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Electronic properties of the sulvanite compounds: Cu_3TMS_4 (TM = V, Nb, Ta)

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Resumen

La familia de compuestos de las sulvanitas se está volviendo importante como posibles candidatos de conductores transparentes tipo-p con aplicaciones potenciales en celdas solares y dispositivos electrocrómicos. Hemos investigado por medio de cálculos de primeros-principios la estructura electrónica de estos materiales. La estructura electrónica nos muestra que estos materiales son semiconductores de bandgap indirecto. Los valores calculados de los bandgaps son 1.02, 1.64 y 1.91 eV para Cu_3VS_4, Cu_3NbS_4 y Cu_3TaS_4, respectivamente. El carácter del máximo de la banda de valencia está dominado por estados-d de Cu y el carácter del mínimo de la banda de conducción es debido a los estados-d de TM. Este incremento en el bandgap es debido al desplazamiento del mínimo de la banda de conducción a energías más altas cuando bajamos en la columna V-B de la tabla periódica.

***Palabras Clave*:** Teoría de los Funcionales de Densidad, Estructura Electrónica, Semiconductores, Sulvanitas

Abstract

The family of the sulvanite compounds are becoming important as possible candidates as p-type transparent conductors with potential applications in solar cells and electrochromic devices. We have investigated by means of first-principle calculations the electronic properties of these materials. The electronic structure shows that these materials are semiconductors with an indirect bandgap. The calculated bandgaps are 1.02, 1.64 and 1.91 eV for Cu_3VS_4, Cu_3NbS_4 and Cu_3TaS_4, respectively. The character of the valance band maximum is dominated by Cu d-states and the character of the conduction band minimum is due to the TM d-states. This bandgap increment is due to the shift of the conduction band minimum to higher energies when we go down in the column V-B of the periodic table.

***Keywords*:** Density Functional Theory, Electronic Structure, Semiconductors, Sulvanites

1. Introduction

Transparent conductors (TCs) are well known materials for industrial applications such as solar cell panels, electro-chromic and opto-electronic devices, etc. These applications are expanded to photovoltaic cells where TCs have a dual function as substrates for the photon absorbent material and as ohmic contact to transport the the photon-generated electrons or holes in the absorbent; they are also utilized as front electrodes in flat panels displays, low-emissivity windows, smart windows, electro-chromic materials in rear-view mirrors of vehicles; as well as gas sensors, biosensors, etc. [1,2,3,4,5]. The above TC applications are based on the fact that the electronic bandgap of a TC is higher than 3.1 eV. So visible photons (having energy between 2.1 and 3.1

eV) cannot excite electrons from the valence band (VB) to the conduction band (CB) and hence are transmitted through it, whereas they have enough energy to excite electrons from donor level to CB (for n-type TC) or holes from acceptor level to VB (for p-type TC). These acceptor or donor levels are created in the TC by introducing non-stoichiometry and (or) appropriate dopants in a controlled manner.

The most studied TCs are the transparent conducting oxides (TCOs), where a very active research on the n-type TCOs as In_2O_3:Sn (ITO), SnO_2:F, ZnO:Al, TiO_2:Nb has been carried out [6,7,8,9]. These doped materials have electron concentrations close to 10^{21} cm^{-3}, which contrast enormously with the electron concentration of these materials without doping (10^{17} to 10^{19} cm^{-3}) [6,7,8,9]. On the other hand, the study of p-type TCOs and TCs in general is very scarce; this is due to either the small number of discovered materials of this kind or because the hole concentration measured in these materials is very low. The best known p-type TCOs are the delaffosites ($CuMO_2$, M = Al, Ga, In) and NiO[10,11]. Other p-type semiconductors which may be find applications in transparent electronic devices are the ternary compounds belonging to the family of sulvanites: Cu_3TMS_4 (TM =V, Nb, Ta), especially Cu_3TaS_4 which has a optical bandgap near 2.8 eV[12]. The sulvanite compounds are materials which show mixed conductivity, with an ionic conductivity a room temperature due to Cu^+ interstitial impurities and a hole conductivity due presumably to Cu vacancies[13]. The sulvanite compounds have a simple cubic crystal structure with space group symmetry $P\bar{4}3m$ and point group symmetry T_d[14]. In spite of the fact that the sulvanites may be important materials for electronic applications, they were scarcely studied and no theoretical studies on these materials were carried out. In this paper for the first time we present a theoretical study of the elec-

