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Authors: Lawal Mohammed., Muhammad A. Saeed, Qinfang Zhang, Auwalu Musa

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# Core-level excitation in polymorph of $AS_2S_3$ and $\beta$-$In_2S_3$

**Lawal Mohammed.[*] [1,2,3], Muhammad A. Saeed[3], Qinfang Zhang[1], Auwalu Musa[4]**

[1]*School of Material Science and Engineering, Yancheng Institute of Technology, Yancheng 224051, P. R. China*
[2]*Physics Department Ahmadu Bello University, Zaria 833201, Nigeria*
[3]*Physics Department Universiti Teknologi, Johor 81310, Malaysia*

Highlights

- Similarities in the shift of the optical band-gap in β-$In_2S_3$ and orpiment.
- Striking comparisons in Arsenic $L_3$ (s, d)-edges peaks for the polymorph of $As_2S_3$ crystals.
- Optical absorption increases due to core-hole for S K (p) and As $L_3$-edges in orpiment.
- This work provides a better quality crystal for optical evaluation.

[4]Physics Department Bayero University Kano 3011, Nigeria

**Abstract**
X-ray absorption near-edge structure (XANES) is one of the most widespread spectroscopies for studying the chemical properties of materials. It is a sensitive probe of the atomic environment, because it can be used to effectively measure the transition probability between core electrons and unoccupied states. In this paper, single level excitonic effects on the core state of the polymorph of $As_2S_3$ and tetragonal $In_2S_3$ were studied using X-ray absorption spectroscopy. Our results for the first time show striking similarities in Arsenic $L_3$ (s, d)-edges peaks for the two phases of $As_2S_3$ orpiment and anorpiment crystals. Optical absorption increases mostly due to core-hole for S K (p) and As $L_3$-edges in orpiment as compared to the other structures. The core-level calculations for these orbitals show good agreement with the experimental ones thus validating the approach used in this study. In orpiment and anorpiment, an indirect energy band gap which has been improved by the mBJ potential to about 1.03 eV and 0.65 eV respectively was observed. We have calculated the imaginary dielectric function and the absorption coefficient with the mBJ potential and core-hole, the optical excitations, is observe to be enhance by core level spectroscopy for all the crystals. Furthermore, the bond length and angles of monoclinic and triclinic $As_2S_3$ as well as the beta-phase $In_2S_3$ compared well with the experimental results. Structural optimization and total energies of all structures are computed using the all electrons full potential linearized augmented plane wave plus local orbitals (FP-LAPW + lo) within the framework of DFT.

*Keywords*: chalcogenide; core hole; X-ray absorption; optical properties; electronic structure

*Corresponding author.
E-mail address: mohammedlawal08@yahoo.com

## 1. Introduction

Chalcogenide semiconductors have many interesting optical and electronic properties [1-3]. Although these properties for arsenic chalcogenide [4] glasses have been studied extensively as materials for optoelectronic devices [5,34] however, the electronic structure of these materials is obtained from the study of their crystalline phases not amorphous. Anorpiment, $As_2S_3$ is a newly discovered mineral that exist in triclinic symmetry [6], it composed of layers of $As_2S_3$ macromolecules similar to that of orpiment. There are many striking similarities between the two phases, yet a little is known about the electronic and optical properties of anorpiment. Therefore, it is difficult to compare these properties with that of more stable monoclinic phase $As_2S_3$. There are few theoretical studies available on crystalline orpiment $As_2S_3$ [7] by employing GGA energy functional to investigate and compare some repulsive forces between $As_2S_3$ and $As_2Se_3$. Furthermore, electronic structure of monoclinic phase was investigated using multiple scattering approximations for clusters in real space [8]. However, none of these studies provide detail insight on the similarities and differences between the polymorph of $As_2S_3$. Therefore, for the first time as per as we know the electronic structure of the triclinic anorpiment is presented.

On the other hand, the β-phase Indium sulfide is the only stable crystallized spinel among the existing three phases that shows potential photovoltaic properties, [9-11]