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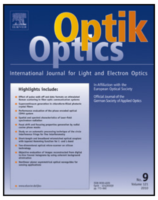

Original research article

FP-LAPW investigation on structural, electronic and optical properties of Eu^{2+}-doped MF_2 (M = Ca and Ba)

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ABSTRACT

The structural, electronic and optical properties of MF_2 (M = Ca and Ba) doped with Eu^{2+} ion have been studied using full-potential linearized augmented plane wave (FP-LAPW) method based on the density functional theory (DFT), as implemented in Wien2k package. Due to the difference in ionic size, the Eu^{2+} incorporation in MF_2 induces a re-accommodation of its nearest neighbors to reach more stable configuration. Along with the generalized gradient approximation (GGA-PBE), the electronic properties also are investigated by Tran-Blaha modified Becke Johnson potenital (mBJ) due to that it gives very accurate band gap of a lot of types of solid. The Eu^{2+} doping causes a slight increase on band gap of CaF_2 and BaF_2, and there is found Eu^{2+}-*4f* state in the forbidden energy region of *host*. In this work, the spin-orbit coupling (SOC) effect on electronic properties of MF_2:Eu^{2+} is also investigated. Finally, the doping effect on optical absorption property is also studied by deriving the absorption coefficient of all materials on consideration from their calculated complex dielectric function in energy range up to 17 eV.

1. Introduction

CaF_2 and BaF_2 compounds are strongly ionic solids which crystallize in fluorite-type structure ($Fm\bar{3}m$ space group) [1]. These materials have been considered excellent candidates for use as *host* for optically active centers (OAC), due to their interesting physical and chemical properties, such as, high optical transparence in large energy range (as result of their wide band gap of 12.1 eV and 11 eV for CaF_2 and BaF_2, respectively [2,3]), chemical stability and low energy phonons (446 and 319 cm^{-1}, respectively [4]), which reduces the non-radiative energy loss.

The OAC can be transition metal or lanthanide ions which are incorporated as dopant in the crystal lattice of solids to obtain desired optical properties. They are characterized by *3d* and *4f* unfilled shell, respectively. While the crystal field plays important role in optical properties of the formers due to the *3d* shell is not well screened, those of the later generally suffer very little effect by outside pertubation because the *4f* shell is well screened by outer ones [5]. One of the most used lanthanides is Europium (Eu) due to that its luminescence generated by transitions between *5d* and *4f* shells which are effectively excited by UV light [6]. Eu ions can be incorporated in *host* lattice in two possible oxidation states: Eu^{3+} and Eu^{2+}. It is well known that interesting optical properties of Eu^{3+} ion are due to *4f*-*4f* transitions [7] and those of Eu^{2+} ion are generated by $4f^7$-$4f^6 5d^1$ transitions [8]. The Eu-doped solids have been applied in optical fiber [9,6], UV based white LED [10], visible lasers [11], among others.

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Experimentally, it is proved that divalent Eu^{2+} is highly soluble in MF_2 compounds. MF_2:Eu^{2+} has been prepared and well characterized with different methods [12–15]. The substitutional incorporation of Eu^{2+} would induce re-arrangement of closest atoms to reach stable geometry of minimum energy. A intense emission centered at 425 nm [16] and 450 nm [14] has been observed for CaF_2:Eu^{2+} and BaF_2:Eu^{2+}, respectively.

In order to optimize the applications of the optical properties of materials, it is very important to study and understand their electronic properties. From theoretical point of view, Cheng at el [17] studied the structural, electronic and optical properties of CaF_2:Eu under pressure using the plane-wave pseudopotential method based on density functional theory and found that there is an impurity band belonging to *4f* electrons, which is introduced in the forbidden energy region of *host* and contributes to the bandgap narrowing by 1.937 eV, otherwise, some peaks corresponding to dopant atom appear at the calculated optical spectras. Aiga et al [18,19] studied the *4f-5d* transitions using the complete active space self-consistent field (CASSCF) and second order perturbation theory (CASPT2) calculations with spin-orbit interactions and the obtained results are in good agreement with experimental absorption spectra. To the best of our knowledge, these mentioned studies are of the very little theoretical works devoted to MF_2 doped with Eu^{2+} in literature. Hence, a deeper investigation of structural, electronic and optical properties of MF_2:Eu^{2+} is still needed.

