

Studying on high efficiency and thermostable quantum cutting materials for solar cells

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Tb^{3+}/Yb^{3+} doped phosphate glass ceramics were prepared by high temperature melting method and heat treatment technology. The excitation and emission spectra of the samples were investigated in details. The samples can cut one blue or green photon into two 1000 nm infrared photon. Our materials can be used as wavelength conversion for solar cells and decrease the temperature of the solar cells, which are helpful in improving the efficiency of the solar cells.

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1. Introduction

To resolve the problem of energy and environment, solar cells have widely been studied [1-3]. Silicon solar cells can generate a single electron-hole pair by absorbing a photon above the band gap of Si ($E_g \approx 1.12\text{eV}$) and the excess energy is lost as heat. Thus, on the one hand the energy utilization efficiencies of solar cells for the high energy photons (like as visible and ultraviolet photons) are very low; on the other hand the overheated parts of solar cell will not work normally. To improve the efficiency of solar cells, two ways are usually used, like as modifying the solar spectrum or improving the structure of solar cell. In recent years, the first approach has attracted people's attention. Both up-conversion (UC) and down-conversion (DC) can modify the solar spectra. UC emissions need to absorb two or more low energy photons and emit a high energy photon, which affect the quantum efficiency of the materials. DC emissions, so-called quantum cutting (QC), may divide one high energy photon into two or more low energy photons. The quantum efficiency of the DC materials is higher compared to that of the UC materials. Considering trivalent Yb^{3+} ion only has a single excited state ($^2F_{5/2}$) in the 4f configuration. The luminous materials doped with Yb^{3+} ion can emit $\sim 1000\text{ nm}$ ($h\nu \approx 1.27\text{eV}$) NIR emission, which is just above the high energy edge of crystalline silicon. Consequently, the materials doped with Yb^{3+} ions have widely been investigated for developing solar cells. The systems doped with RE^{3+}/Yb^{3+} ($RE = Tm^{3+}, Er^{3+}, Tb^{3+},$ or Pr^{3+}) can obtain two $\sim 1000\text{ nm}$ infrared photons by absorbing one high energy photon [4-8], whose energy is no less than that of a blue light photon. Subsequently, the visible photons, like as red and green emissions, are not still be used. And the heat loss of solar cells is serious, which will bring the side-effect for the

instruments. From 1929, Pringsheim postulated that anti-Stokes fluorescence might be used to cool a material. The rare-earth doped materials had widely been studied for obtaining solid-state cooling by anti-Stokes emission. The results show that the fluorescence cooling by anti-Stokes emission is feasible. However, until to now, this technology does not apply to the solar cells. Here we firstly report that the utilization efficiencies of the visible light can be improved by using the thermal radiation, and the temperature of the solar cell can be controlled by the fluorescence cooling by anti-Stokes emission.

The rare earth ion have fruit energy levels in the visible and infrared wavelength region. The luminescence characters of the materials doped with rare earth ions are relaxed to the host matrix [9-13]. The host materials with low phonon energy, like as fluoride and crystal hosts [14-18] are chosen usually, which can reduce the non-radiative transition by multi-phonon relaxation and are expect to improve the luminous efficiency of the materials. The phosphate materials own good thermal and chemical stabilities, high rare-earth ions doped concentration, and large emission cross-section, and so on. However, the large energy phonon energy ($\sim 1200\text{ cm}^{-1}$) of phosphate materials usually restricts their applications. However, the large phonon energy is helpful to increase the energy transitions when the energy levels are not matching. Subsequently, in this letter, we prepared Tb^{3+}/Yb^{3+} doped phosphate glass ceramics and studied the luminescence characters in details. The materials can not only increase the utilization to the visible light, but also restrain the heat problem of the solar cells.