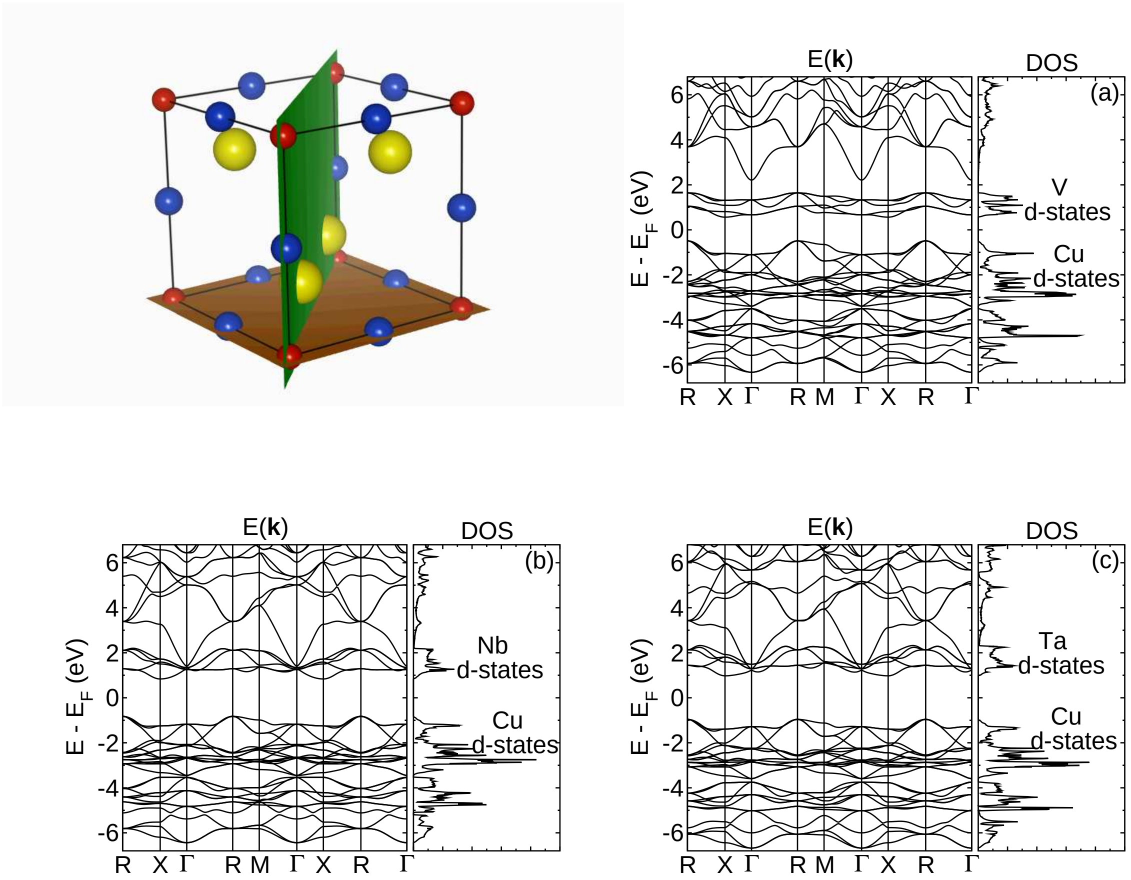

Figure 1. Crystal structure and electronic band structure for the sulvanite compounds. Blue, red and yellow balls denotes Cu, TM and S ions, respectively. The planes (001) and (-110) are shown in brown and green, respectively. The dispersion relation $E(\mathbf{k})$ and the total DOS for (a) Cu_3VS_4, (b) Cu_3NbS_4 and (c) Cu_3TaS_4. The Fermi level is set to zero.

