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Enhanced luminescence via Li^+ doping from a Sm^{3+}/Eu^{3+} Co-doped cerium oxide phosphor

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ABSTRACT

The $Sm^{3+}/Eu^{3+}/Li^+$ co-doped cerium oxide phosphor has been synthesized through co-precipitation and hydrothermal method. The structure and phase of these crystals have been characterized by X-ray diffraction, and it turned out to be the cubic fluorite cerium oxide structure. The spectroscopic investigations of the synthesized phosphors reveal that the Sm^{3+}-doped phosphor emits visible radiation in the red regions upon excitation with 365 nm. However, the addition of Eu^{3+} to the Sm^{3+}-doped phosphor decrease the magnetic-dipole transitions of Sm^{3+}, and then it emit an intense red emission corresponding to the characteristic transitions of Eu^{3+}. It is also found that the presence of Li^+ in the Sm^{3+}/Eu^{3+} co-doped cerium oxide phosphor obviously enhance the emission intensity of Eu^{3+}, whereas the increase of Sm^{3+} emission intensity is not obvious. A plausible mechanism of Li^+ for that luminescence enhancement of Eu^{3+} is suggested based on experimental studies. There may be a energy transfer from the excited 5d state of Ce^{3+} to the $^4F_{7/2}$ of Sm^{3+} ions, and the $^4F_{7/2}$ of Sm^{3+} ions further relaxed to the $^4G_{5/2}$ level by nonradiative relaxation. The two times enhancement in the electric-dipole transitions of Eu^{3+} is found, and thus $Sm^{3+}/Eu^{3+}/Li^+$ co-doped cerium oxide phosphor may be provided with a potential application for the high efficient dye-sensitized solar cell.

1. Introduction

Solar energy, an important source of renewable energy, is extremely valuable as global demands for energy [1,2]. Considerable research has been focused on improving the efficiency of solar cells. In 1991, the dye-sensitized solar cell was introduced by O'Regan and Gratzel, and then the development of dye-sensitized solar cell were suggested due to their low cost and relatively high efficiency [3]. Generally, the dye-sensitized solar cell are mainly comprised of a mesoporous network of TiO_2 nanoparticles and a dye sensitiser [4]. However, there are two types of spectral losses found for incoming solar radiation. One is weak light scatters in the visible light region, and thus a large portion of light will passe through the TiO_2 film, which results in a considerable loss of incident light. On the other hand, Ru-based dyes commonly have a narrow absorption spectral range in the visible regime, which gives rise to an energy loss of the incident light for ultraviolet (UV) [5]. Therefore, it is significant to increase light absorption and extend the light absorption range to improve the existing conventional dye-sensitized solar cell performance [6].

The dye-sensitized solar cell based on cerium oxide is the subject of investigation because of cubic structure of cerium oxide with high refractive index for visible light [7]. On the other hand, the rare-earth (RE) ions doped cerium oxide show unique down-conversion (DC) and up-conversion (UC) properties [8], which offer the opportunity to improve light harvesting and thereby the efficiency of the solar cells. Among the rare-earth elements, Eu^{3+} doped cerium oxide [9] were investigated for improving dye-sensitized solar cell efficiency, exhibiting down-conversion luminescent properties through energy transfer to the Eu^{3+} ions in the cerium oxide host. However, aliovalent substitution in cerium oxide lattice can result in the incorporation of considerable defect (mainly oxygen vacancies) due to the charge imbalance [10–13]. These defect can alter the local site symmetry of the primary dopant ion and ultimately influence the relaxation phenomenon [14,15]. Meanwhile, The role of oxygen vacancies on the photo-

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luminescent properties are still ambiguous [16–18].

Double or triple doped matrixes [19] is used as a prevalent way to improve the optical efficiency. Sm^{3+} is as one of the good activators, and Eu^{3+} and Sm^{3+} co-doped compounds were investigated in some host lattices [20]. For example, Xin Min et al. [21] found that the emission intensity of $LaMgAl_{11}O_{19}$:Eu^{3+} can be greatly enhanced by the co-doping of Sm^{3+}. In addition, alkali metals ions has been proven to be a prevalent way to improve the emission intensity of the down-converted emissions from different materials to a great extent [22]. For example, K Y Junga et al. [23] have investigated the effects of alkali metals doping on CeO_2:Eu^{3+} nanocrystals and showed that co-doping Li^+ enhanced their luminescence intensity. Further, in another work, Min et al. [24] shown that Na^+ ions are well inserted in the oxygen vacancy and produce the effect of the charge compensation and the improvement of crystallinity.

