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4 to 5 pages

FP-LAPW study of Structural, Electronic properties of perovskite: Hybrid Functionals Investigations

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Abstract

The study of structural, electronic and optical properties of $EuAlO_3$ cubic perovskite is carried out by full-potential linearized augmented plane wave (FP-LAPW) + On-site hybrid method within density functional theory (DFT). The exchange-correlation potential was treated with a solid version of the generalized gradient approximation of GGA-PBEsol to calculate the total energy. Moreover, GGA-PBEsol+U based potential and hybrid exchange-correlation functional were also used for the electronic and optical properties. Quantities such as the lattice parameter are consistent with the available data. The spin-polarized electronic band structure and the calculated density of states, by GGA+U, show that the studied compound has a half-metallic behavior while the hybrid method shows that it is a semiconductor.

Keywords: FP-LAPW. Optical properties, Hybrid exchange-correlation functionals, GGA+U, GGA-PBEsol.

1. Introduction

The perovskite structure has a high potential for a variety of device applications, especially the cubic structures, they have attractive properties such as superconductivity, insulator-to-metal transition, ionic conduction characteristics, dielectric proper-ties, and Ferro elasticity[1-3].In this work we have specified study of rare earth aluminium, these materials have interesting uses like phosphorescence and luminescence properties and laser materials[4,5]. We studied the ground-state structural and optoelectronic properties of EuAlO3 cubic perovskite by using a full-potential linearized augmented plane wave (FP-LAPW) technique based on density functional theory (DFT) [6-8]. The spin-polarized electronic band structure and the calculation of densi-ty of state show that most of the compounds have a half-metallic and a ferrimagnet-ic nature that was confirmed in previous published works, whereas the properties of cubic structures of RAlO3 perovskites were calculated [9].These materials have been the subject of experimental and theoretical interests due to their applications in spintronic[10-16], which is the potential to simultaneously tune both charge and spin in solid-state materials.

2. Computational Details

The calculation is performed using the generalized gradient approximation (GGA-PBEsol) [17], GGA+U and Hybrid functional (ecce) approximation for more accuracy in calculation of band structures and optical properties [18] implemented in the packageWien2k [19]. We represent a crystal structure of $EuAlO_3$ cubic phase with space group 221. We choose $R_{mt}\times K_{max}= 8$, where K_{max} is the plane's wave cutoff with energy -7.0 Ry, R_{mt} is the smallest of all atomic sphere radii. The radii of Eu, Al and O atomic sphere were set to 2.1,1.68 and 1.62 a.u. respectively. The k-integration over the Brillouin zone was selected by using the Monk Horst-Pack method [20]. We have used 35 k points in the irreducible wedge of the BZ for the cubic structure, and 27x27x27 for the self-consistent calculation that is considered to be converged when the total energy difference is less than 0.00001 Ry.

3. Results and discussion

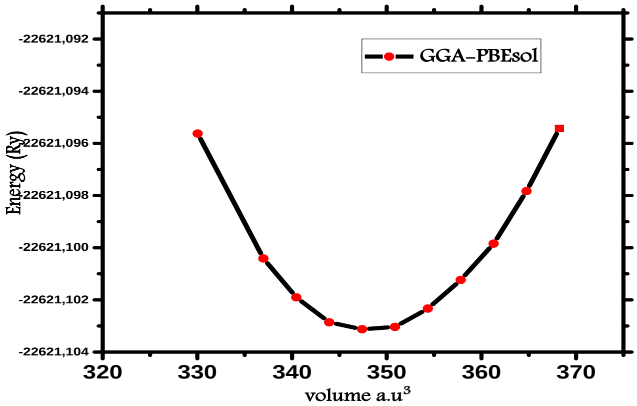
3.1. Structural optimization

The optimization plot of $EuAlO_3$ compound is shown in Fig. 2 obtained from the GGA-PBEsol calculation, it was fitted by the Murnaghan equation of state [21], so as to determine the equilibrium structural parameters. The calculated equilibrium lattice constants, bulk modulus B_0 and E_0 energy minimal are collected in Table 1, together with available experimental information.

