Journal of Luminescence 203 (2018) 152–159

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

A red-emitting phosphor of $Li_5La_3Ti_2O_{12}$:Eu^{3+} with garnet-like structure and near-UV/blue light excitation

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ARTICLE INFO

Keywords:
Garnet-like structure
Europium
Luminescence
Phosphor
Optical materials and properties
Energy transfer

ABSTRACT

A series of novel red-emitting phosphor of $Li_5La_{3-3x}Eu_{3x}Ti_2O_{12}$ (x = 0.01–0.25) were synthesized via the facile solid-state reaction method. The Rietveld refinements verified that all the samples crystallized in a garnet-like cubic structure. The band gap energy of $Li_5La_3Ta_2O_{12}$ is 3.87 eV, which can be greatly narrowed by Eu^{3+}-doping. This benefits the red-shift of optical absorption from UV- to near-UV light region. Importantly, the sample presents dominant absorption in near-UV (390–395 nm) and blue-light (460–465 nm) region. $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.01–0.15) has a bright red-luminescence with the strongest $^5D_0 \rightarrow {}^7F_2$ transition at 613 nm. The energy transfer was discussed on the Eu^{3+}-doping concentration. The experimental red-emitting lamps were fabricated using a 395 and a 460 nm LED-chips, respectively, in combination with the single phosphor of $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.2) driven by 2 mA current. The results indicate that the phosphor could be a promising candidate used in solid-state lightings and displays.

1. Introduction

The inorganic compounds with garnet-like structure have been regarded as the excellent hosts for optical applications because of its rigid lattices and large heat conductivity [1,2]. Garnet structure ahs a formula of $C_3B_2A_3O_{12}$, where *A*, *B* and *C* cations can vary with different types, sizes and valences inducing a large group of compounds. This effect can result in different changes in symmetry, electronic structures and crystal field strength, which can have great influences on the energy splitting and electronic transitions in RE-activator-containing garnet-type host.

To fabricate and design luminescence devices, scintillating counter, up-conversion materials or laser hosts, considerable efforts have been paid to the luminescence properties of rare earth ions (RE) (e.g., Eu^{3+}, Tb^{3+}, Pr^{3+}, and Er^{3+} etc) activated garnet-type oxides. For example, YAG:Ce^{3+}, the well-known garnet, has been widely applied as a yellow-emitting phosphor and commercially available for lighting devices [3,4]. In recent years, there are many investigations on RE-doped garnets including yellow, green, blue, and red-emitting phosphors with potential which can be used in both WLEDs. Among them, there are continuous interests in the development of Eu^{3+}-activated garnets for red-emitting phosphors [5,6].

In this work, we reported $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.01–0.25) phosphor and its optical properties. Mazza [7] firstly reported $Li_5La_3Ta_2O_{12}$ with a cubic symmetry and a space group of *Ia*-3. This garnet framework has two special characteristics: firstly Li^+ ion occupies the octahedral hole in the unit-cell, which is empty in the normal garnets; secondly the large trivalent ions like La^{3+} is supported for the first time by a garnet-like structure [7]. Therefore, the Li-stuffed garnet has proton-exchange in the lattice. This gives $Li_5La_3Ta_2O_{12}$ to be an excellent solid electrolyte for conducting property. Li^+ ion diffusion involves the jumps between the tetrahedral and octahedral Li^+ sites across the tetrahedron face connecting them [8]. The present reports indicate that $Li_5La_3Ta_2O_{12}$ could be a promising candidate for all-solid-state battery with good chemical stability [9–13].

Recently, we successfully synthesized the pure and Eu^{3+}-activated $Li_5La_3Ta_2O_{12}$ by facile solid-state reaction method. And the samples present strong absorption in UV- and near-UV region. In the host, the La^{3+} ions serve suitable sites for the Eu^{3+} ions with similar ionic radius and valence for substitution. This encourages us to investigate the luminescence activities. Eu^{3+} is an activator is based on its specialties, i.e., its emission lines are very simple compared with the other RE ions. Eu^{3+} ions substituted for host cations in a host usually exhibit a bright red emission and it can be easily excited by UV- and near UV-radiation which is strongly absorbed by the charge transfer (CT) transition of Eu^{3+}.