In this Article, we have studied the emission from Sm^{3+}/Eu^{3+}/Li^+ co-doped cerium oxide phosphor upon excitation with 365 nm radiation. The structural and optical properties, along with the mechanism involved in CET, are investigated in detail. It was found that UV–visible absorption decrease with concentration of Li^+ due to the increase of oxygen vacancies in as-prepared CeO_2:Sm^{3+}, Eu^{3+}. Interestingly, although oxygen vacancies increases with concentration of Li^+ ions, luminescence intensity of CeO_2:Sm^{3+}, Eu^{3+} increase instead of being reduced as shown in earlier literature [25]. It is found that the change in the amount of oxygen vacancies promotes the enhancement of Ce^{3+} concentration which played an important role in the energy transfer mechanisms instead of O^{2-}-Ce^{4+} CT band in the CeO_2:Sm^{3+}, Eu^{3+}, Li^+, which suggest a plausible mechanism for enhancement of the luminescence of CeO_2:Sm^{3+}, Eu^{3+}, Li^+.

2. Experimental

2.1. Preparation of samples

CeO_2:1 mol % Sm^{3+}, x mol % Eu^{3+} (i.e., x = 0, 1, 3, 5, 7, 10); CeO_2:1 mol % Sm^{3+}, 5 mol % Eu^{3+}, y mol % Li^+ (i.e., y = 0, 1, 3, 5, 7); and CeO_2:1 mol % Sm^{3+}, y mol % Li^+ (i.e., y = 0, 1, 3, 5, 7) phosphor samples were prepared by co-precipitation and hydro-thermal method. This paper did not present all sample synthesis processes, and the CeO_2:Eu^{3+}, Sm^{3+}, Li^+ phosphor samples was used as an example. The raw materials were $Ce(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}5H_2O$, polyethylene glycol 2000, $NH_3{\cdot}H_2O$ (AR) and $LiNO_3$. All of them were used as-received without further purification. The $Ce(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}5H_2O$ and $LiNO_3$ was first dissolved in deionized water, and formed a corresponding aqueous solution. The co-precipitation process was as follows: Polyethylene glycol (2000) and deionized water were added to single-mouth flask with magnetic stirring for 20 min at 40 °C. $Ce(NO_3)_3$, $Eu(NO_3)_3$, $LiNO_3$ and $Sm(NO_3)_3$ aqueous solution were added and continuous stirring for 30 min. Subsequently, $NH_3{\cdot}H_2O$ solution was slowly added and vigorously stirred for 1 h, and the mixed solution turned into white turbid liquid. The hydro-thermal process was as follows: the above white turbid liquid was transferred into a 100 ml hydro-thermal reactor and maintained at 180°Cfor 12 h. After naturally cooling to room temperature, the precipitate was separated and washed with ethanol and deionized water by centrifuging, respectively. The obtained precipitate were dried at 80 °C for 24 h under vacuum. The crude product was fired with air at 1000 °C for 2 h and CeO_2:Eu^{3+}, Sm^{3+}, Li^+ nanocrystals were obtained.

2.2. Characterization method

The X-ray Powder Diffraction (XRD) was conducted on a Bruker ADVANCED8 Advance X-ray diffractometer with CuKα X-rays at a scanning rate of 4°/min^{-1}, speed 0.5 s, and angle from 10 to 80° as well as tube voltage 40 kV and tube current 30 mA. Raman Spectra was measured by Invia-Reflex Confocal Micro Raman spectroscopy. The preparation of sample was as follows: a trace amount of CeO_2:Eu^{3+}, Sm^{3+}, Li^+ was dispersed in ethanol and was evenly mixed. The mixture was dropped with a dropper to the prepared copper grid and dried to conduct experiment. The absorption characteristics of the synthesized samples were studied in the wavelength range 200–800 nm using a Shimadzu, UV-3600 UV–vis spectrophotometer using barium sulphate as the reference. The photoluminescence of the phosphors was measured by HITACHI F-2700 Fluorescence Spectrometer (operation voltage 400 V, with a slit width of 5 nm).