Table 1. Calculated lattice constant (a_0), bulk modulus (B_0) , ground-state volume (V_0), and ground-state energy(E_0) of $EuAlO_3$ by the GGA-PBEsol approximation

	a_0 (A°)	V_0(a.u.^{3})	B_0 (GPa)	E_0(Ry)
This work	3,720	347.4434	194.1115	-22621,103174
Others [9,22]	3.72 3.64	341.00	199.82	
Experimental [22]	3.72			

Fig. 1. Energy as a function of volume for $EuAlO_3$



3.2 Electronic Properties

Fig. 2. Spin Up/Dn electronic band structures of $EuAlO_3$ obtained using a) GGA-PBEsol, b) GGA+U, c) hybrid functional

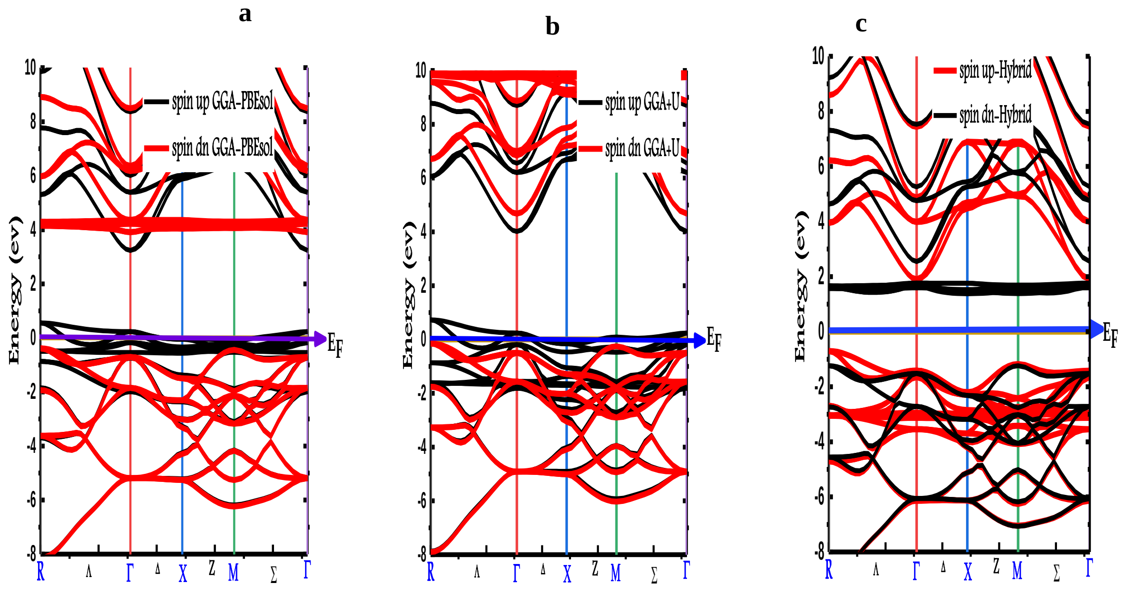
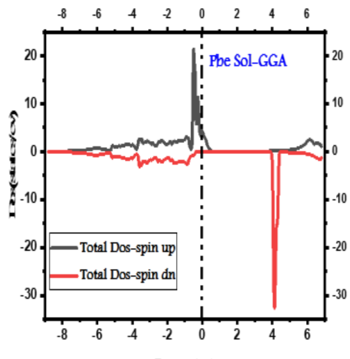
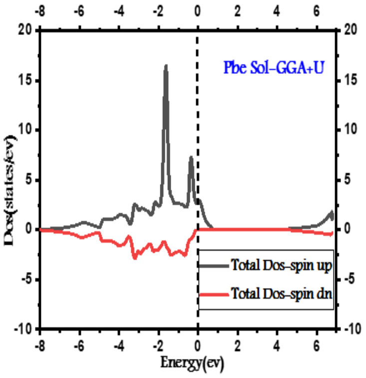


Fig. 3. Spin Up/Dntotal and partial contribution of Eu-f and O- p of states density obtained using a) GGA-PBEsol, b) GGA+U, c) hybrid functional



a



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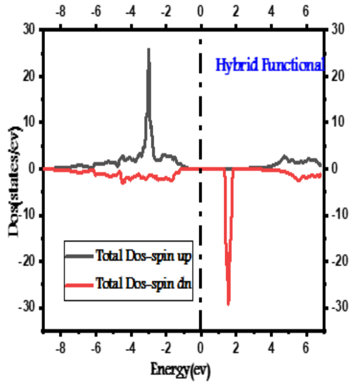

