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Preparation of Er^{3+}/Yb^{3+} co-doped zeolite-derived silica glass and its upconversion luminescence property

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Abstract

A novel upconversion luminescence transparent glass has been successfully synthesized from Er^{3+}/Yb^{3+} co-doped zeolite powder by Spark Plasma Sintering (SPS) method through the order–disorder transition process. XRD was used to detect the order–disorder transition process of each phase after SPS. These zeolite-derived silica glasses showed enhanced upconversion luminescence under the excitation of 980 nm diode laser, which was caused by the change of phonon energy according to the results of Raman spectrum, and the corresponding energy transfer mechanism was also discussed in detail.

Keywords: Zeolites; Silica glass; Spark plasma sintering; Upconversion; Phonon energy

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1. Introduction

Aluminosilicate zeolites are a kind of crystalline microporous material which have large surface area and low density. Due to to their excellent loading capacities, they have been widely used as host materials for guest molecules, ions and nanomaterials [1]. Until now, several different kinds of zeolites, such as ZSM-5, zeolite Y, zeolite B and zeolite L, have been chosen as luminescent hosts showing unique photochemical and photophysical activities [2]. Our previous work showed for the first time that aluminosilicate zeolite could undergo an order–disorder phase transition to become transparent glass during spark plasma sintering (SPS). Interestingly, compared with the conventional glass obtained by the melt-quench method, the zeolite-derived silica glass has better mechanical property and stronger ultraviolet photoluminescence properties at about 360 nm [3].

Upconversion luminescence glasses with wide varieties of host materials such as germanate, tellurite, fluoride and chalcogenide have been intensively investigated [4]. Possibly due to the high phonon energies (1060–1150 cm^{-1}) of silica glass, there is only one example of upconversion luminescence silica glass reported by Zhang et al. [5]. It is important to mention that silica glass shows excellent chemical and mechanical properties compared to the other kinds of glasses, which are essential for industial application. It would be a promising upconversion luminescence host if the high phonon energy can be reduced.

To realize the upconversion luminescence, Er^{3+} and Yb^{3+} have been chosen to dope into zeolite as guest ions. Among several possible choices of rare earth ions, Er^{3+} ion is very attractive due to its convenient and exploitable energy structure. Meanwhile, Er^{3+}/Yb^{3+} co-doping is one of the most efficient methods to enhance upconversion luminescence,

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because Yb^{3+} ion with a large cross-section around 980 nm can act as a sensitizer of Er^{3+} ion to promote the efficient energy transfer from Yb^{3+} to Er^{3+} [6,7].

On the basis of our previous work, here, we loaded Er^{3+}/Yb^{3+} into ZSM-5 to ensure the homogeneous dispersion of luminescence center. The SPS is used to compact the powder to avoid the concentration quenching during the melt-quench process [8] and achieve good mechanical properties. Notably, this Er^{3+}/Yb^{3+} co-doped zeolite-derived high silica glass exhibits a distinctive upconversion luminescence property, which has never been reported previously. Furthermore, the collapsed microporous structure of ZSM-5 is likely to induce significant reduction of the phonon energy, which is beneficial for improving upconversion efficiency.

2. Experimental procedure

ZSM-5 (Si/Al = 50) powder was provided by our research team [9]; Er^{3+}/Yb^{3+} was co-doped into ZSM-5 by wetting the ethanol solutions of $Er(NO_3)_3 \cdot 6H_2O$ and $Yb(NO_3)_3 \cdot 6H_2O$ into ZSM-5 power under ultrasonic treatment. The mixture was ultrasonicated for 2 h and then dried at 80 °C for 12 h, followed by calcination at 400 °C to move the NO_3^{3-}. By adjusting the relative ratio of $Er(NO_3)_3 \cdot 6H_2O$ and $Yb(NO_3)_3 \cdot 6H_2O$, a series of Er^{3+}/Yb^{3+} co-doped ZSM-5 samples with different Er^{3+}/Yb^{3+} molar ratios were prepared.

The Er^{3+}/Yb^{3+} co-doped ZSM-5 powder was loaded into a cylindrical graphite die with an inner diameter of 10 mm. A sheet of graphite paper was placed between the punch and the powder as well as between the die and the powder for easy removal. During the SPS process, a heating rate of 100 °C/min was launched at temperatures above 600 °C, and a uniaxial pressure of 55 MPa during the sintering cycle. Finally, the samples were obtained after sintering at 1200 °C for 1 min.

