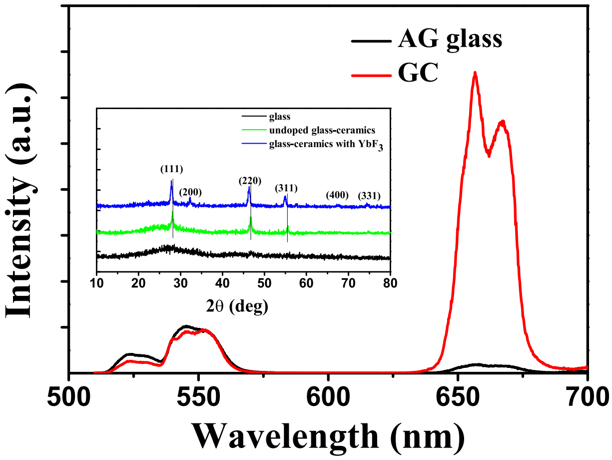

Fig. 2. The emission spectra of AG glass and GC of the P3 sample under the 380 nm excitation. The inset shows the XRD patterns of the glass, glass-ceramic without doped rare earth ions and glass-ceramic doped with Yb^{3+}.