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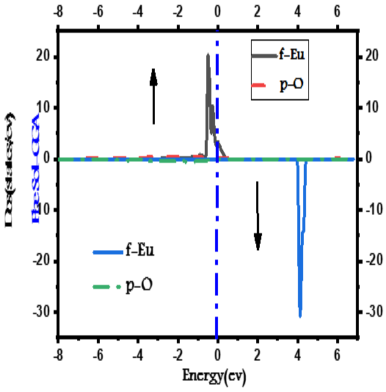
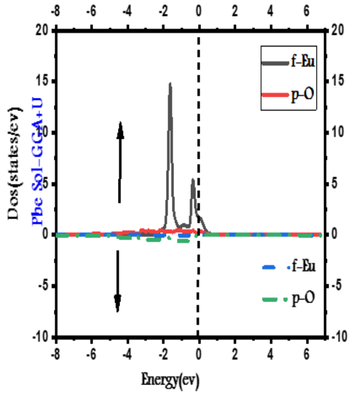
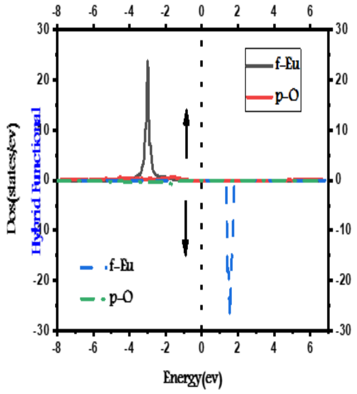
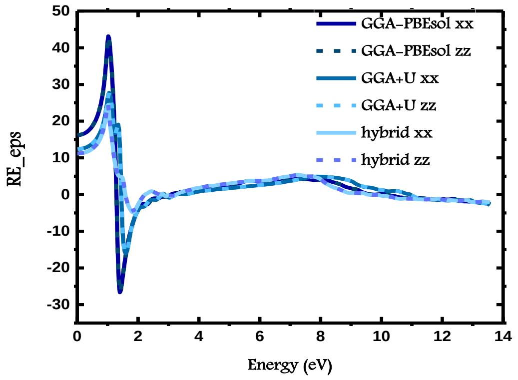


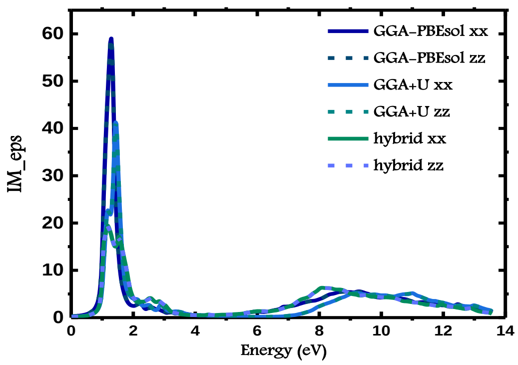




The spin polarized total and partial DOS spectra of $EuAlO_3$ show a halfmetallic character in Fig. 3 (a, b) at the Fermi level E_F set at 0 eV. This is in agreement with other result[9], and when applying the GGA + U[23], a special considerations is required for the correlation effect of f electrons of Eu, where a Hubbard term (U) is introduced for the strong on-site Coulomb repulsion among the localized states[24].With the application of U in the calculation, the rare earth 4f states shift leading to an increase in the band gap of the systems as shown in Fig. 3b. As described above, $EuAlO_3$ is a direct band gap semiconductor (spin down) in fig 2(a, c) and the band gap value of GGA-PBEsol and GGA+U are 4,30 ,4,84 eV respectively, somewhat determined by the energy of the conduction band. The Eu-f band is important in determining the band gap of $EuAlO_3$. In fact, the band gap depends on the energy of the Eu -4f, O-2p antibonding level. The both spins present a semiconductor character in Fig. 2(c) by using hybrid functional with a direct band gap and have a value of 3.70 eV, which results in a complete spin polarization of the charge carriers. Otherwise, the partial density of states in Fig. 3(c) shows that the major contribution to the valence and conduction bands in the majority spin channel around the Fermi level is mainly due to the orbital 4f of europium atom with a very small contribution of 2p orbital of oxygen.