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https://doi.org/10.1016/j.jlumin.2018.06.036
Received 11 February 2018; Received in revised form 11 May 2018; Accepted 14 June 2018
Available online 15 June 2018

$Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.01–0.25) phosphors have been synthesized via the facile solid-state reaction. X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) were used to investigate its structure evolution and morphological properties. The luminescence spectra of Eu^{3+} and the possible applications were investigated.

2. Experimental

The polycrystalline $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.01, 0.05, 0.1, 0.15, 0.2, 0.25) phosphors have been synthesized via the solid-state ceramics reaction with the stoichiometric raw chemicals of Li_2CO_3, Ta_2O_5 and RE_2O_3 (RE = La, Eu). A 7 wt% excess of Li_2CO_3 was used in order to compensate the loss of Li^+ ions due to volatilization during the heat at high temperature. Firstly, the mixtures in stoichiometric amount were preheated up to 450 °C during 6 h and kept at this temperature for 5 h. The powders were thoroughly mixed and then heated at 850 °C for 5 h. The powders were carefully mixed and were sintered at 950 °C for 8 h in air atmosphere to get the final phosphors.

XRD measurement was performed via Rigaku D/Max diffractometer (30 mA, 40 kV) (Rigaku Corporation) by Bragg–Brentano geometry equipped with Cu-Kα radiation (λ = 1.5405 Å). Surface characteristics were tested via a SEM together with EDS. The photoluminescence (PL) spectrum was taken via the spectrometer (Perkin-Elmer LS-50B). The luminescence decay curve was measured via the excitation of forth harmonic wavelength of YAG:Nd pulsed laser (Spectron Laser Sys. SL802G). The emission signal was dispersed by a monochromator (75 cm, Acton Research Corp. Pro-750) coupled with a PMT (Hamamatsu R928). The emission quantum efficiency (QE) was evaluated on a spectrometer Edinburgh FS-920 (UK, Edinburgh) equipped via an integrating sphere. The monochrometer was connected with a computer together with a CCD sensor via light guides. The QE value could be obtained via the software installed in the system for the measurement.

The experimental lamps were fabricated by the combination of 395 nm- and 460 nm-LED-chip and $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.2) phosphor via the package of complex polymers. In the package process, the epoxy resin based glues (1 g) and the phosphor (0.15 g) were thoroughly mixed for several minutes. The precursor mixtures were carefully packaged on the LED chips. The devices were dried at 60 °C for 1 h, and followed by another heat at 135 °C for 100 min. Finally a lampshade was installed on the lamp.

3. Result and discussions

3.1. Phase formations and particle morphology

The crystal formation and structure of polycrystalline $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.01–0.25) phosphors were investigated by XRD measurements. The typical structural refinement for x = 0.2 using the GSAS program is shown in Fig. 1. The refined profiles of the other samples have similar profiles. The refinements verified that the phosphors crystallized with a pure cubic phase formation in a space group Ia-3 (206). The refined structural data and the corresponding coordinates are listed in Tables 1 and 2, respectively. The lattice parameters are in agreement with the literature [7]. The Eu^{3+} doping has not any obvious influence on the crystal features except for the small degrease of the unit cell size because the fact that the Eu^{3+} has a smaller radius than La^{3+} ion.

