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Novel pyrochlore-type $La_2Zr_2O_7$: Eu^{3+} red phosphors: Synthesis, structural, luminescence properties and theoretical calculation

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ABSTRACT

The Eu^{3+} ion activated pyrochlore-type $La_2Zr_2O_7$ red emitting phosphor was prepared through solid-state reaction. The electronic structure of $La_2Zr_2O_7$ was investigated with density functional theory (DFT) calculation. The phase purity, crystalline structure, morphology and lattice parameters of the Eu^{3+} ion doped $La_2Zr_2O_7$ through powder X-ray diffraction and Rietveld refinement were also elucidated in details. The as-prepared $La_2Zr_2O_7$: Eu^{3+} phosphors presented excellent red light emission with intense absorption bands in the near-ultraviolet and blue light regions. The optimized doping concentration of Eu^{3+} ions was found to be 0.05 with an ideal CIE coordinate index of (0.62, 0.38). Finally, the excellent thermal stability of $La_2Zr_2O_7$: Eu^{3+} phosphor was also determined according to the temperature dependent emission spectra, excited at 393 nm. All these results indicated that the $La_2Zr_2O_7$: Eu^{3+} phosphors had high potential for applications in solid-state white light-emitting diodes as suitable red-emitting components for white light emitting diodes (w-LEDs), combined with near-ultraviolet or blue lighting chips.

1. Introduction

As fossil fuels and are becoming increasingly scarce and the climate change is severe, one of the best ways to relieve the energy crisis and global warming threat is to improve the energy efficiency [1,2]. For lighting devices, white light emitting diodes (w-LEDs) exhibit 70% energy saving compared to conventional incandescent bulbs, due to the corresponding high efficiency and long lifetime [3,4]. Nowadays, commercial w-LEDs are usually fabricated through combinations of ultraviolet or blue LED chips with phosphors. As an example, high-efficiency yellow phosphors (such as YAG:Ce^{3+} phosphors) are readily available for commercial lighting, when combined with blue LED chips; also, UV/NUV LED chip excited RGB phosphors exhibit high application potential for w-LEDs [5]. High efficiency red or orange phosphors are of valuable scientific significance for these two devices, due to requirements for high performance w-LEDs with higher color rendering index and the poor stability of traditional sulfide-based red phosphors (such as Y_2O_2S: Eu^{3+}) under the UV/NUV light excitation [6,7]. Therefore, it is essential to exploit novel red phosphors with high efficiency and excellent stability to solve these problems.

Since Eu^{3+} ions demonstrate excellent absorption band in the NUV and blue light regions as well as urgent orange-red emission spectrum originating from the 4f-4f transition, the Eu^{3+}-doped phosphors have been considered as potential red-emitting components in w-LEDs [8–10]. Compared to the commercial sulfide red phosphors, the Eu^{3+} doped oxide-based red phosphors have attracted tremendous interest due to their outstanding advantages, such as in easy preparation, excellent stability, high absorption and luminescent efficiency [11–14]. Among these compounds, the rare earth (Re, such as Y, La, Gd) zirconate $Re_2Zr_2O_7$ ternary oxides have been extensively investigated for applications as hosts for fluorescence centers and thermal barrier coatings for gas turbines as well as diesel engines in recent years [15,16]. As for the moderate size of La^{3+} ions, the $La_2Zr_2O_7$ displays a fully ordered pyrochlore-type structure with a space group of *Fd-3m*, also presenting certain important properties including high stability, low thermal conductivity, and good ability to accommodate defects [17–19]. Nowadays, reported materials with $La_2Zr_2O_7$ as a host for phosphors are mainly the $La_2Zr_2O_7$: Eu^{3+} nanoparticle, the $La_2Zr_2O_7$: Eu^{3+} nano-rod and the $La_2Zr_2O_7$: Eu^{3+}@ YBO_3 core@ shell nanoparticle [8,20–22]. By contrast, these $La_2Zr_2O_7$-based phosphors are