All the samples were surface-polished to small disks with 10 mm in diameter and 2 mm in thickness for optical measurements.

The crystallinity of powders was checked by X-ray powder diffractions (XRD) (D/Max-2550 V, Rigaku, using Cu Kα radiation ($\lambda = 1.5406$ Å)). The upconversion spectrum of the as-prepared phosphors was measured by a spectrofluorometer (Flotolog-3, Jobin Yvon, using Hamamatsu R928 photomultiplier tube) at room temperature. The Raman spectrum was collected by a Raman Microscope (DXR, Thermo scientific, using DXR 532 filter). All emission spectra were corrected for the spectral response of the measuring system.

3. Results and discussion

As can be seen from Fig. 1, the sample without Er^{3+}/Yb^{3+} ions doped (a) is transparent, while the sample co-doped with 0.6 mol% Er^{3+} and 6 mol% Yb^{3+} (b) is translucent, less transparent than the samples without rare earth ion, which can be attributed to the additon of Er^{3+}/Yb^{3+} ions.

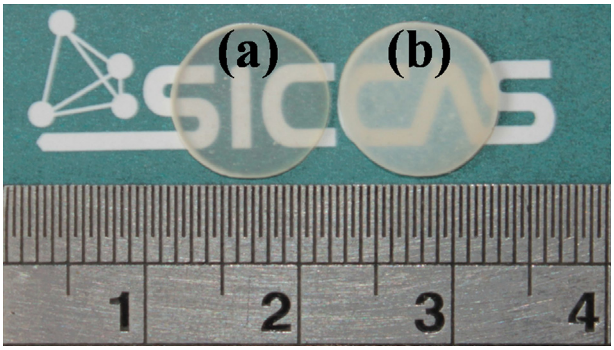

Fig. 1. The zeolite-derived silica glass samples without rare earth ion doping (a) and with 0.6 mol% Er^{3+} and 6 mol% Yb^{3+} co-doped (b).

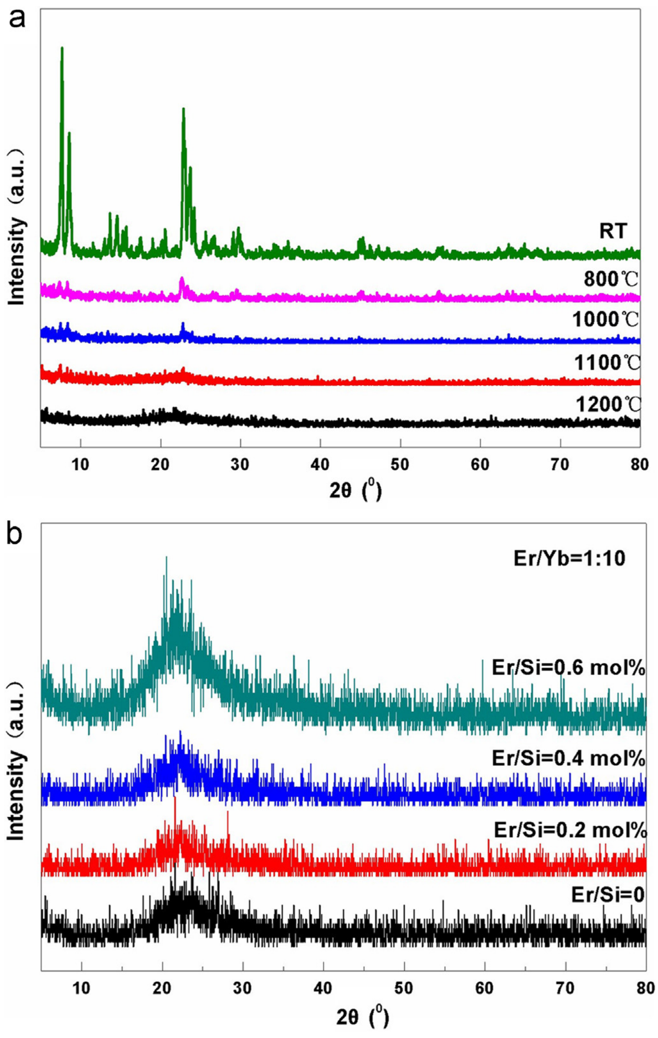

Fig. 2. XRD patterns of the ZSM-5 powders sintered at different temperatures by SPS (a) and (b) zeolite-derived glass samples with different amounts of co-doped Er^{3+}/Yb^{3+}.