Fig. 2 is the structure along [001] direction drawn on the atomic coordinates listed Table 2. The structure belongs to cubic symmetry with the space group (No. 230) in which cations at special positions [La, (0.125, 0, 0.25); Li/Ta (0, 0, 0); Li (0.375, 0, 0.25)]. Compared with the common garnet structure, $Li_5La_3Ta_2O_{12}$ has excess 16 Li+ ions located in the 16-fold positions of type 1/8, 1/8, 1/8. These positions are vacant in a conventional garnet stoichiometry structure with chemical formula of $C_3B_2A_3O_{12}$. The average distance of La-O in $Li_5La_3Ta_2O_{12}$ is 2.5607 Å. In the lattices, two neighbors of $[LaO_8]$ dodecahedra are separated by $[LiO_4]$ tetrahedral or $[TaO_6]$ octahedral.

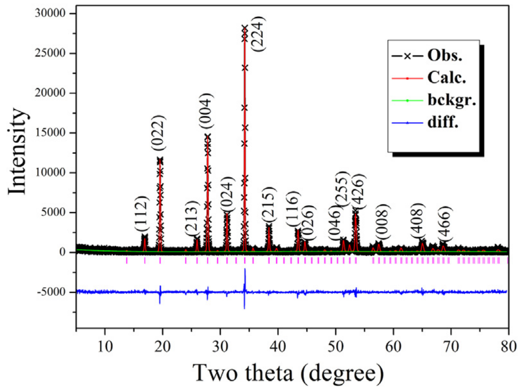

Fig. 1. The representative Rietveld refinement for the synthesized $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.2) phosphor.

The typical SEM picture of the final phosphor $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.2) phosphor sintered at 950 °C was displayed in Fig. 3(a) and (b). The other samples have similar situation. It has ununiform grains with the size of 40–50 nm. The particles are loosely connected, which are easily separated with each other. Fig. 3(c) and (d) shows EDX analysis of $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ phosphors with x = 0, and 0.2. The elemental components can be detected. The pure sample only shows the signals from Li, La, Ta and O in the lattices, while In the Eu-doped samples, the EDS signals from Eu^{3+} ions were clearly detected.

3.2. The optical absorption

To investigate the influence of Eu^{3+}-substitution on its band nature, the optical absorption spectra of $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.01–0.25) phosphors were measured (Fig. 5). All the spectra have an obvious absorption in UV- to near-UV wavelength region (< 400 nm). It is from the intrinsic electronic transitions in the band gap of the tantalum host, which is usually assigned to the well-known CT bands in TaO_6 groups. It can be seen that the optical transition of $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.01) occur at about 320 nm. The optical absorption edge has an obvious red-shift with the increase of Eu^{3+} substitution in the lattices. The band energy (E_g) is estimated by the equation $E_g = 1240/Abs$, where Abs is the abrupt absorption estimated from the absorption edge.

The band energies of $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.01–0.25) phosphors are shown in Fig. 4. The undoped sample has a band energy of 3.88 eV, which is consistent with the reported nature for $Li_5La_3Ta_2O_{12}$ in references (3.9 eV) [14]. Eu^{3+}-doping obviously narrows the host band gap. This is beneficial for the optical absorption in the red-emitting phosphors because Eu^{3+} has a vital drawback, i.e., a very low ($< 10^{-6}$) oscillation strength in the near-UV region due to its *f–f* forbidden transitions. This strictly limits the application of near-UV and blue LED-chips as excitation sources in of Eu^{3+}-doped phosphors [15].

Usually the absorption edge of a semiconductor should be steep with the abrupt profile. It can be observed that $Li_5La_3Ta_2O_{12}$ shows the common steep a optical absorption edge; however, the deviation from the steep profile was observed around 350–400 by Eu^{3+}-doping. This could be created by some possible defects [16]. The distortion due to the Eu^{3+} doping could induce more defects such as oxygen vacancies (V_O). For example, the defects V_O could act as donors with the local levels under the conduction band. This probably enhances the optical absorption in the visible light.

3.3. The luminescence characteristic

Fig. 5(a) presents the PL excitation spectra of $Li_5La_{3-3x}Eu_{3x}Ta_2O_{12}$ (x = 0.01–0.25) at 300 K by monitoring the $^5D_0 \rightarrow {}^7F_2$ (613 nm). The