In the present work, we carried out first principles calculations to study the structural, electronic and optical properties of MF_2 compounds doped with Eu^{2+} ion pretending to give a more complete understanding about these materials.

2. Computational details

In this work, all calculations have been performed using the full-potential linearized augmented plane wave method (FP-LAPW) within the framework of density functional theory (DFT) as implemented in the Wien2k package [20], this method has been proven to be very efficient for solving the Kohn-Sham equations of crystalline systems. The standard generalized gradient approximation as proposed by Perdew et al [21] (GGA-PBE functional) is adopted for treatment of exchange-correlation effects. It is well known that as other standard functionals, PBE describes well the form of the electronic band structure of solids, but it always underestimates their band gap, hence, we also employ the mBJ exchange potential in combination with PBE correlation one (mBJ-PBE). mBJ is the Tran-Blaha modified version of exchange potential proposed by Becke-Jhonson [22] to improve the band gap calculated with standard functionals, and it has been proven to give very accurate band gap of a lot of solid types, such as wide band gap insulators, *sp*-semiconductors and strongly correlated *3d* transiton-metal oxides [23,24]. The results obtained with mBJ potential can be compared with those of hybrid functionals, but it has a big advantage being computationally cheaper.

To separate core states from valence states, the cut-off energy is set to −6 Ryd. The maximum quantum number (l_{max}) for atomic wave functions inside the atomic spheres is 10, and the cut-off energy for plane wave expansion of wave functions in the interstitial region is taken to be $K_{max} = 7/R_{MT}$, where R_{MT} is the muffin-tin radius. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-4} Ryd. The MF_2 properties are calculated with a k-mesh of 6 × 6 ×6 in the first Brillouin zone, while the MF_2:Eu^{2+} are investigated by generating a supercell of 2 × 1 ×1 and a k-mes of 5 × 10 × 10 is employed.

It is worth mentioning that in the optical calculations, we used the k-mesh much denser than that in electronic calculations.

3. Results and discussion

3.1. Structural properties

As mentioned above, at ambient conditions, CaF_2 and BaF_2 crystallize in fluorite-structure, $Fm\bar{3}m$ space group with cations and anions are located at (0; 0; 0) and (0.25; 0.25; 0.25) positions, respectively. The experimental lattice parameter of CaF_2 and BaF_2 is 5.46 and 6.20 Å, respectively [1]. Firstly, the structure of CaF_2 and BaF_2 is optimized by calculating the total energy of 11 points from $-10V_0$ to $10V_0$, where V_0 is the experimental volume, and then the obtained results are fitted to the equation of state of Murnaghan [25] to find out the volume with minimum energy. The optimized lattice constant by our calculations is 5.5307 and 6.2917 Å, this result is in good agreement with experimental one and other theoretical works [1–3].

From the optimized structure of MF_2, we generate a supercell of 2 × 1 ×1 for modelling the Eu doping. Then, the M atom at the center, that is (0.5; 0.5; 0.5) position, of the supercell is replaced by an Eu atom to obtain $Ca_7Eu_1F_{16}$ and $Ba_7Eu_1F_{16}$ materials as shown in Fig. 1.

Due to the difference of ion radius between the dopant and replaced atoms, it is expected a re-arrangement of atoms nearest to Eu. Hence, the geometry of MF_2:Eu^{2+} is optimized by relaxing all atoms in the cell and maintaining constant the volume. The obtained results are listed in Table 1.

The ionic radius of Ca^{2+}, Ba^{2+} and Eu^{2+} is 1.14, 1.49 and 1.31 Å, respectively [26]. So, Ca^{2+} is 15% smaller than Eu^{2+}, while Ba^{2+} is 12% bigger than Eu^{2+}. Therefore, once a Ca atom is substituted by an Eu atom, we can expect an estrangement of nearest atoms, while an opposite trend would be observed in case of BaF_2:Eu^{2+}. As seen in Table 1, our results do obey the size criterion mentioned. In case of CaF_2:Eu^{2+}, the size effect is more clearly noted than in BaF_2:Eu^{2+}, this is due to that the