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Effect of Li^+ ion concentration on upconversion emission and temperature sensing behavior of $La_2O_3:Er^{3+}$ phosphors☆

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ABSTRACT

The effects of Li^+ co-doping concentration on the structure, upconversion luminescence and temperature sensing behavior of $Er^{3+}:La_2O_3$ phosphors were investigated. X-ray diffraction and scanning electron microscopy observations reveal that Li^+ ion co-doping can change the lattice parameter of La_2O_3 host and increase the particle size of the samples. The optical investigation shows that co-doping of Li^+ ions can enhance the upconversion emission of Er^{3+} ions in La_2O_3 matrix effectively. Most importantly, the temperature sensing sensitivity of the samples is found to be dependent on Li^+ co-doping concentration, when the emission intensity ratio of the $(^2H_{11/2} \rightarrow {}^4I_{15/2})$ and $(^4S_{3/2} \rightarrow {}^4I_{15/2})$ transitions of Er^{3+} is chosen as the thermometric index. Both of the optimum upconversion luminescence and temperature sensing sensitivity are obtained for 7 mol% Li^+ co-doped sample. When the Li^+ concentration is beyond 7 mol%, both the quenching in upconversion intensity and the degradation of temperature sensitivity are observed, which may be due to the serious distortion in local crystal field around Er^{3+} ions caused by the excess Li^+ ions.

1. Introduction

Trivalent rare earth (RE^{3+}) doped upconversion (UC) luminescence materials have been extensively studied owing to their applications in the fields such as lasers, three dimensional displays, remote temperature sensor, solar cells, cell imaging and so on.[1–16] Recently, temperature sensing behavior of RE^{3+} doped UC luminescence materials, which can provide non-contact temperature measurement, is becoming a hot research subject due to the advantages of rapid response, low signal to noise ratio as well as the applicability in electromagnetically and thermally harsh environments. Among the optical thermometry methods, the fluorescence intensity ratio (FIR) technique has attracted more attentions, which is based on the measurement of luminescence intensity from the transitions of thermally coupled energy levels. This is because the technique can offer more accurate measurement in terms of its independence of the external factors, such as fluorescence losses, fluctuation of pumping intensity and electromagnetic compatibility, etc.[9,11,12]

Among the RE^{3+} ions, Er^{3+} ion is one of the most studied ions for the temperature sensor application.[3–5,8,12] Normally, its two thermally coupled levels $^2H_{11/2}$ and $^4S_{3/2}$ are adopted for temperature sensing. However, the poor UC emission efficiency and requirement of high pump power still impede the practical applications of Er^{3+} single-doped phosphors. Considerable efforts have been made to improve the UC efficiency of Er^{3+} ions. Besides using Yb^{3+} ion as the sensitizer, some non RE^{3+} ions (such as Li^+, Mg^{2+}, Zn^{2+}, etc.) also have been applied as co-dopants to increase the UC luminescence.[6,17–19] Recently, it is found that co-doping of the smallest metallic ion of Li^+ into the RE^{3+} ions doped systems can effectively improve the UC efficiency through tailoring the RE^{3+} ions' local environment. Ref. 18 has reported that co-doping of Li^+ ion into the $Y_2O_3:Er^{3+}$ nanocrystals can enhance the green UC intensity by ~20 times. However, few papers have reported the Li^+ ion co-doping effect on the luminescence temperature sensing property of Er^{3+} ion to date, not to mention the influence of Li^+ ion concentration.

Lanthanum oxide (La_2O_3) is a suitable host matrix for UC luminescent materials due to its relatively low phonon energy (~400 cm^{-1}), high thermal stability and good chemical and mechanical durability, as well as relatively low cost, etc.[6,20] The aim

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of the present work is to investigate the influence of Li^+ ion concentration on UC emission enhancement and the optical temperature sensing behavior of La_2O_3:Er^{3+} phosphors. For this purpose, we have synthesized a series of Er^{3+}/Li^+ co-doped La_2O_3 phosphor by gel combustion technique using glycine as reducer and fuel. The structure, morphology and optical properties of these samples have been studied systematically. The possible mechanism for the UC emission enhancement has been discussed. The relationship between the Li^+ ion concentration and the temperature sensing behavior of Er^{3+} in the samples has been investigated in detail, when the FIR value between $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions is chosen as an index for probing the temperature.

2. Experimental

2.1. Material preparation

La_2O_3 doped with 2 mol% Er^{3+} and 0–10 mol% Li^+ ions powders were synthesized by gel combustion synthesis method. The starting materials were $La(NO_3)_3\cdot 6H_2O$ (99.9%), $Er(NO_3)_3\cdot 5H_2O$ (99.9%), $LiNO_3$ (AR) and glycine. Firstly, $La(NO_3)_3\cdot 6H_2O$, $Er(NO_3)_3\cdot 5H_2O$ and $LiNO_3$ were dissolved into deionized water to obtain transparent solutions, respectively. Then those metal nitrates were mixed according to the required proportion. Glycine was added to the mixture and the molar ratio of nitrate to glycine was 1:3.5. The precursor solution was vigorously stirred under room temperature for homogeneous mixing and its pH value was adjusted to 6. The precursor solution was heated at 90 °C until it became gelatinous. After that, the gel was heated at 120 °C to dehydration and further removed to an electric furnace kept at a temperature of 450 °C. The combustion process took place and white foamy powders were obtained. Finally, the precursor powders were calcined at 1000 °C for 2 h to improve crystallinity and reduce the impurities.

