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Red luminescence of Lu_2O_2S:Ce and Y_2O_2S:Ce at room temperature

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Abstract

Lu_2O_2S:Ce (8.90 g/cm^3) and Y_2O_2S:Ce (4.92 g/cm^3) powder crystals have been prepared by oxalate co-precipitation first and then solid state reaction at 1150 °C in reducing atmosphere. X-ray diffraction (XRD) patterns show that they are of hexagonal structures. Photoluminescence (PL) of them is red and can be observed at room temperature. The emission spectrum of Lu_2O_2S:Ce has one broad band peaking at 650 nm; Y_2O_2S:Ce has two peaking at 346 and 600 nm. Gaussian components of these peaks suggest that they originate from the 5d–4f transition of Ce^{3+}. Photoluminescence, photoluminescence excitation (PLE) and diffuse reflectance spectra of Lu_2O_2S:Ce and Y_2O_2S:Ce as well as their luminescent mechanism have been studied.

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Keywords: Rare earth luminescent material; Luminescence; Scintillator

1. Introduction

Current applications in high energy physics strongly stimulate the search for promising high density, fast and radiation hard scintillation materials. For some applications, the readout of scintillation crystals with photomultiplier tubes (PMT's) presents problems: e.g. in applications where a high voltage or strong magnetic fields is unwanted. The detection of scintillation light with silicon photodiodes is then an alternative. Commonly used silicon photodiodes exhibit an efficient sensitivity in the range from 500 to 1000 nm, which generates a need for long wavelength scintillators (LWS) [1]. All Eu- and Tb-doped compounds show long decay time constants (τ) in the range of 10^2–10^4 μs [2]. So the problem is to find materials with a short decay time among the long wavelength phosphors.

The luminescence of Ce^{3+}, due to the 5d–4f electric dipole allowed transition, has relatively shorter decay time (20–40 ns) among trivalent lanthanide ions [3]; the density of Lu_2O_2S is 8.90 g/cm^3, higher than that of the recently widespread used scintillators, such as $Bi_4Ge_3O_{12}$ (7.13 g/cm^3) and $PbWO_4$ (8.28 g/cm^3). Thereby, the research on Lu_2O_2S:Ce may be of great significance in the exploration of promising scintillators.

In dozens of host materials, the emission of Ce^{3+} is efficient, but in some rare earth oxide and oxysulfide hosts, it is completely quenched, such as Y_2O_3, La_2O_3 [4], La_2O_2S [4,5], Gd_2O_2S [5] and Lu_2O_3 [6]. On the other hand, information about the luminescence of Y_2O_2S:Ce and Lu_2O_2S:Ce has barely been found in one article, describing them as red broad bands, though the 5d–4f emission of Ce^{3+} in most hosts is in the blue range or shorter [7], and such red luminescence is too weak to be observed unless at low temperature below 170 K [5].

In the present work, we have developed the synthesis method of Lu_2O_2S:Ce and Y_2O_2S:Ce and detected their red luminescence at room temperature; we also studied their crystal structures, photoluminescence (PL), photoluminescence excitation (PLE) spectra, diffuse reflectance spectra as well as their luminescent mechanism.

2. Experiments

Lu_2O_2S:Ce and Y_2O_2S:Ce powder phosphors were synthesized in the same method by oxalate co-precipitation [8] first and then solid state reaction in reducing atmosphere. The precursor $(R_{1-x},Ce_x)_2O_3$ (R = Lu or Y) was obtained by sintering the oxalate co-precipitate $(R_{1-x},Ce_x)_2(C_2O_4)_3$ (R = Lu or Y) at 900 °C in reducing atmosphere for 40 min. After the mixture of precursor, S, Na_2CO_3

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and Na_3PO_4 at a weight ratio of 100:30:30:5 was fully milled together, it was filled into a small ceramic crucible and pressed tightly, with 2–3 mm sublimed sulfur on the surface. The small crucible (50 ml) was then put into a bigger one (100 ml) with a certain amount of active carbon in it to create a reducing atmosphere when sintering. The double-crucible was sintered in a muffle at 1150 °C for 25 min.

The reducing atmosphere was created to protect Ce^{3+} from being oxidated to Ce^{4+}. After washed with dilute nitric acid and dried at 100 °C for 2 h, the samples (Y_2O_2S:Ce or Lu_2O_2S:Ce) turned out to be light-yellow powders and the body color darkens with the increase of doping concentration.

The X-ray diffraction (XRD) was carried out by a Rigaku D/MAX-rA diffractometer with Cu Kα ($\lambda = 0.15418$ nm) as the incident radiation. Photoluminescence spectra were performed on a Hitachi 850-type fluorescence spectrophotometer with a Xe lamp as the excitation light source. The diffuse reflectance spectra were recorded by a Schimadzu model UV-240 spectrophotometer. All of the measurements were performed at room temperature.

