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Concentration effect and temperature quenching of upconversion luminescence in $BaGd_2ZnO_5$:Er^{3+}/Yb^{3+} phosphor

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Abstract: Er^{3+}/Yb^{3+} codoped zincate $BaGd_2ZnO_5$ phosphors were synthesized via a traditional solid state reaction. The crystal structure and phase purity were checked by means of X-ray diffraction (XRD), and the results showed that pure phase $BaGd_2ZnO_5$ phosphors with various Er^{3+}, Yb^{3+} concentrations were obtained. The influence of Er^{3+} and Yb^{3+} doping concentrations on the green and red upconversion emissions was studied. It was found that both green and red upconversion emissions under 980 nm excitation were two-photon processes independent from the rare earth doping concentrations. However, the upconversion luminescence intensities greatly depended on the rare earth doping concentration. Furthermore, the population processes of upconversion luminescence and the quenching mechanisms were analyzed. The temperature-dependent green upconversion luminescence was studied, and the temperature quenching process of two green upconversion emissions was modeled. The thermal quenching processes of the green upconversion emissions could be well explained by the model we proposed.

Keywords: $BaGd_2ZnO_5$:Er^{3+}/Yb^{3+} phosphor; solid state reaction; upconversion; crossover; rare earths

Upconversion luminescence in rare earth (RE) ions doped materials has been widely studied since it was first discovered in 1966 by Auzel[1]. A consensus that higher upconversion luminescence quantum yields can be obtained in the rare earth ions doped fluoride-based materials such as RE doped fluoride crystals ($LiYF_4$), fluoride glasses (ZBLAN) and fluoride powders ($NaYF_4$, $NaLuF_4$) has been fetched from a large number of investigations in the past several decades[2–6]. The upconversion luminescence of RE doped crystals and glasses was thought to be a possible route for realizing short wavelength lasing operation. With the development of semiconductor technology the short wavelength laser outputs have already been achieved directly from the electrically pumped semiconductor lasers, thus the research interest in RE doped bulk materials for upconversion luminescence has been depressed in a certain degree in recent years. Nevertheless, the research interest in RE doped fluoride nanoparticles driven by their applications in biomedicine and sensing technology is increasingly growing nowadays, and the syntheses, structural and morphological characterizations, luminescence mechanisms and applications of RE doped nanoparticles have been widely studied[7–11]. Though the RE doped fluoride-based materials exhibit higher upconversion luminescence quantum yields than that of most oxide-based RE doped upconversion luminescence materials, their chemical and physical stability is weaker, therefore, restricting the applications under some execrable conditions such as high temperature and corrosive environments. Thereby, developing novel oxide-based RE doped upconversion luminescence materials with high quantum yields is till necessary.

In the aspect of searching for high quantum yield oxide-based upconversion luminescence materials, Etchart and his co-workers have made a breakthrough that 5% and 2.6% of the upconversion luminescence yields were achieved, respectively, in Er^{3+}/Yb^{3+} and Ho^{3+}/Yb^{3+} codoped oxide compounds Ln_2BaZnO_5 (Ln=Y, Gd) derived from solid state reaction[12,13]. Since then, the RE doped zincate luminescence materials have received much attention. In addition to the solid state reaction, some other preparative routes including sol-gel reaction[14,15], microwave-assisted sintering technique[16], chemical auto-combustion[17], modified solid-state reaction[18,19] etc. have been developed for preparing the zincate phosphors. Moreover, the influence of flux and RE doping concentration on the crystal structure and spectroscopic properties has also been studied for the purpose of upconversion and white light illumination applications[19–22].

Though many efforts have been paid to the RE doped

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zincate phosphors, the temperature and RE concentration dependence of fluorescence properties in the zincate-based oxide phosphors is still not comprehensively perceived. Therefore, in this work, we studied on the influence of RE doping concentration on the upconversion luminescence, and discussed the temperature quenching mechanisms for upconversion luminescence in Er^{3+}/Yb^{3+} doped $BaGd_2ZnO_5$ phosphor.