2. Experimental

The phosphate glass samples with the compositions of $60\text{P}_2\text{O}_5\text{-}10\text{AgO}\text{-}(20\text{-}x)\text{Sb}_2\text{O}_3\text{-}10\text{Tb}_2\text{O}_3\text{-}x\text{Yb}_2\text{O}_3$ (mol%) were prepared by high-temperature melting method, where $x=0, 0.05, 0.1, 0.2,$ and $0.4,$ respectively. The detailed preparation technology of the phosphate glass ceramics has been given in previous papers [19,20]. The start raw materials: $\text{NH}_4\text{H}_2\text{PO}_4, \text{AgNO}_3, \text{Sb}_2\text{O}_3, \text{Tb}_4\text{O}_7$ and $\text{Yb}_2\text{O}_3,$ were mixed thoroughly, and then put into a high fuse. Initially, the furnace was heated to 600 K at the rate of $1\text{Kmin}^{-1},$ and held at the temperature for 2 h to release the volatile components. Finally, the furnace temperature was raised to 1620K at the rate of $2\text{K min}^{-1},$ and control at the temperature for 3h to melt the raw materials completely. A clear, viscous melt was poured onto a preheated stainless-steel plate in air. The glass samples were heated at 720K for 6h to release the thermal stress. In order to obtain the glass ceramics, the precursor glasses are heated at 800K for 6h. Finally, the samples were incised and surface-polished for optical measurements. The emission and excitation spectra were measured with a model F111AI fluorescence spectrophotometer under the excitation of a xenon lamp (model Xe900).

3. Results and discussion

The excitation and emission spectra of the $\text{Tb}^{3+}/\text{Yb}^{3+}$ doped phosphate glass ceramics at room temperature are shown in Fig. 1. The monitoring wavelength of the excitation spectrum in the 300-700 nm region is 1000 nm and the excitation wavelength of the emission spectrum in the 900-1200 nm region is 472 nm. The excitation peak at 472 nm should come from the ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$ transition of Tb^{3+} ion. The emission peak at 1000 nm should be due to the ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition of Yb^{3+} ion. At higher temperature, the excitation and emission spectra of the $\text{Tb}^{3+}/\text{Yb}^{3+}$ doped phosphate glass ceramics were also measured. Fig. 2 is the excitation and emission spectra of the sample at $100^\circ\text{C}.$ The excitation peaks at 472 and 548nm are observed, which should be attributed to transitions of Tb^{3+} ions: ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$ and ${}^7\text{F}_5 \rightarrow {}^5\text{D}_4.$

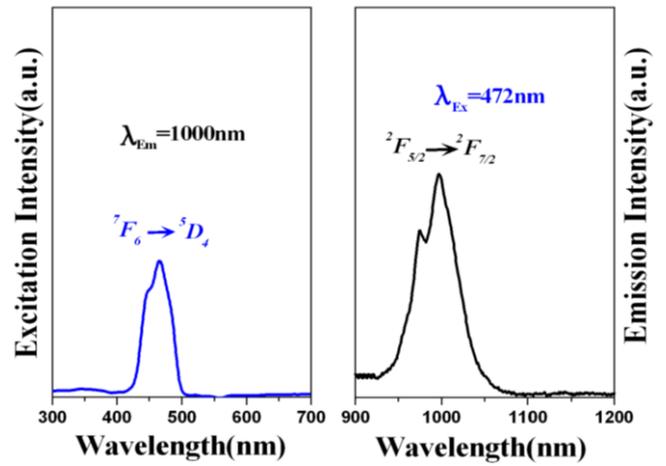


Fig. 1. Excitation and emission spectra of the $\text{Tb}^{3+}/\text{Yb}^{3+}$ doped phosphate glass ceramics at room temperature