Fig. 2(a) shows the XRD patterns of zeolite powder sintered at different temperatures by SPS. As the sintering temperature increases, the intensity of the main peaks characteristic of ZSM-5 decreases, indicating that the order to disorder procedure has occurred in the SPS sintering under high temperature and pressure. As the temperature increases up to 1200 °C, all the characteristic peaks disappear, indicating the completion of

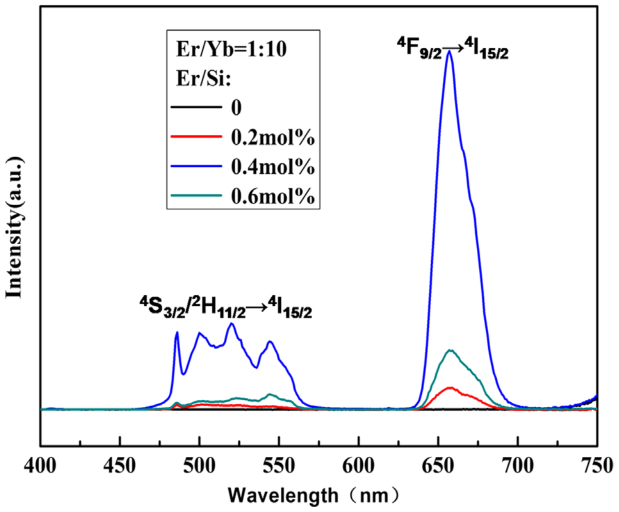

Fig. 3. Visible upconversion emission spectra of Er^{3+}/Yb^{3+} co-doped zeolite-derived glasses under 980 nm excitation.

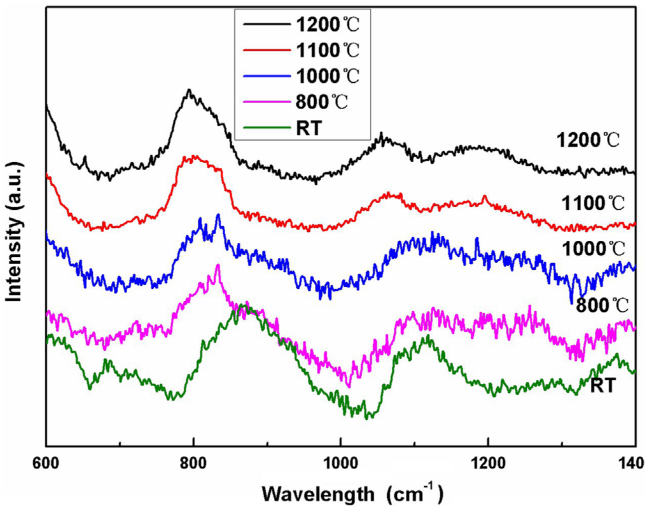

Fig. 4. Raman spectra of ZSM-5 powders sintered at different temperatures by SPS.

order–disorder process and the formation of zeolite-derived silica glass through SPS.

Fig. 2(b) shows the XRD patterns of Re-doped zeolite-derived high glasses. There is no distinct diffraction peak in the 2θ range of 5–80°, which demonstrates that all the samples have been transformed completely into glass phase after sintering as expected. Besides, no diffraction peaks of Er_2O_3 and Yb_2O_3 can be detected, which suggests that Er^{3+}/Yb^{3+} ions have been homogeneously dispersed in zeolite-derived silica glasses and no aggregation of Er^{3+}/Yb^{3+} ions into nanoparticles is observed during the SPS process which could otherwise give out diffraction peaks.

Fig. 3 shows the emission spectra of pure and Er^{3+}/Yb^{3+} co-doped ZSM-5-derived glass with different Er^{3+}/Yb^{3+} co-doping concentrations in the range of 400–750 nm under the excitation of 980 nm diode laser. The pure ZSM-5-derived glass exhibits no emission bands, while there are two distinct broad emission bands of all Er^{3+}/Yb^{3+} co-doped samples centered at 548 nm and 666 nm under the same experimental condition, which can be ascribed to the transition of $^4S_{3/2}/^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ respectively [10,11]. This indicates that all the Er^{3+}/Yb^{3+} co-doped zeolite-derived glass samples possess remarkable upconversion luminescence features. However, the emission intensity of red light firstly increases and then decreases with the increase of the Er^{3+}/Yb^{3+} co-doping concentration, which suggests that optimal upconversion intensity of the Er^{3+}/Yb^{3+} co-doped zeolite-derived glass could be obtained at a relatively low Er^{3+}/Yb^{3+} co-doping concentration of 0.4 mol%. The intensity decreases at high doping concentration which may be caused by the concentration quenching effect due to the Er^{3+}/Yb^{3+} ions clustering [12,13].