2.2. Characterizations

The Fourier transformation infrared (FTIR) spectroscopic measurement was performed on a Bruker tensor 27 FTIR spectrometer. X-ray diffraction (XRD) measurements were carried out with a Bruker D2 PHASER diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm). The morphology of the products was observed by scanning electron microscopy (SEM) (HITACHI TM 3000). The particle sizes of the samples were calculated from the average of at least 50 particles. The UC photoluminescence (PL) spectra were measured by a Jobin-Yvon Frolog3 spectrofluorometer under the excitation of a 980 nm laser diode (LD). The temperatures of the powders were controlled by a temperature controlling system (TAP-02) assembled in our lab. With this system the sample temperature can be well adjusted and controlled in the temperature region from room temperature to 573 K.

3. Results and discussion

3.1. FTIR analysis

Fig. 1 shows the FTIR spectrum of La_2O_3:2 mol% Er^{3+}/7 mol% Li^+ to verify its composition and possible impurities. As shown, the absorption peaks at 543 and 648 cm^{-1} are mainly due to La–O vibrations in La_2O_3 structure. The peak at 887 cm^{-1} owing to C–O asymmetric stretching and the one at 1658 cm^{-1} due to O–H vibration are also observed, which may arise from the incomplete combustion of the organic fuel glycine.[21]

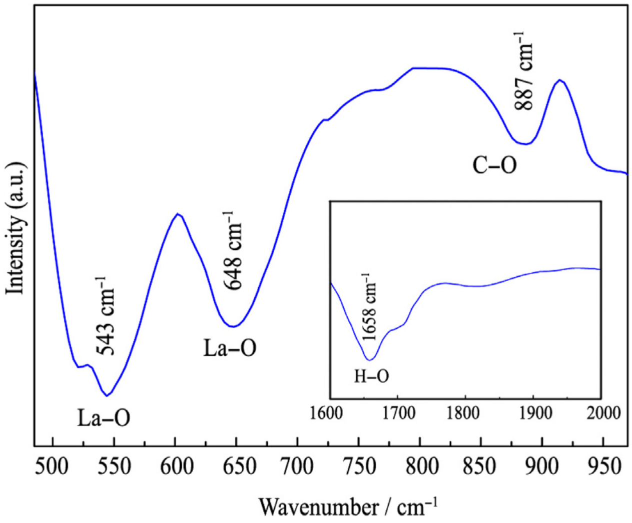

Fig. 1. FTIR spectrum of La_2O_3:2 mol% Er^{3+}/7 mol% Li^+ powders calcined at 1000 °C for 2 h.

3.2. XRD analysis

Fig. 2(a) shows the XRD pattern of the La_2O_3:2 mol% Er^{3+}/7 mol% Li^+ powders synthesized at 1000 °C. All diffraction peaks are well indexed to the hexagonal phase of La_2O_3 (JCPDS No.05-0602). No secondary phases can be detected in the pattern, suggesting that Er^{3+} and Li^+ ions are completely doped into La_2O_3 host lattice. Moreover, the sharp diffraction peaks reveal that the sample has possessed a high degree of crystallinity.

The XRD patterns of La_2O_3:2 mol% Er^{3+} powders co-doped with different Li^+ concentrations calcined at 1000 °C are shown in Fig. 2(b). To illustrate the influence of Li^+ ions on the La_2O_3 structure, a relatively narrow range of 2θ between 25° and 32° is presented. It can be noticed that the diffraction peaks of La_2O_3 shift towards higher angle sides with Li^+ concentration up to 7 mol%, indicating the reduction of La_2O_3 lattice parameter. Hence, we calculated the lattice parameters of the samples based on the square fitting of the peaks.[22] It is found that the lattice parameters are: $a = b = 0.3935$ nm, $c = 0.6130$ nm for La_2O_3:2 mol% Er^{3+}; while $a = b = 0.3929$ nm, $c = 0.6126$ nm for La_2O_3:2 mol% Er^{3+}/7 mol% Li^+. Since the ionic radii of Li^+ ion is smaller than that of La^{3+} ion, the substitution of La^{3+} by Li^+ ions can cause the shrinkage of the La_2O_3 lattice. Reversely, the peaks move towards lower angles with further increasing Li^+ concentration over 7 mol%, which can be attributed to the expansion of the host lattice by the presence of some Li^+ ions at interstitial sites of La_2O_3 lattice. Therefore, Li^+ ions dominate to substitute the La^{3+} ion sites, and then they may enter into the interstitial sites with further increasing concentrations. The results are consistent with those reported in Y_2O_3:Er^{3+}/Li^+ phosphors.[17–19] It is obvious that both types of Li^+ ion occupancies can slightly alter the crystal symmetry of La_2O_3 host and tailor the environment around Er^{3+} ions.

3.3. SEM observation

SEM study was performed to find out the influence of Li^+ ions on the particle size and morphology of the samples. Fig. 3(a) and (b) shows the SEM images of La_2O_3:2 mol% Er^{3+} and La_2O_3:2 mol% Er^{3+}/7 mol% Li^+ powders, respectively. It can be seen that the average particle sizes of La_2O_3:2 mol% Er^{3+} and La_2O_3:2 mol% Er^{3+}/7 mol% Li^+ powders are about 122 and 329 nm, respectively. Thereby, the particle size shows a significant increase after co-doping with Li^+ ions. The increase in particle size can lead to the