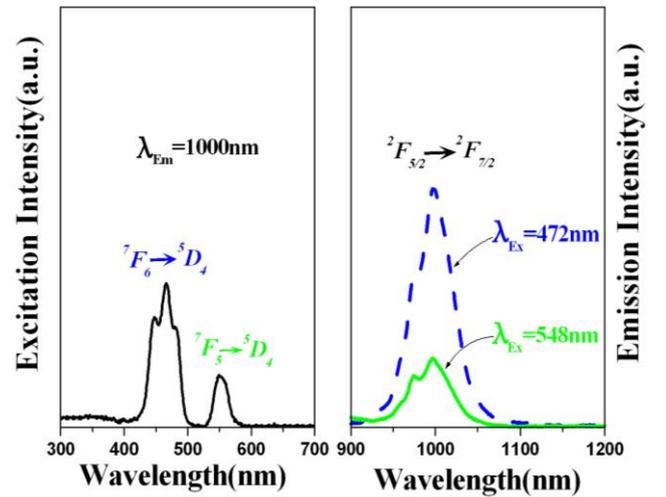


Fig. 2. Excitation and emission spectra of the $\text{Tb}^{3+}/\text{Yb}^{3+}$ doped phosphate glass ceramics at 100°C (color online)

Fig. 3 shows the energy level diagrams of the Yb^{3+} and Tb^{3+} ions, as well as the proposed population processes. The population processes of the 1000 nm infrared emission can be described as follows. The Tb^{3+} ions in the ground state can be excited to ${}^5\text{D}_4$ state under 472 nm excitation. Subsequently, The Yb^{3+} ions in the ground state can be pump to ${}^2\text{F}_{5/2}$ state by energy transition: ${}^7\text{F}_6(\text{Tb}^{3+}) + 2 * {}^2\text{F}_{7/2}(\text{Yb}^{3+}) \rightarrow {}^5\text{D}_4(\text{Tb}^{3+}) + 2 * {}^2\text{F}_{5/2}(\text{Yb}^{3+}),$ from where the 1000 nm infrared emission arises. At lower temperature, the 1000nm emission is not observed under 548 nm excitation. However, the strong 1000 nm emission can be found at higher temperature. The reasons can be interpreted as follows. The energy transfer of $h\nu + {}^7\text{F}_5(\text{Tb}^{3+}) \rightarrow {}^5\text{D}_4(\text{Tb}^{3+})$ is very weak because of the poor population of ${}^7\text{F}_5$ state at lower temperature. However, the vibration of phonon becomes strong with the increasing of the temperature, which is helpful to the population from ${}^7\text{F}_6$ to ${}^7\text{F}_5$ state. Thus, the ${}^7\text{F}_5$ state can populate lots of

particles at higher temperature. Then the ion can be excited to 5D_4 state by absorbing a 548 nm photon.

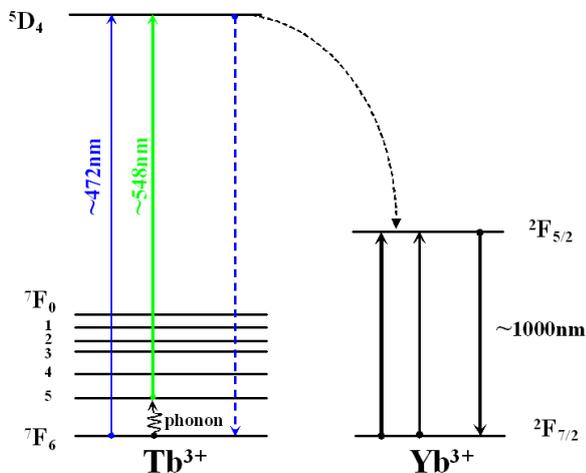


Fig. 3. Energy level diagrams of the Yb^{3+} and Tb^{3+} ions, as well as the proposed population processes (color online)

4. Conclusions

By high temperature melting method and heat treatment technology, the Tb^{3+}/Yb^{3+} doped phosphate glass ceramics were prepared. The sample can cut one blue emission photon into two 1000 nm infrared photons. Especially, the sample can cut one green emission photon into two infrared photons at higher temperature, which can not only improved the luminous efficiency of the 1000 nm emission, but also decrease the temperature of the materials by fluorescence cooling. Our materials will be valuable to develop wavelength conversion for high efficient solar cells. The quantum efficiency of the luminescence was still lower in the Tb^{3+}/Yb^{3+} doped phosphate glass ceramics. In the next work, we will improve the efficiency by controlling the host components and ion contractions.

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