J. At. Mol. Sci.
doi: 10.4208/jams.072813.091013a

Vol. **5**, No. 2, pp. 110-122
May 2014

First-principles calculations of the electronic structures and optical properties of Mg- and Sr-doped CaF_2

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Received 28 July 2013; Accepted (in revised version) 10 September 2013
Published Online 28 February 2014

Abstract. Based on the density functional theory (DFT), the first-principles methods are used to study and compare the electronic structures and optical properties of Mg-, Sr-doped CaF_2 systems with those of CaF_2 bulk in detail. In contrast to CaF_2 bulk, the band gaps of doped systems become narrower and the new peaks of density states appear. The orbital interactions between Mg, Sr atoms and Ca atom are enhanced near the Fermi level, besides, the doped systems all show single dielectric properties and their absorption coefficients for ultraviolet light are reduced greatly, for Ca_7SrF_{16} system, there is a small absorption peak at 25.44 eV. Compared with CaF_2 bulk, doped systems have much lower extinction coefficients and much higher light transmittance in the ultraviolet region. In addition, their reflection and loss peaks all display red shift and the peak value reduce.

PACS: 31.15.E-, 71.20.-b, 78.20.-e

Key words: density functional theory, electronic structure, optical property, dope

1 Introduction

Calcium fluoride (CaF_2) crystals have been widely used as optical medium materials for many years due to their excellent properties such as high transmittance and broad transmittance range (from far UV to mid-IR), low refractive index, high chemical resistance and high laser damage threshold [1]. Recently, large size CaF_2 crystals are required as an important lens material for photolithographic processing of silicon integrated circuits (IC) at wavelengths in the deep ultraviolet (DUV) region [2]. Calcium fluoride crystals

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have so many advantages that attract a number of scholars to research into them [3-8]. Calcium fluoride has typical fluorite structure consisting of a simple cubic array of fluorine ion (F-) with every alternate cube occupied by calcium ion (Ca^{2+}). This kind of fluorite structure enables high doping concentration of foreign ions, especially for doped with transition-metal and rare-earth ions. For CaF_2 doped systems, the changes in electronic structures and optical properties can introduce new characters different from those of CaF_2 bulk. For example, in the case of CaF_2:Yb single crystal thanks to its broad emission bands, it shows very good performances as tuneable laser and as ultra-short pulse laser generator [9,10]. Recently, the synthesis and upconversion luminescence properties of Er^{3+}:CaF_2 nanoparticles co-doped with Yb^{3+} as sensitizer were reported [11]. Lately, high power diode-pumped femtosecond laser as well as self-Q-switched laser based on Yb doped and Na-Yb co-doped CaF_2 crystals were developed [12]. Light emitting structures based on nanocrystalline Si/CaF_2 system were developed featuring a great dependence of the photoluminescence properties from the nanoparticles size [13]. Additionally, there are other literatures about synthesis of CaF_2 nanoparticles or hollow sphere doped with rare-earth and alkaline-earth ions, such as Eu^{3+} [14,15], Tb^{3+} [16,17] and Ce^{3+} [18] were successively reported. Besides, Magnesium(Mg) and Strontium(Sr) doped calcium fluoride nanocrystals were synthesized by co-precipitation method by C. Pandurangappa [19], for Mg:CaF_2 and Sr:CaF_2 nanocrystals, their morphological features, optical absorption spectrum and photoluminescence spectrum were studied in detail. However, in the experiment, there would be interaction among elements in the interface between metals and calcium fluoride films, which may affect the structures and optical properties of CaF_2 doping systems, so there are limitations in the experimental research and the computational simulation at the atomic level is particularly important. Currently, theoretical reports on the physical mechanism about the crystal structures, electrical and optical properties of Mg-, Sr-doped CaF_2 systems are very rare.

In this paper, using the first-principles methods based on the density functional theory (DFT), we have studied the electronic structures and optical properties of CaF_2 bulk and Mg-, Sr-doped CaF_2 systems. To be specific, we have calculated the total density of states (DOS) and partial density of states (PDOS), the real and imaginary parts of complex dielectric functions, absorption coefficients, refractive indexes, extinction coefficients, reflectivity and loss functions. The present results are compared with the available experimental results. Our results would play a guiding role in preparation and development in the field of application about Mg-, Sr-doped CaF_2 systems.

2 Theoretical systems and calculation method

2.1 Theoretical systems

CaF_2 bulk belongs to cubic fluorite structure, its space group is Fm 3m and lattice constants $a(b,c)$ are 5.4630 Å [20]. The unit cell of CaF_2 is composed by four calcium atoms and eight fluorine atoms, there is equal bond length between each calcium atom and each