3.3 Optical Properties





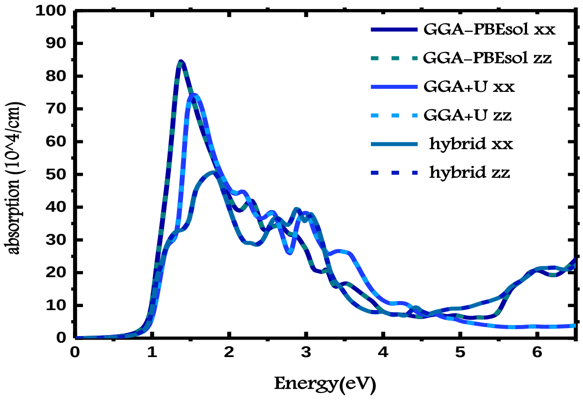


Fig. 4. a- Real and imaginary parts of the dielectric function, b- absorption coefficient α(ω) using : GGA-PBEsol, GGA+U and hybrid functional

We calculated the optical proprieties of these compound by using GGA-PBEsol, GGA+U and hybrid functional in two direction (E//x , E//z) these interaction are described by the dielectric function ε(ω) [24]:

$$\varepsilon(\omega) = \varepsilon 1(\omega) + i\varepsilon 2 \qquad (1)$$

In Fig 4.a shows the calculated real (dispersive) part ε_1 and the imaginary (absorptive) part ε_2 as a function of the photon energy. The imaginary part of the dielectric constant ε_2 is related to the electronic transitions from the occupied to the unoccupied states[25], it shows a set of peaks from 1.26 eV for GGA-PBEsol, 1.16-1.43 eV for GGA+U and 1.18 to 8.06 eV for Hybrid. These transitions are very probable because of the large number of bands in the top of valence as well as the energy difference which is very small between these bands and which supports these transitions. When the excitation energy exceeds the corresponding value at the top of the valence band, the peaks of the transitions rapidly decrease and they rise once this energy reaches the value corresponding to the minimum value of the conduction band. The band gap energy mainly originates from the electronic transition between the occupied O-2p energy levels and the unoccupied Eu-4f orbitals. And for the real part of the dielectric function ε1(ω) describes the dispersion of photons in the material which is calculated at the zero-frequency limit. It has a strong relationship with the bandgap energy as described by the Penn model [26]:

$$\varepsilon 1(0) = 1 + \left(\frac{hw}{E_g}\right)^2 \qquad (2)$$

This equation shows that ε1(0) changes inversely with the band gap energy E_g. The :calculated ε1(0) agree well with the Penn model that is found to be 15.58 for GGA-PBEsol, 12.13 for GGA+U and 11.17 for Hybrid and those values they are same in both direction which mean our compound is isotropic. In Fig 4.b we noted the peaks of absorption they are identically in both direction for deferent approximation as shows in fig 5.a, the absorption coefficient α(ω) can be calculated directly with dielectric function ε(ω) by using the following relation [27]:

$$\alpha(\omega) = \sqrt{2}\ \omega \left[\sqrt{\varepsilon_1{}^2(\omega) + \varepsilon_2{}^2(\omega)} - \varepsilon_1(\omega)\right]^{1/2} \qquad (3)$$

The absorption spectra begin 1.36,1.55,1.80 for GGA-PBEsol, GGA+U, hybrid functional respectively, which lies in the range 1– 6 eV and are all located from visible to near UV energy spectrum, these peaks are related to electron transition from valence to conduction.

4. Conclusion

In this paper, we have investigated the structural, optoelectronic properties of $EuAlO_3$ perovskite within the highly accurate density functional theory using the full-potential linearized augmented plane wave method as implemented in WIEN2K code. The electronic properties like band structure and density of states have been calculated by taking spin polarization into account. The band and DOS reveal the half-metallic nature of approximation GGA and GGA+U that can be used in spintronic device fabrication. However, with hybrid functional (ecce), our results show a semiconducting behavior for the real and the imaginary parts of the dielectric functions. They can be used to reproduce optical constants and show $EuAlO_3$ isotropic characteristic, absorption index which has spectra in the ultraviolet range and implies that this material is suitable can be utilized for photoluminescence and photocatalysis applications.

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