First-principles study of electronic, electrical and optical properties of HoMn$_2$O$_5$

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Abstract. In this work, we have studied the electronic, electrical and optical properties of HoMn$_2$O$_5$ using first-principles density functional theory within the generalized gradient approximation (GGA). The electrical conductivity decreases with increasing temperature and it exhibits metal-like behavior. The maximum conductivity values as a function of relaxation time reach $1.144.10^{-22} (\Omega^{-1} m^{-1} s^{-1})$ at 300 K. The optical calculation presents this material a good absorbing light in the visible region which is good for many optoelectronic and photovoltaic applications.

1. Introduction

Multiferroics materials, which exhibit simultaneous magnetic and ferroelectric order [1-3], have attracted much attention recently because of the interesting physics of systems with coupled multiple order parameters and because of their potential for cross electric and magnetic functionality: magnetic field induced polarization and depolarization [4], colossal magnetodielectric effects in DyMn2O5 [5], Colossal magnetostriction effect in HoMn2O5 [6], magnetocaloric effect [7,8], spintronic devices[9-12]. Thus, electrically accessible magnetic memory and processing and vice versa are important possibilities. Fundamental interest in multiferroicity also derives from the strong interplay between magnetic frustration, ferroelectric order and fundamental symmetry issues in phase transformations that characterize these materials [13-16]. Multiferroics with magnetic and electric ordering united in a single phase were thought to be rare [17,18]. RMn$_2$O$_5$ (R = Tb, Dy, Ho, Y, etc.) belongs to a very special class of multiferroics because the ferroelectricity is driven by the magnetic ordering [19–21], the multiferroic compounds in this study is improper ferroelectric [22]. One of the most important features in the magnetocaloric effect is multiferroics, where a ferroelectric and an (anti)ferromagnetic order coexist and both the ordered temperatures strongly associate with each other [23,24]. The presence of magnetic ions Ho$^{3+}$ with high magnetic moment could enhance the magnetocaloric effect in HoMn2O5 [7]. HoMn$_2$O$_5$ has an orthorhombic structure with Pbam symmetry at room temperature,
where edge-sharing $\text{Mn}^{4+}\text{O}_6$ octahedra align along the c-axis and pairs of $\text{Mn}^{3+}\text{O}_5$ pyramids link the $\text{Mn}^{4+}\text{O}_6$ chains in the ab-plane[25] shown in Fig.1.

![Figure 1: Orthorhombic structure of HoMn$_2$O$_5$ bulk](image)

**2. Computational Details**

Electronic structure calculations are performed through full potential linearized augmented plane waves (FP-LAPW) method based on the density functional theory implemented in the WIEN2k code [26]. For the exchange–correlation functionals, we have utilized the generalized gradient approximation (GGA) [27]. Total energies were converged within $10^{-5}$ (eV) precision in each self-consistency cycle. In addition, we have employed the BoltzTraP code to calculate the electrical properties [28,29], which is based on the analytical expressions of the electronic bands. We have calculated the electrical conductivity and mobility verses the temperature variation. HoMn$_2$O$_5$ crystallize in orthorhombic structure with space group Pbam (55). The lattice parameters a=7.272 Å, b = 8.493 Å, and c=5.679 Å. The atoms and Wyckoff positions are described in Table.1

| Atom    | Wy. | x    | y    | Z    |
|---------|-----|------|------|------|
| Ho      | 4g  | 0.1367 | 0.1714 | 0    |
| $\text{Mn}^{4+}$ | 4f  | 0    | 0.5  | 0.2611 |
| $\text{Mn}^{3+}$ | 4h  | 0.4126 | 0.3496 | 0.5  |
| $\text{O}_1$  | 4e  | 0    | 0    | 0.2702 |
| $\text{O}_2$  | 4g  | 0.1637 | 0.4438 | 0    |
| $\text{O}_3$  | 4h  | 0.1503 | 0.43 | 0.5  |
| $\text{O}_4$  | 8i  | 0.3948 | 0.2063 | 0.2457 |