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mostly synthesized through an overly complicated chemistry solution method, such as sol-gel, hydrothermal, co-precipitation and combustion. Moreover, the resultant nanostructures always present poor crystallinity. It has been reported that the crystallization degree tailoring is significant for the corresponding luminescence properties and emission efficiencies improvements [23]. Adversely, as an effective way to improve the crystallinity of nanostructures, the calcination at higher temperature easily produces nanoparticle bonding, forming high-sized aggregates and severely affecting the luminescence performance. Therefore, the high-temperature solid-state reaction method was utilized. This was a low cost and efficient route, as well as a simple process to produce phosphors with good crystallinity and dispersity [24,25]. In addition, the first-principle calculation was recently utilized to study the electric structure of matrix host materials, as well as to predict or further investigate the mechanism of changes in the mechanical and thermal properties of $La_2Zr_2O_7$ materials [19,26,27]. This calculation regarding the relationship between the electronic structure and luminescence properties of $La_2Zr_2O_7$ based materials is inadequate. Consequently, the Eu^{3+} doped pyrochlore-type $La_2Zr_2O_7$ red emitting phosphors were synthesized through the high temperature solid-state reaction method, as presented in this paper, whereas the crystal structure, the electronic structure, the photoluminescence properties and the thermal stability were also investigated in details with aim to fill in the gaps both theoretically and actually.

2. Material and method

The $La_{2-x}Zr_2O_7$: xEu^{3+} (x = 0, 0.001, 0.005, 0.01, 0.03, 0.05, 0.08, 0.1, 0.2) phosphor samples were synthesized through the high temperature solid-state reaction method. During the procedure, all La_2O_3 (99.9%), ZrO_2 (99.9%), and Eu_2O_3 (99.9%) were utilized as the raw materials, while the La_2O_3 powders were weighed immediately following heating at 1100 °C for 1 h. These reactants were uniformly mixed in the agate mortar, according to their theoretical stoichiometry. Subsequently, the mixed powders were placed in a corundum crucible with a corundum lid, as well as calcined at 1500 °C for 4 h in the air. Finally, the samples were cooled down to room temperature and ground into powders again for further measurements.

The X-ray diffraction (XRD, D8 Advance diffractometer, Bruker Corporation, Germany) measurements of the samples were carried out with Cu Kα (λ = 1.5406 Å) radiation, to investigate their crystalline phases in the 2θ range from 10° to 70°. The powder diffraction patterns for the Rietveld analysis of $La_2Zr_2O_7$: $0.2Eu^{3+}$ were collected with a step size of 0.02° and 20 s of counting time per step, whereas the Rietveld refinement was conducted with the TOPAS 4.2 [28]. Field-emission scanning electron microscopy (FESEM, S-4800, HITACHI, Japan) and transmission electron microscopy (TEM/HRTEM, JEM-2100HR, JEOL, Japan) equipped with energy dispersive X-ray spectroscopy (EDS) were adopted to study the morphology and microstructure of the $La_2Zr_2O_7$: $0.05Eu^{3+}$ sample. The room temperature photoluminescence excitation (PLE) and emission (PL) spectra were recorded with a fluorescence spectrophotometer (F-4600, Hitachi, Japan) with a photomultiplier tube, operating at 400 V and with a 150 W Xe lamp as the excitation source. The decay curves were measured with a spectrofluorometer (TBX-PS, Horiba Jobin Yvon, France), where a 460 nm pulse laser was the excitation source. The Coherent Infrared Energy (CIE) chromaticity coordinates were calculated with a custom-made software, while the quantum yield was measured with a fluoromax-4 spectrofluorometer (Horiba Jobin Yvon, France), with an integral sphere at room temperature. The temperature-dependent emission spectra were recorded with the spectrophotometer (F-4600, Hitachi, Japan), combined with a custom-made heating attachment and a computer-controlled electric furnace.

