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Crystal structure and two types of Eu^{3+}-centered emission in Eu^{3+} doped $Ca_2V_2O_7$

Ling Li [a,b], Xiaoguang Liu [a,b], Hyeon Mi Noh [b], Sung Heum Park [b], Jung Hyun Jeong [b,*], Kwang Ho Kim [c]

[a] Hubei Collaborative Innovation Center for Advanced Organochemical Materials, Ministry-of-Education Key Laboratory for the Synthesis and Applications of Organic Functional Molecules, Hubei University, Wuhan 430062, China
[b] Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea
[c] School of Materials Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea

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ABSTRACT

The dependence of $Ca_2V_2O_7$:Eu^{3+} photoluminescence on the crystal structure was discussed experimentally and theoretically. The important chemical parameters, especially, standard deviation of the bond environmental factor were calculated firstly. Two broad excitation bands with the peaks at 311 and 400 nm covering from 250 to 475 nm and two different types of f–f transition–emission of Eu^{3+} can be found. Detailed discussion demonstrated that two different emission mechanisms exist in $Ca_2V_2O_7$:Eu^{3+}: (1) was from the $Eu1^{3+}$ ions occupying the Ca1 sites and (2) was from the $Eu2^{3+}$ ions in the Ca2 sites. The energy transfer was in two ways: one was from O–V1 charge transfer (CT) to Eu2 and another was from O–V2 CT to Eu1.

1. Introduction

Vanadates form a very interesting class of compounds, which have many applications in the fields of luminescence, catalysis, and electrochemistry. Particularly as a kind of luminescence material, vanadates have been widely investigated because they have broad and intense O^{2-}–V^{5+} charge transfer (CT) bands, usually observed in the near-UV region (300–400 nm), and they are very efficient in transferring their energies to a luminescent center by non-radiative pathways [1–12]. $Ca_2V_2O_7$ has a triclinic crystal structure. Vanadium atoms have two different 2i sites, and both of them are coordinated to four different oxygen atoms [13]. Thus, two different O^{2-}–V^{5+} charge transfer (CT) bands can be expected. In this $Ca_2V_2O_7$ crystal, Ca^{2+} ions occupy two different 2i sites. Eu^{3+} ions probably occupy two different Ca^{2+} sites in Eu^{3+} doped $Ca_2V_2O_7$ crystal. It is well known that the emitting light color of Eu^{3+} changes with the symmetry and coordination environment of Eu^{3+} [14]. They can induce different emissions due to the different ralative intensity of f–f transitions. Thus it would be very interesting to investgate the emission of Eu^{3+} and the energy transfer from the O–V charge transfer to the luminescent center Eu^{3+} in $Ca_2V_2O_7$:Eu.

There are a few reports on taking Eu^{3+} as an activator to investigate the luminescence properties of $Ca_2V_2O_7$:Eu^{3+}. Gu et al. [15], Taxak et al. [16] and Kumar et al. [17] employed the hydrothermal, combustion and citrate-gel combustion methods to synthesize europium doped $Ca_2V_2O_7$, respectively. Different luminescent properties of $Ca_2V_2O_7$:Eu^{3+} were found using different synthesis methods. In the hydrothermal method, the strong broad band peak at 280 nm was attributed to the absorption band of charge transfer from oxygen to the Eu^{3+}, and only one strong f–f transition emission at 610 nm was found [15]. In the combustion method, two excitation peaks at 305 and 400 nm were detected, which were assigned to the O–V CT and f–f transitions of Eu^{3+}, respectively [16]. And two strong f–f transition emission bands with the peaks at 613 and 621 nm were reported [16]. In the citrate-gel combustion method only one broad excitation band ranging from 200 to 350 nm was found, which was assigned to the charge transfer band from O^{2-} to V^{5+}, and also a highly intense peak at 612 nm was found [17]. It makes us feel interesting to investigate the photoluminescence properties of $Ca_2V_2O_7$:Eu. To our knowledge, the photoluminescence properties of Eu^{3+} doped $Ca_2V_2O_7$ synthesized through a solid state reaction method and the correlation between the crystal structure and the photoluminescence, as well as the detail energy transfer mechanism were still not reported. In our work, $Ca_2V_2O_7$:0.5%Eu^{3+} was synthesized using the solid state reaction method which showed that interesting photoluminescence

* Corresponding author. Tel.: +82 51 629 6285; fax +82 51 629 5549.
E-mail address: jhjeong@pknu.ac.kr (J.H. Jeong).

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properties and mechanisms of $Ca_2V_2O_7$:Eu^{3+} were reported. Different types of Eu^{3+} red emission were found. The energy transfer mechanism was discussed quantitatively based on the dielectric theory of complex crystals.

2. Experimental

2.1. Preparation

$Ca_2V_2O_7$:0.5%Eu^{3+} phosphors were synthesized through the solid-state reaction route according to Ref. [18].

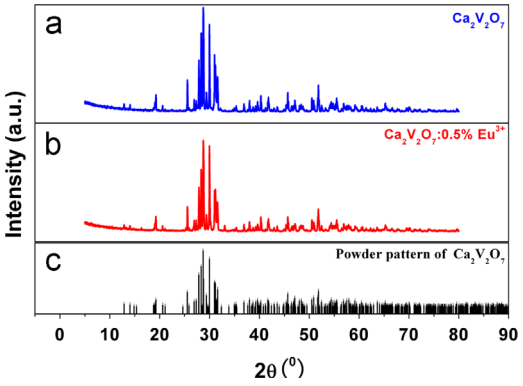

Fig. 1. (a) and (b) are XRD patterns of undoped $Ca_2V_2O_7$ and $Ca_2V_2O_7$:Eu^{3+} samples annealed at 950 °C, respectively. (c) The full powder pattern of pure $Ca_2V_2O_7$ through the Diamond software.