**Table 1**: Wyckoff and atomic positions
3. Results and discussion

3.1. Electronic properties

In the case of ferromagnetic phase, the density of states of HoMn$_2$O$_5$ is plotted versus energy with spin polarized calculation illustrated in Figure 2. The highest valence band is located at -18 (eV) formed completely by O(2s), and the top of the valence band between -7 (eV) and Fermi level, formed states of hybridized Ho(4f), Mn$^{3+}$(3d) and Mn$^{4+}$(3d) atoms with a small contribution of 2p states of O. Near of the Fermi level the density of state is mainly formed by states of Ho(f). Between 0.5 and 5 (eV) the conduction band is constituted by strong hybridization of Mn$^{3+}$(3d) and Mn$^{4+}$(3d) orbitals. The top of the conduction band occupied by the Ho (4d) orbitals.

![Figure 2. Density of states of HoMn$_2$O$_5$](image)

3.2. Electrical properties

For the conductivity coefficient calculation, the relaxation time term $\tau$ should be treated as a constant parameter [30]. Figure 3 presents the calculated temperature dependent electrical conductivities for orthorhombic HoMn$_2$O$_5$ compound as a function of relaxation time $\sigma$ ($\tau$) within the temperature interval from 300 K to 800 K. The maximum conductivity values as a function of relaxation time reach 11.44.10$^{-2}$($\Omega^{-1}\text{m}^{-1}\text{s}^{-1}$) at 300 K.
Within the framework of the Boltzmann transport equation in constant relaxation time ($\tau$) approximation, the electrical conductivity ($\sigma$) is expressed in the form of the ratio $\sigma / \tau$. To calculate the electrical conductivity $\sigma$, we must determine the relaxation time $\tau$. We assume that the relaxation time $\tau$ is independent to the direction, and treat relaxation time as a constant at a certain specific temperature and carrier concentration. The results follow the trend that the electrical conductivity decreases with increasing temperature and it exhibits metal-like behavior. From the $\sigma / \tau$ values, we obtain a set of the temperature dependent relaxation times as shown in Figure 3. The relaxation time shows a decreasing trend with increasing the temperature due to the reduction of mobility at the higher temperature. As we see that by increasing the temperature the conductivity of the investigated material decreases, which confirm the metal-like behavior.

3.3. Optical properties

In order to study the optical properties, we have investigated the optical absorption using the GGA approximation. The optical properties of HoMn$_2$O$_5$ were investigated on the basis of electronic structure, the absorption phenomena depends directly on the number of light-absorbing particles.
According to the Figure 4, the calculation made shows the variation of optical absorption as a function of wavelength (nm). Based on the calculated optical absorption in different directions xx and zz, we noted that HoMn2O5 is an anisotropic system. The radiation(hν) which penetrates the material in E//xx direction present a different behavior to E//zz, which can be explained by the structural non-symmetry of HoMn2O5 matrix, in particular in the UV region. The absorption is high in the range of UV and decreases slightly in the region of visible light. From 300 nm the absorption becomes low, in this range the material did not absorb much radiation(hν). The large peaks which appears in the optical absorption spectrum correspond to the inter band transitions between HoMn2O5 states, and the peaks are shifted to high energies, this can explain the reason in which this material is an absorbent in the UV region.
According to the Figure 5, we show the variation of the reflectivity as a function of wavelength (nm), the average of reflectivity is 30% in the visible light region, it means that HoMn₂O₅ is not a good transparent in this region, this is mainly due to the absorbance of energy.

4. Conclusion

The electronic and optical calculations are performed within the density functional theory using the full potential linearized augmented plane waves (FP-LAPW) method employing GGA as embodied in the WIEN2k code, while the electrical properties calculation was carried out applying the semiclassical Boltzmann transport theory utilizing the BoltzTraP package. The electrical properties were obtained from the calculated band structures by performing additional postprocessing calculations applying the BoltzTraP package. Electrical conductivity for HoMn₂O₅ has maximum values of $(\sigma/\tau)=11.44 \times 10^{22}$ $(\Omega^{-1}m^{-1}s^{-1})$ at 300 K. Our calculation showed that this material is absorbent at UV region so it could be used as candidate in several optoelectronic and photovoltaic applications.

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