3. Results and discussion

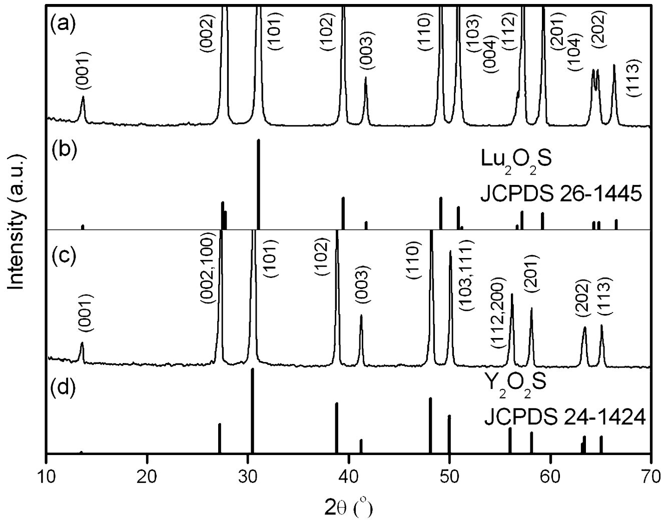

Fig. 1. XRD patterns of hexagonal Lu_2O_2S:Ce (1.5 mol%) (a), Y_2O_2S:Ce (1.0 mol%) (c), synthesized by oxalate co-precipitation and solid state reaction two-step method and pure Lu_2O_2S (b) and Y_2O_2S (d) from JCPDS card.

XRD patterns of the Lu_2O_2S:Ce (1.5 mol%) and Y_2O_2S:Ce (1 mol%) phosphors have been presented in Fig. 1a and c. Compared with the JCPDS cards, it is obvious that both samples are of hexagonal structures, with space group $P\bar{3}m1$. The lattice constant of them are $a = 0.371$ and 0.378 nm, $c = 0.649$ and 0.659 nm, respectively.

Figs. 2 and 3 exhibit the PL and PLE spectra of Lu_2O_2S:Ce (1.5 mol%) and Y_2O_2S:Ce (1.0 mol%) as well as the Gaussian components of their emission peaks. From Fig. 2, we can see that the emission spectrum of Lu_2O_2S:Ce (1.5 mol%) appears to be one broad band with peak at about 650 nm, no matter the irradiation wavelength is 250 or 460 nm; while for Y_2O_2S:Ce (1.0 mol%), under the irradiation of 267 nm, there are two obvious emission bands with peaks at about 346 and 600 nm. In Fig. 3, curves a_1 (peak at 650 nm) is the emission band of Lu_2O_2S:Ce (1.5 mol%), with excitation wavelength 460 nm; a_2 (peak at 346 nm) and a_3 (peak at 600 nm) are those of Y_2O_2S:Ce (1 mol%), with excitation wavelength 267 nm. The fitted peaks are at about 619 and 706 nm for a_1, 336 and 361 nm for a_2 (see the inserted figure in Fig. 3), 577 and 652 nm for a_3. Transforming into wavenumber, the differences of the fitted peaks are about 1991 cm^{-1} for b_1 and c_1, 2061 cm^{-1} for b_2 and c_2, and 1994 cm^{-1} for b_3 and c_3, basically consistent with the energy difference of the split 4f state of Ce^{3+} ion (about 2000 cm^{-1}), and therefore curves b_1–b_3 and c_1–c_3 correspond to the transition of 5d state to 4f $^2F_{5/2}$ and 4f $^2F_{7/2}$ of Ce^{3+}, respectively.

Diffuse reflectance spectra taken from the undoped and Ce-doped Lu_2O_2S and Y_2O_2S samples are given in Fig. 4. Comparing the difference between host and Ce-doped samples, we can see that a relative strong absorption peak at 460 nm appears only in Ce-doped materials. The schematic diagrams of energy levels of Lu_2O_2S:Ce and Y_2O_2S:Ce deduced from the PL, PLE and diffuse reflectance spectra are showed in Fig. 5. The relative energy levels of Ce^{3+} compared with energy gap are also denoted. Emissions from the lowest 5d level (D_1 for Lu_2O_2S:Ce and D'_1 for Y_2O_2S:Ce) to 4f $^2F_{7/2}$ and 4f $^2F_{5/2}$ can be seen in both

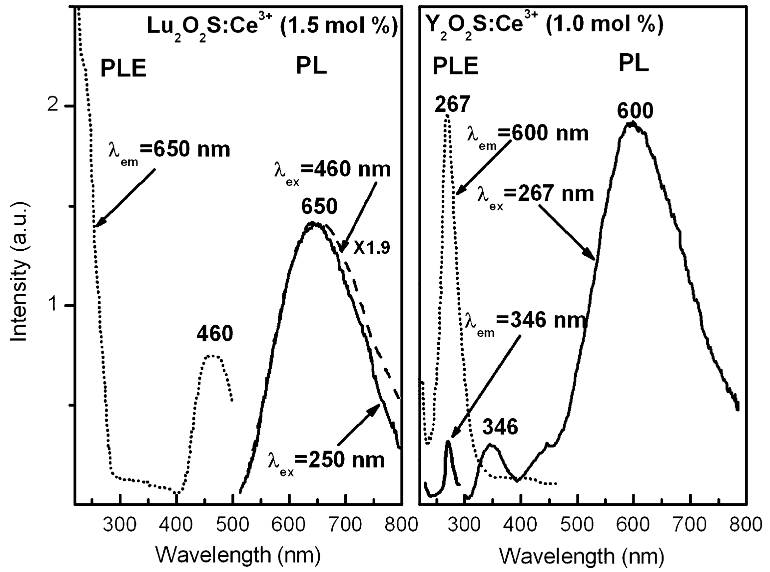

Fig. 2. PL and PLE spectra of Lu_2O_2S:Ce (1.5 mol%) (left) and Y_2O_2S:Ce (1.0 mol%) (right) at room temperature.