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Improvement of photoluminescence properties of Eu^{3+} doped $SrNb_2O_6$ phosphor by charge compensation

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ABSTRACT

In this paper, a series of Eu^{3+}-doped $SrNb_2O_6$ phosphors have been successfully prepared by a high-temperature solid-state reaction technique. The as-prepared samples exhibit strong red emission peak at around 612 nm, which is attributed to the $^5D_0$-$^7F_2$ transition of the Eu^{3+} ion. Both the emission intensity and color rendering effect can be obviously improved in $SrNb_2O_6$:Eu^{3+} phosphors by self-compensation or co-doping with Li^+ ions. Meanwhile, the decay time of phosphors can also be extended by charge compensation. The Judd–Ofelt theory is used to calculate the optical transition strength parameters and quantum efficiencies of the obtained samples. In addition, Eu^{3+} and Li^+ concentration-dependent excitation and emission spectra are investigated in detail. The critical distance is determined to be about 11.48 Å and the strongest red emission intensity is achieved in the $Sr_{0.7}Nb_2O_6$:0.15Eu^{3+},0.15Li^+ phosphor. The CIE-1931coordinate (0.633, 0.366) of this sample is very close to that of the standard red light (0.67, 0.33). All of the results indicate that charge compensation approach can greatly improve the photoluminescence properties of Eu^{3+}-doped $SrNb_2O_6$ phosphors, which will further promote their applications in solid state lighting.

1. Introduction

Rare-earth ions have gained extensive attention due to their abundant energy levels as well as unique and fascinating optical properties. Currently, rare-earth ions doped luminescent materials have been widely used in many aspects, such as displays, solid-state lighting, optical temperature sensors, biomarkers, optical heaters, drug carriers and photovoltaic devices [1–6]. In particular, rare-earth ions based phosphors, which could provide with good spectral characteristics featuring with high efficient luminescent performance, high stability, low energy consumption, long lifetime and environmentally friendly characteristics, are referred as the next generation of illumination source [7–9]. As one of the most frequently used red-emitting activators, Eu^{3+} ion is widely studied owing to its intense red remission at around 610–615 nm arising from the $^5D_0 \rightarrow {}^7F_2$ transition [10]. Up to now, the Eu^{3+}-doped red emitting phosphors have been found in vanadates [11], phosphates [12], borates [13], metasilicate [1,14], tungstates [15] and molybdates [16,17]. However, some available approaches, such as changing composition of host and adjusting the quantity of charger, are still needed to further improve the luminescent properties of Eu^{3+} ions to enhance their performance in the currently existing applications [11,18]. Among them, charge compensation is the most commonly used method because it can be easily realized. As is well known, the alkali metal ions, such as Li^+, Na^+ and K^+, which have low oxidation states and different particle radius, can significantly enhance the photoluminescent properties of rare-earth ions activated phosphors by co-doping methods [19,20]. In comparison with other alkali metal ions, the Li^+ ions are widely employed to enhance the emission intensity of Eu^{3+}-doped materials, meanwhile, some impressive achievements have been obtained in some systems, such as $Sr_5(PO_4)_3F$ [21], $Ca_3(PO_4)_2$ [22], Sr_2CeO_4 [23,24], $CaMgSi_2O_6$ [25], $CaMoO_4$ [26] and $ZnMoO_4$ [27]. On the other hand, self-compensation, which can produce vacancy artificially, is another method to achieve charge compensation.

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Nowadays, niobates are thought to be promising luminescent hosts due to their unique properties including high chemical stability, good mechanical performance, wide transparency range, commendable electro-optical, photoelastic and nonlinear properties, which endow them with important applications in the fields of photocatalytic technology, microwave resonators pyroelectric, electro-optic, ferroelectric and photorefractive devices [3,28]. Over the last decades, the luminescent behaviors of rare-earth ions based niobates, such as, $CaNb_2O_6$ [9], $LaNbO_4$ [29], $YNbO_4$ [30] and $GdNbO_4$ [31], have been intensively studied. In comparison, the interest in the strontium metaniobate ($SrNb_2O_6$) is also increasing as a result of its suitability for pyroelectric, electro-optic, ferroelectric and photorefractive devices [32]. However, as far as we know, the research on photoluminescence (PL) and energy transfer behaviors of Eu^{3+}-doped $SrNb_2O_6$ phosphors are rarely reported.