The electronic structures of $La_2Zr_2O_7$ were examined through density functional theory calculations with the Vienna ab initio simulation package (VASP) [29]. Projector-augmented-wave potentials were utilized to describe the electron-ion interactions, whereas the exchange-correlation effects were treated within the generalized gradient approximation under the scheme of Perdew-Burke-Ernzerhof (PBF) [30]. The self-consistent field energy convergence threshold was 0.02 eV $Å^{-1}$. A kinetic energy cutoff of 500 eV was adopted for the plane wave basis and a k-point sampling of 7 × 7 × 7 Monkhorst-Pack mesh was utilized in the sampling of the Brillouin zone [31]. The Broyden-Fletcher-Goldfarb-Shanno minimization scheme was applied to the geometry optimization [32].

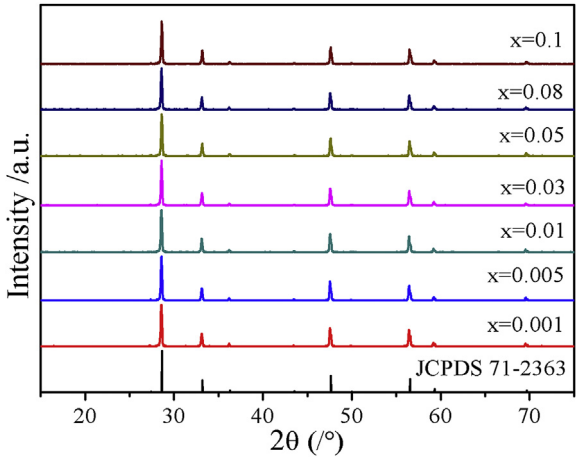

Fig. 1. XRD patterns of $La_2Zr_2O_7$:xEu^{3+} phosphors and JCPDS card (No. 71–2363) $La_2Zr_2O_7$.

3. Results and discussion

The phase purity of the $La_2Zr_2O_7$: xEu^{3+} samples were identified through XRD as presented in Fig. 1. The standard JCPDS card (No. 71–2363) of $La_2Zr_2O_7$ was also presented for comparison. It could be observed that all diffraction peaks were well-matched with the standard card, indicating a single phase without impurity and good crystallinity for the $La_2Zr_2O_7$: xEu^{3+} phosphors. These XRD results confirmed that the Eu^{3+} ions could enter the host lattice completely, forming the same structure of $La_2Zr_2O_7$, whereas the substitution of La^{3+} by Eu^{3+} ions did not cause any significant phase changes. According to present studies, the Eu^{3+} ions were expected to replace the La^{3+} ions due to the same valence states and similar radius values ($R_{La3+,\ CN=8}$ = 1.16 Å, $R_{Eu3+,\ CN=8}$ = 1.07 Å) [33]. Moreover, the crystal phase for the $La_2Zr_2O_7$: xEu^{3+} sample was found to be pyrochlore, due to the apparent peaks at 36.3° and 43.6°, which were considered as the main characteristic of the pyrochlore phase, being distinguished from the fluorite phase [20].

Furthermore, the probability of transitions between different 4f energy levels of Eu^{3+} ions is usually affected by the crystal field, due to the spectral selection rule [23,34]. Therefore, the crystal structure of the $La_{1-8}Zr_2O_7$: $0.2Eu^{3+}$ sample was herein refined from the high resolution powder synchrotron diffraction through Rietveld method with the Topas 4.2 program. Fig. 2(a) presents the measured and calculated data of XRD profiles for the Rietveld refinement, in which, the pyrochlore $La_2Zr_2O_7$ was taken as the starting structure parameter. It could be observed that almost all peaks were indexed and the refinement was good with a few impurities of ZrO_2 (~6(1)%) and EuO (~2.7(2)%). Also, the $La_{1-8}Zr_2O_7$: $0.2Eu^{3+}$ was observed to be well crystallized as a cubic unit cell with the space group of *Fd-3m* (227), which proved to be good evidence for the Eu^{3+} ions occupying the La^{3+} sites. Table 1 presents the details of crystallographic data and refinement parameters. As it could be observed, the refinement finally converged into R_p = 10.71%, R_{wp} = 15.95%, χ^2 = 1.43. Even though the R_{wp} was a high value, it did not occur due to bad refinement, but it occurred due to the noisy background. The results also demonstrated that the La^{3+}