In order to test the feasibility of the zeolite-derived silica glass as host material for the upconversion luminescence, Raman spectroscopy is used to measure the exact phonon frequencies [14]. Fig. 4 shows the Raman shifts of ZSM-5 powder sintered at different temperatures by SPS. The intensity represents the phonon density of states in glasses while wavenumber stands for the phonon energy. A notable difference of different samples on the band at *ca.* 1000–1200 cm^{-1} could be obviously detected. The peaks of the samples sintered at 1200 °C and 1100 °C present low decrease in intensity and red-shift in wavenumber compared with the sample sintered at less than 1100 °C. This change illustrates a clear evidence of the reduction of the high phonon energy, which is corresponding to the LO asymmetric Si–O–Si stretching mode [15–17]. The pressure dependence of Raman spectra of amorphous SiO_2 has been studied by Hemley [18], Grimsditch [19] *etc.*, who explained that the Raman band shifted and decreased in intensity at the highest energy band under high pressure. This change is irreversible in the Raman spectrum because of the irreversible changes in the Si–O–Si bond angle and distortion of the individual $[SiO_4]$ tetrahedra at high pressure.

ZSM-5, a microporous aluminosilicate, is built up of corner-sharing $[SiO_4]$ tetrahedra. The microporous structure of the ZSM-5 collapsed during the order–disorder transition as the ZSM-5 powder transformed into dense silica glass. The collapse of the pores in the zeolite structure can result in reduced average Si–O–Si bond angles and distortion of the $[SiO_4]$ tetrahedra [16]. It is reported that as the melting temperature increased, only the low energy segment in the Raman band shifted, and no clear change could be found in the high energy region in normal silica glass by the melt-quench method [20]. In our work, the collapse of the microporous structure is found to play an important role in decreasing the high phonon energy. Usually, high phonon energy will lead to stronger vibrations and nonradiative relaxation, which may be deteriorative to the upconversion performance. Meanwhile, low phonon energy reduces the nonradiative decay rates and shortens the distances between the Er^{3+}/Yb^{3+} ions, which favors the energy transfer process. This zeolite-derived silica glass obtained by the order–disorder transition process shows reduced phonon energy which is helpful to enhance upconversion efficiency.

The upconversion fluorescence process is as follows: the $^4I_{11/2}$ level lies around halfway between the ground state ($^4I_{15/2}$) and the excited state ($^4F_{7/2}$). The green fluorescence comes from the energy level transition of $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and the red fluorescence is caused by $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition upon 980 nm excitation through two-photon absorption followed by multiphonon relaxation. The efficiency of these energy level transitions is strongly dependent on the characteristics of the glass host, such as multiphonon decay rates, population of metastable energy levels, energy transfer and cross relaxation rates decided by resonances in the energy level structure and active ions concentration. It has been established that rare earth doped glasses of low phonon energy exhibited low multiphonon decay rates in non-radiative loss, and thus enhanced the efficiency of the upconversion luminescence [12,21]. In other words, the zeolite-derived glasses with reduced phonon energy host materials are beneficial to minimize the multiphonon relaxation without radiative loss and maximize the radiative emission to obtain high upconversion efficiency.

4. Conclusions

Zeolite-derived silica glass co-doped with Er^{3+}/Yb^{3+} has been prepared by using SPS technique. During the SPS process, the zeolite structures collapse under high pressure and temperature and undergo an order–disorder transition process to form the glass. The Er^{3+}/Yb^{3+} silica glass exhibits distinctive upconversion luminescence properties due to the reduced high phonon energy of the silica glass, which can hardly be found in a normal silica glass host. The order–disorder transition treatment of aluminosilicate zeolites offers a new and effective way to reduce the phonon energy of the host material to enhance the upconversion efficiency. And it is believed that aluminosilicate zeolites are promising host materials for silica-based upconversion luminescence materials.

Acknowledgments

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