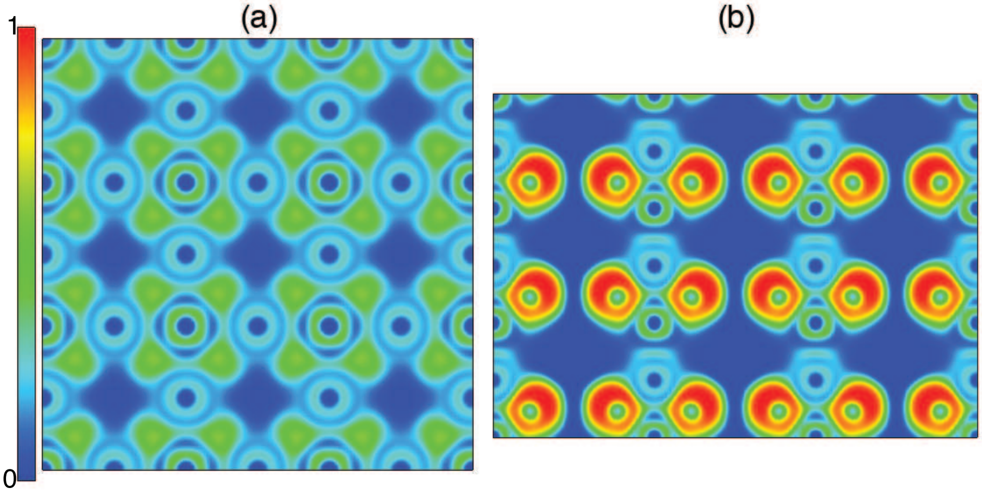

Figure 2. Electron localization function (ELF) for Cu_3VS_4. (a) ELF on the plane (001) and (b) ELF on the plane $(\bar{1}10)$.

tronic structure of the sulvanite compounds Cu_3TMS_4 (TM =V, Nb, Ta).

2. Method of Calculation

All total energies and atomic forces were calculated via first-principles density functional theory (DFT) using the projector augmented wave method (PAW) and the generalized gradient approximation (GGA-PBE) as implemented in the VASP code[15] to solve self-consistently the Kohn-Sham equations. The energy cutoff in the planes waves expansion was 480 eV. Brillouin-zone integration was performed on a $6 \times 6 \times 6$-$\mathbf{k}$-mesh with a Gaussian broadening for the atomic relaxation and a Γ-centered $12 \times 12 \times 12$-$\mathbf{k}$-mesh using the tetrahedron method for the calculation of total energies, charge density, and electron localization function.

3. Results and Discussion

The calculated electronic structure (the dispersion relation $E(\mathbf{k})$ and the total density of the states (DOS)) is shown in Fig. 1. We can see that all three compounds are semiconductors with indirect bandgap and the calculated values are 1.02, 1.64 and 1.91 eV for Cu_3VS_4, Cu_3NbS_4 and Cu_3TaS_4, respectively. The calculated bandgaps are underestimate with respect the experimental known values of 1.3 and 2.8 eV for Cu_3VS_4 and Cu_3TaS_4, respectively. This error is usual in DFT-GGA calculations, where bandgaps are underestimate. For all three compounds the bands that are between -6.5 to -3 eV below the Fermi level are build up mainly of S p-states. Moreover, the valance band maximum (VBM) is located at the R-point $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ and its character is dominated by Cu d-states with t_2 symmetry and the conduction band minimum (CBM) is located at the X-point $\left(\frac{1}{2}, 0, 0\right)$ and its character is dominated by TM (=V, Nb, Ta) d-states with symmetry e. We can observe that the VBM in these materials remains fixed with reference to the Fermi level whereas the CBM is shifted to higher energies when we go down in the column V-B of the periodic table. This displacement of the CBM is responsible for the increment of the bandgap in the sulvanite compounds.

The electron localization function (ELF), which is a useful tool for the characterization of bonds in molecules and solids. It has been shown that the spatial organization of this scalar function provides a basis for a well-defined classification of bonds. According to the definition, ELF can take values in the range between 0 and 1, where 1 corresponds to perfect localization and 0.5 to the case of a uniform electron gas. Pure ionic bonding would manifest itself by high values of the ELF close to the nuclei and very low (close to 0) and uniformly distributed ELF values in the interstitial region. Pure covalent bonding between two atoms would be the presence of a local maximum of the ELF on the line connecting those atoms, with a typical maximum value of the ELF in the range between 0.6 and 1.0 depending on how strong it is. Metallic bonding, which represents an intermediate case between the covalent and the ionic bonding, usually demonstrates a more or less uniform ELF distribution in the interstitial region with typical values of order 0.3 to 0.6. Figures 2 (a) and (b) show the calculated ELF for Cu_3VS_4 on the planes (001) and $(\bar{1}10)$, respectively (those planes are shown in Fig. 1).

We can observe that the values of ELF between the Cu and V ions (plane (001)) shows a metallic character. On the other hand, the values of ELF on the plane $(\bar{1}10)$ show a well recognized ionic character for the CuS_4 and VS_4 tetrahedral.

In conclusion, we have calculated the electronic structure of the sulvanite compounds Cu_3TMS_4 (TM =V, Nb, Ta), finding that they are semiconductors with indirect bandgap and the analysis of the ELF reveals the ionic character of these semiconductors materials.

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