1 Experimental

1.1 Sample preparation

Several $BaGd_2ZnO_5$:Er^{3+}/Yb^{3+} phosphors were prepared via a solid state reaction by using $BaCO_3$(AR), ZnO (AR), Gd_2O_3 (99.99%), Yb_2O_3 (99.99%) and Er_2O_3 (99.99%) as raw materials. In one series of samples the Er^{3+} doping concentrations were 0.5 mol.%, 1 mol.%, 3 mol.%, 5 mol.%, 7 mol.%, 10 mol.%, 15 mol.%, 20 mol.%, and the Yb^{3+} concentration was fixed to be 10 mol.% unchanged. In another series of the samples, the Er^{3+} concentration was set to be 7 mol.%, but Yb^{3+} concentrations were 0, 1 mol.%, 5 mol.%, 15 mol.%, 20 mol.%, 30 mol.%, 40 mol.% and 50 mol.%. In this paper the concentration is defined as the molar ratio of replaced Gd^{3+} content to total contents of rare earth ions in the phosphors. In a typical procedure, all raw materials were weighed stoichiometrically, and then were well mixed and ground in an agate mortar. After that the mixture was moved into an alumina crucible, and then heated in an electric muffle furnace at 1200 ºC for 4 h. Lastly, when the furnace cooled down to room temperature, the product was collected and ground again. More detailed synthesis procedure can be found in Ref. [23].

1.2 Sample characterization

The crystal structures and phases of the synthesized samples were checked on a powder diffractometer (Shimadzu XRD-6000, Japan), provided with a Cu tube with Kα radiation (λ=0.15406 nm). The upconversion emission spectra were measured by using a 980 nm optical fiber laser (BWT KS3-11312, Beijing Kaipulin Co., China) as the excitation source, and the data were recorded on a fluorescence spectrophotometer (Hitachi F-4600, Japan). The sample temperature was controlled and measured by using an apparatus assembled in our lab.

2 Results and discussion

2.1 Crystal structure characterization

In order to examine the crystal phase of the final products, the XRD patterns for all the samples were measured. It was found that all the samples exhibited similar diffraction patterns which are in good agreement with the pattern appearing in JCPDS card No. 49-0518. As examples, the patterns for the 1 mol.% Er^{3+}/10 mol.% Yb^{3+} codoped and 7 mol.% Er^{3+}/10 mol.% Yb^{3+} codoped samples are shown in Fig. 1, where a diffraction pattern plotted by using the data reported in the JCPDS card No. 49-0518 is also given for the comparison purpose. From the XRD patterns it can be concluded that the final products derived from our synthesis route are pure phase $BaGd_2ZnO_5$ in the degree that the XRD technique can discriminate. Meanwhile, higher concentration doping of rare earth ions does not cause the change of crystal structure of the final products thanks to the replacements between rare earth ions[24].

2.2 Dependence of upconversion luminescence intensity on Er^{3+} and Yb^{3+} doping concentrations

In order to examine the influence of Er^{3+} concentration on the upconversion luminescence, the upconversion spectra for the samples with fixed Yb^{3+} concentration (10 mol.%) and various Er^{3+} concentrations (0.5 mol.%, 1 mol.%, 3 mol.%, 5 mol.%, 7 mol.%, 10 mol.%, 15 mol.% and 20 mol.%) were measured under the same experimental conditions upon 980 nm excitation, and are shown in Fig. 2(a). In the spectra three upconversion emission peaks of Er^{3+} located at 529, 553 and 667 nm corresponding to the transitions from $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ to $^4I_{15/2}$ were observed[5,6,13]. The integrated emission intensities for green and red emissions for each sample were calculated from the upconversion spectra. The insert of Fig. 2(a) shows the dependence of upconversion luminescence intensity on the Er^{3+} concentration. It can be seen that both the green and red emission intensities first increase with Er^{3+} concentration, and reach their maximum at around 7 mol.% of Er^{3+} concentration, then decrease with further increasing Er^{3+} concentration.

Fig. 2(b) shows the upconversion spectra for the samples with 7 mol.% Er^{3+} and various Yb^{3+} concentrations (0, 1 mol.%, 5 mol.%, 10 mol.%, 15 mol.%, 20 mol.%, 30 mol.%, 40 mol.% and 50 mol.%). The intrinsic emissions as appearing in Fig. 2(a) are also observed. It can be seen that the upconversion emission intensity changes

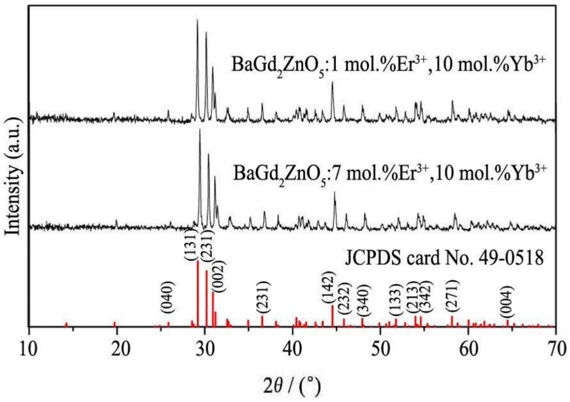

Fig. 1 XRD patterns of the $BaGd_2ZnO_5$ phosphors and the diffraction pattern plotted by using the data reported in JCPDS card No. 49-0518