In present work, a series of $Sr_{1-2x}Nb_2O_6$:xEu^{3+},xLi^+ ($x = 0.00–0.175$) phosphors were synthesized by the conventional high-temperature solid-state reaction method. The phase structure, morphology, lifetime and photoluminescent properties of the obtained samples were investigated in detail. Furthermore, the energy transfer mechanism between the Eu^{3+} was also systematically studied.

1.1. Sample preparation

The $Sr_{1-2x}Nb_2O_6$:xEu^{3+},xLi^+ phosphors were prepared through a high-temperature solid-state reaction technique. According to the appropriate stoichiometric ratio, the starting materials, such as $SrCO_3$ (GTSCIEN, 97.00%), Nb_2O_5 (DAEJUNG, 99.90%), Li_2CO_3 (ALDRICH, 99.997%) and Eu_2O_3 (Aladdin, 99.99%), were weighed and ground finely in an agate mortar for 30 min with an appropriate amount of ethanol. Then, the homogeneous mixture was kept in a crucible and sintered in a muffle furnace at 1250 °C for 7 h. After cooled to the room temperature, the obtained white samples were ground to a fine powder for further characterization.

1.2. Characterization and optical measurements

The X-ray diffraction (XRD) measurement was performed to verify the phase purity by a Philips X'Pert MPD (Philips, Netherlands) X-ray diffractometer at 40 kV and 30 mA. The diffraction patterns were scanned within an angular range of 10–70° (2θ). The morphology and particle size of phosphors as well as the energy dispersive X-ray (EDX) spectrum were characterized using a scanning electron microscope (SEM) system (JSM-6490, JEOL Company). X-Ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5000 *VersaProbe* spectrometer using a monochromatic Al K_α radiation source. UV–vis diffuse reflectance spectra (DRS) were collected by a V-670 (JASCO) UV–vis spectrophotometer. The PL and PL excitation (PLE) spectra were recorded by a Photon Technology International (PTI, USA) fluorimeter with a 60 W Xe-arc lamp as the excitation light source. The quantum yields (QY) of the samples were measured with use of an integrating sphere and a FLS 920 fluorescence spectrophotometer. All measurements were performed at room temperature in air atmosphere.

2. Results and discussion

2.1. The phase formation and structure

The typical SEM images of pure $SrNb_2O_6$, $Sr_{0.85}Nb_2O_6$:$0.15Eu^{3+}$, $Sr_{0.775}Nb_2O_6$:$0.15Eu^{3+}$ and $Sr_{0.7}Nb_2O_6$:$0.15Eu^{3+}$,$0.15Li^+$ phosphors are shown in Fig. 1. It can be found that all the samples are made of irregular particles with average particle size around 5 μm, which are caused by the inherent characteristics of the high-temperature solid-state method. It should be noted that the $SrNb_2O_6$, $Sr_{0.85}Nb_2O_6$:$0.15Eu^{3+}$ and $Sr_{0.775}Nb_2O_6$:$0.15Eu^{3+}$ phosphors show the similar morphology properties, while the $Sr_{0.7}Nb_2O_6$:$0.15Eu^{3+}$, $0.15Li^+$ phosphor shows the agglomeration and coarse surface. The different charge compensation has an obvious impact on the surface and particle size of the resultant phosphors, especially alkali metal ions. In this work, the Li_2CO_3 does not only act as charge compensating agent but also serves as liquid flux. It can accelerate the grain growth of the particles to generate highly crystalline phosphor. Also, it will help the doped activators to penetrate deep inside the matrix and form homogeneous distribution in the matrix at high temperature [15].

