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Spectral redshift mechanism of N doped $Sr_2SiO_4:Eu^{2+}$ phosphors

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ABSTRACT

By using the first principle methods, the electronic structure and spectral characteristics of N-doped and un-doped $Sr_2SiO_4:Eu^{2+}$ phosphors is studied. It is found that after nitrogen doping the shorter bond lengths of Eu—N leads to the splitting of Eu5d states due to the crystal field effect, and the stronger covalencies of Eu—N bonds results in the down shift of Eu5d states because of the nephelauxetic effect. These two factors come together to bring about the red-shift of the of the PL properties. Lower Eu5d energy level and wider energy band of Eu5d states for Eu(II) site occurs due to shorter bond length and greater covalency of Eu(II)—N bond. Consequently, the Eu(II) site was effectively substituted with nitrogen. By increase of nitrogen content, the number of Eu—N bonds increases and the luminescence intensity for the phosphors increase correspondingly.

1. Introduction

Rare earth doped silicate phosphors have been more and more applied in white light emitting diodes because of their low energy consumption, long lifetime and mercury free [1–4]. As a kind of important silicate materials, alkaline earth silicon compounds doped with divalent europium ions, which have high chemical and thermal stability, high quantum efficiency, and broad excitation spectra, are good candidates for high efficient luminescence phosphors because divalent europium is more stable in the host and more easily diffuses into the lattice sites [5,6]. Among them, Eu^{2+}-doped Sr_2SiO_4 phosphor (SSO) has shown promising prospect in producing white light using the GaN LED [7–11]. However, the maximum excitation band of SSO is around 370 nm, too short for the blue LED chip. Recently, it has been reported that N-doped $Sr_2SiO_4:Eu^{2+}$ (SSON) phosphors can be more efficiently excited and improve the intensity of its excitation and emission than their oxosilicate counterparts, while its emission spectra shows red-shift [12–18]. Gu et al. achieved red-shift in the emission spectra of SSO, and the excitation band could be tuned to fit the blue LED chips simultaneously by doping N into the host [12]. Lee & Park discovered that N^{3-} ions were partially incorporated into the oxygen sites of SSO, resulting in the solid solutions of SSON and showing strong red-shift of the emission spectra (green to red) due to Eu—N bonds [13,17]. It is interesting to understand how N atoms influence the electronic structure of SSO and improves its luminescence properties. However, no detailed study has been done on the interaction mechanism among the N atoms and Eu^{2+} of the phosphors.

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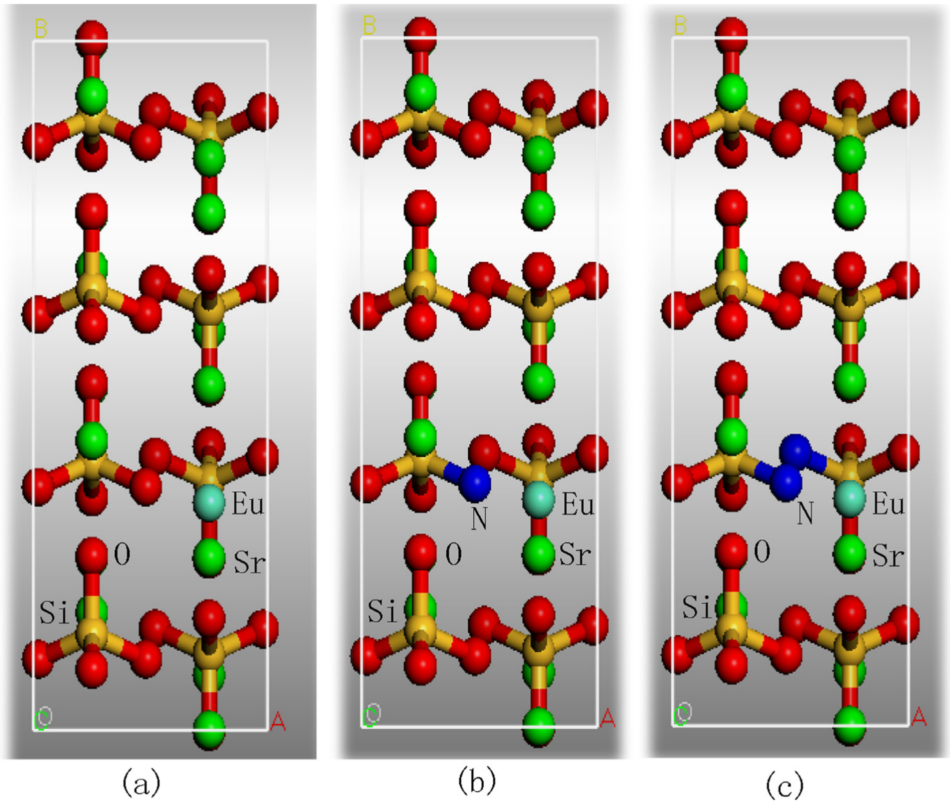

Fig. 1. Structure of super-cells of (a) SSO, (b) SSO1N and (c) SSO2N.

In recent years, more and more studies show that it the density functional theory (DFT) can satisfactorily provide detailed information on electronic properties of rare earth doped phosphors and the relationship with photo-luminescence properties [19–23]. In this work, the electronic structure of N-doped and un-doped Sr_2SiO_4:Eu^{2+} were investigated by employing first-principles calculations based on the DFT. Besides, lengths and population of bonds, density of states (DOS) as well as absorption spectra were computed. Subsequently, the effects of N doping on the electronic properties and the absorption properties of SSO were presented.

2. Theoretical simulation

The crystal structures' optimization and electronic structures of the SSO and SSON phosphors were performed within the Cambridge Serial Total Energy Package (CASTEP) plane wave code based on the first principles [24–26]. The calculations employed the plane-wave pseudopotential method. In order to obtain accurate electronic structure, the PBE method by Generalized Gradient-corrected Approximation (GGA) was used for the exchange correlation potential. During the calculation, the 430 eV for cutoff energies, 4 × 2 × 3 for the numbers of k-point can ensure the convergence for the total energy, and self-consistent field tolerance thresholds were 1.0×10^{-6} eV/atom. All the calculations were considered converged when the maximum force on the atom was below 0.03 eV $Å^{-1}$, maximum stress was below 0.05 GPa, and the maximum displacement between cycles was below 0.001 Å. The reliability of the calculations was demonstrated by the results of the convergence test and a 1.9 eV scissors operator was used to plot the band structure and absorption spectra of the phosphors.

Based on the experimental data, Eu doped α'-Sr_2SiO_4 (SSO) (ICSD #35667) as the control group [27]. Firstly, a 1 × 2 × 1 supercell of a Sr_2SiO_4 was built and replaced one Sr with Eu in the cell as the SSO model. Then, all the oxygen atoms coordinated with Eu were substituted by one and two nitrogen atoms to establish SSO1N and SSO2N models, respectively (shown in Fig. 1). These models were optimized and the optimized lattice structures were chosen for calculating electronic structures and density of states of these phosphors. It is well known that Sr_2SiO_4 has two different cation sites: Sr(I) coordinated by 10 oxygen atoms and Sr(II) surrounded by 9 oxygen atoms. Thus, it is generally accepted that the Eu atoms occupy both two Sr sites in the lattice when Eu atoms are doped in Sr_2SiO_4, which are named as Eu(I) and Eu(II) [28].