2.2. Characterizations

The phase purity of the as prepared phosphor was checked by powder x-ray diffraction (XRD) analysis by using a D/MAX 2500 instrument (Rigaku) with a Rint 2000 wide angle goniometer and Cu Kα1 radiation (λ=1.54056 Å) at 40 kV and 100 mA. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a fluorescence spectrophotometer (Photon Technology International) equipped with a 60 W Xe-arc lamp as the excitation light source.

3. Result and discussion

Fig. 1(a) and (b) shows the XRD patterns of $Ca_2V_2O_7$ and $Ca_2V_2O_7$:Eu samples, respectively. Their diffraction peaks were matched perfectly well with the standard $Ca_2V_2O_7$ phase, which comes from the powder pattern of $Ca_2V_2O_7$ through the Diamond software [13]. No peaks from other phases are detected, indicating that Eu^{3+} ions have been effectively incorporated into the $Ca_2V_2O_7$ host by substituting Ca^{2+} sites.

Fig. 2 shows the photoluminescence excitation (PLE) and emission (PL) spectra of $Ca_2V_2O_7$:Eu^{3+} samples. When monitored at a wavelength of 621 nm or 615 nm, the excitation spectra of $Ca_2V_2O_7$:Eu^{3+} consist of two broad excitation bands with peaks at 311 and 400 nm covering spectral range from 250 to 475 nm. They may be originated from two different mechanisms: the charge transfer transition from O^{2-} to V^{5+} (O–V CT) or the charge transfer transition from O^{2-} to Eu^{3+} (O–Eu CT). As shown in Fig. 3, in the crystal structure of $Ca_2V_2O_7$, Ca^{2+} ions occupy two nonequivalent crystallographic sites (Ca1 site

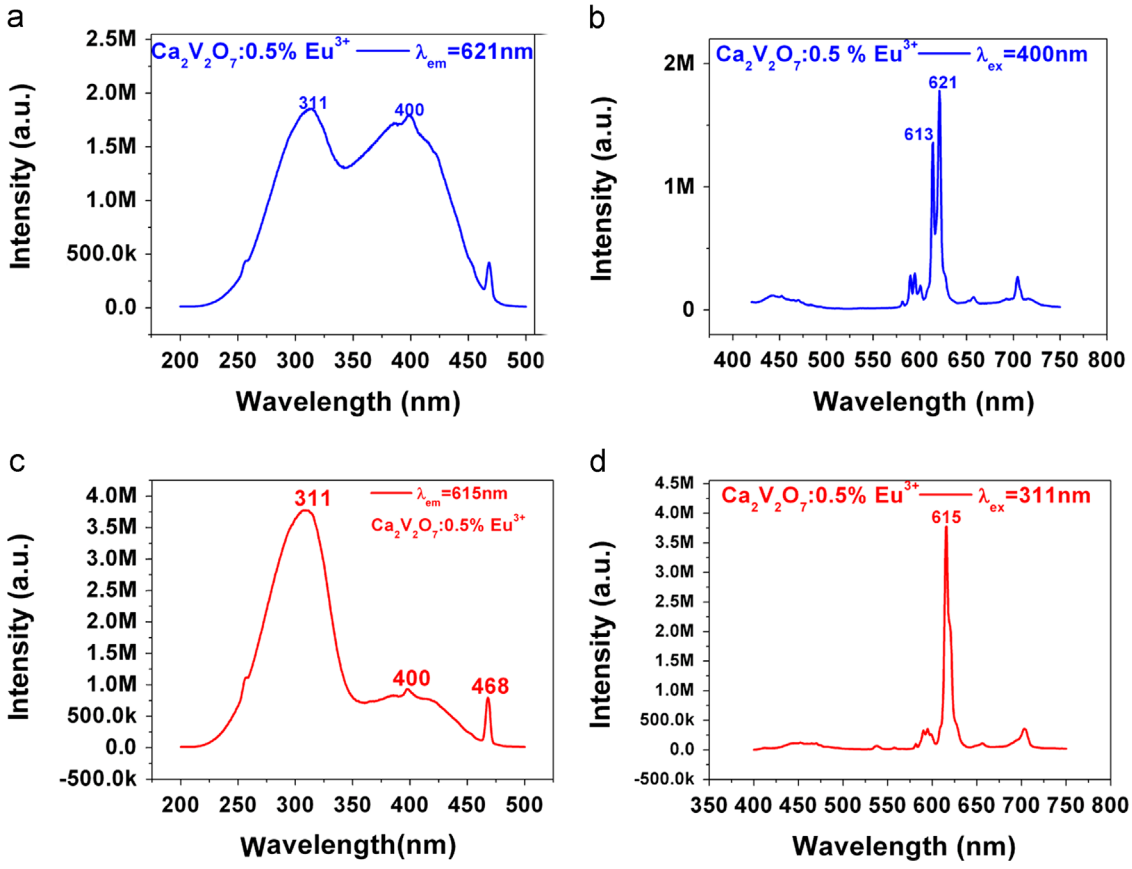

Fig. 2. Photoluminescence excitation (PLE) and emission spectra of $Ca_2V_2O_7$:Eu^{3+} phosphors. (a) and (c): excitation spectra monitored by 621 and 615 nm, respectively; (b) and (d): emission spectra excited at 400 and 311 nm, respectively.