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First Principles Study of Copper Sulfides (for applications as photoconductors)

J.A. Ferreira[1,a], M.H. Braga[2,3,b]

[1]LNEG, Laboratório Nacional de Energia e Geologia, S. Mamede Infesta, Portugal

[2]Los Alamos Neutron Scattering Center, Los Alamos National Laboratory, NM, USA

[3]CEMUC, Engineering Physics Dep., Engineering Faculty, Porto University, Portugal

[a]jorge.ferreira@lneg.pt (corresponding author), [b]mbraga@fe.up.pt

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Abstract. The Tetrahedrite's family constitutes a complete solid-solution series, and is among the most frequent complex sulfides in Nature. This kind of structure can be generically expressed by the composition, $Cu_{12}Sb_4S_{13}$. We have calculated the electronic band structure of $Cu_{12}Sb_4S_{13}$ and $Ag_6Cu_6Sb_4S_{13}$ (with band gaps of 1.24 and 1.20 eV, respectively) to demonstrate that different elements occupying certain sites of the crystal structure will make a difference in what concerns the conduction process in Tetrahedrites. We will use this effect and *ab initio* calculations to show that the electronic properties of these compounds make them promising candidates as solar cells photovoltaic materials since not only they possess a direct band gap but their energy falls within the range of energies of photovoltaics. Moreover, we can optimize these properties by doping and substituting ions furthermore. Mechanical properties were also calculated for both compounds and will be compared.

Introduction

Tetrahedrite is a copper antimony sulfosalt mineral, $Cu_{12}Sb_4S_{13}$, with I -43m crystal symmetry, seeming to be a promising candidate for solar cells photovoltaics. The Copper-Antimony-Sulfur compound can occur as a stable mineral [1] (Fig. 1) (at ambient conditions), or being synthesized from the constituent elements in stoichiometric proportion [2,3].

Fig1: A specimen of natural Tetrahedrite, from Huaron Mine, Peru.

The crystal structure of the Tetrahedrite can be interpreted as a derivation of the crystal structure of the Sphalerite, which presents a cubic structure F -43m, with composition ZnS. This compound can be transformed into a Tetrahedrite, I -43m. This transformation can be explained and supported by the principles assisting the geometrical crystallography. It only implies a transformation from F to I cell type, keeping the point group (-43m). The latter transformation requires doubling the unit cell size from a_0= 5.25 Å to a = 10.50 Å. The transformation is described as following: the cubic crystal structure of the Tetrahedrite has two formula units per cell, being derived from the Sphalerite structure by replacing a tetrahedral cluster of sulfur atoms by four packing vacancies (4Vac) in each sixteen packing sulfur positions. Then the vacancies, 4Vac, are replaced by one single S-atom according to the sequence (1), where S^t corresponds to the generic tetrahedral position and S^o is the final octahedral position assumed by one in sixteen atoms of sulfur (Fig. 2).

$$[S^t_{16}] \rightarrow [S^t_{12}\,Vac_4] \rightarrow \{[S^t_{12}][S^o]\} \quad (1)$$