The unit cell structure of $SrNb_2O_6$, which possesses an orthorhombic columbite structure (space group P21/c) with cell parameters of $a = 7.772$ Å, $b = 5.592$ Å, $c = 10.989$ Å, V = 474.51 Å^3, N = 4, is shown in Fig. 2. Based on the crystal structure, it is clear that there is only one cationic site with Wyckoff position 4e for activators to accommodate, while each cation has different coordination environments, such as the Sr atom, which is the center of hendecahedron, surrounded by eight oxygen atoms with the average distance of 2.605 Å, and the Nb atom, which is the center of octahedron, is surrounded by six oxygen atoms with the average distance of 1.998 Å. Taking into consideration of the ionic radii and charge balance, Eu^{3+} [r = 1.066 Å for coordination number (CN) = 8] ions are expected to substitute the Sr^{2+} ions (r = 1.26 Å for CN = 8) instead of the Nb^{5+} (r = 0.64 Å for CN = 6) ions. Thus, we can conclude that the Eu^{3+} ions would occupy the sites of Sr^{2+} ions in the $SrNb_2O_6$ host lattices. The structure of [$-NbO_6-SrO_8-NbO_6$] is the minimum unit cell, in which the SrO_8 polyhedra and NbO_6 octahedron share the common edge, while two Nb atoms are connected by sharing point, forming a 3D framework.

Fig. 3 shows the XRD patterns of the representative samples of pure $SrNb_2O_6$, $Sr_{0.85}Nb_2O_6$:$0.15Eu^{3+}$, $Sr_{0.775}Nb_2O_6$:$0.15Eu^{3+}$, $Sr_{0.7}Nb_2O_6$:$0.15Eu^{3+}$,$0.15Li^+$ phosphors together with the standard pattern (JCPDS 28-1243) of $SrNb_2O_6$. As illustrated in Fig. 3(a), all the diffraction peaks of compounds are matched well with the standard pattern of $SrNb_2O_6$, indicating that the obtained samples are single phase and the Eu^{3+} ions are completely dissolved in the $SrNb_2O_6$ host lattices. From the zoomed XRD patterns (Fig. 3(b)), it is also observed that the XRD peaks move to larger angles with the addition of Eu^{3+} and Li^+ ions. This is because the Sr^{2+} ions with larger ionic radius are replaced by the smaller Eu^{3+} and Li^+ (0.92 Å) ions. Based on Bragg equation $2d\sin\theta = n\lambda$ (here d is the interplanar distance, θ stands for half diffraction angle, n represents the integer and λ is the wavelength of X-ray), the interplanar distance would be shortened when the larger (Sr^{2+}) ions are substituted by smaller (Eu^{3+}, Li^+) ions, resulting in the shifting of the diffraction peaks. In order to further determine the structure of the obtained phosphor, the lattice constants of $SrNb_2O_6$ phosphors were refined by the GSAS software and the final consequence are showed in Fig. 4. The reliability factors of the refinement are wRp = 3.72%, Rp = 2.72%, and $\chi^2 = 4.75$, which indicated that the phosphor well possess pure orthorhombic phase without any impurity phases. Fig. 5 shows the EDX spectra of the samples modified with different charge compensation methods. Fig. 5(a–c) show the EDX spectra of the $Sr_{0.85}Nb_2O_6$:$0.15Eu^{3+}$, $Sr_{0.775}Nb_2O_6$:$0.15Eu^{3+}$ and $Sr_{0.7}Nb_2O_6$:$0.15Eu^{3+}$,$0.15Li^+$ phosphors, respectively. The elements of Sr, Nb, O, and Eu could be clearly identified, whereas the Li could not be detected due to its light element property (see Fig. 5(a–c)). The experimental weight percentages and calculated weight percentages of the elements in the samples are displayed in the inset of Fig. 5. Clearly, the experimental values are close to calculated values, indicating that Eu^{3+}-doped $SrNb_2O_6$ phosphors were successfully synthesized. To