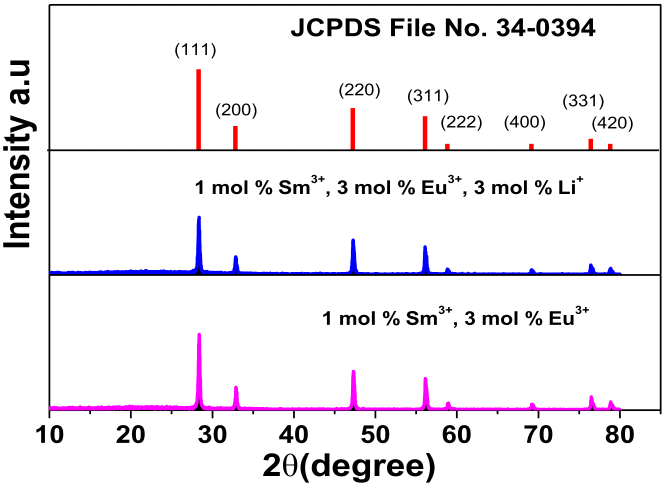

Fig. 1. XRD patterns of CeO_2:1 mol % Sm^{3+}, 3 mol % Eu^{3+} and CeO_2:1 mol % Sm^{3+}, 3 mol % Eu^{3+}, 3 mol % Li^+ phosphors.

3. Results and discussion

3.1. Structural characterization

Fig. 1 show the XRD patterns of CeO_2:1 mol % Sm^{3+}, 3 mol % Eu^{3+} and CeO_2:1 mol % Sm^{3+}, 3 mol % Eu^{3+}, 3 mol % Li^+ phosphor. It is observed that the diffraction peaks correspond to the (111), (200), (220), (311), (222), (400), (331) and (420) planes of the cubic fluorite cerium oxide structure (JCPDS Card No. 34–0394). Meanwhile, there was also no formation of diffraction peaks corresponding to other oxides, indicating that the small amounts of Sm^{3+}, Eu^{3+} and Li^+ ions into the host does not destroy the crystal structure of cerium oxide. On the other hand, it can be noted from Fig. 1 that the Li^+ doped CeO_2:Sm^{3+}, Eu^{3+} nanocrystals phosphors obviously exhibits a decrease in intensity of diffraction peaks, indicating that the Li^+ co-doped sample hadn't improve the crystallization of the samples. The result may be ascribed to the increase of oxygen vacancies. It is established in the literature [25] that, on substitution of monovalent ion for Ce^{4+}, oxygen vacancies is formed due to the charge imbalance on the substitution of Ce^{4+} with monovalent ion, and the charge compensation mechanism described in the Kröger Vink notation as: $CeO_2 + Li_2O \rightarrow 2Li'''_{Ce} + 3V_{\ddot{O}} + O_O^X$. On the other hand, according to the Scherrer equation, the strongest peak (111) at 28.7° were used to calculate the average crystallite size of sample, as is shown in Table 1. CeO_2:1 mol % Sm^{3+}, 3 mol % Eu^{3+} crystals is determined to be around 38.3 nm, and whereas the average crystal size of CeO_2:1 mol % Sm^{3+}, 3 mol % Eu^{3+}, 3 mol % Li^+ crystals estimated by the Scherrer equation decreased to 35.5 nm. Compared with the CeO_2:1 mol % Sm^{3+}, 3 mol % Eu^{3+} crystals, the calculated cell parameter values of the Li^+ doped sample is 0.5436 nm, and a little larger than that of CeO_2:1 mol % Sm^{3+}, 3 mol % Eu^{3+} (0.5432 nm), which may be due to the oxygen vacancies induced by the doping Li^+ ions. Earlier literature [26] on ions doped cerium oxide also reported that the lattice expansion effect result from increased oxygen vacancies and Ce^{3+} ions with aliovalent substitution in