

Experimental and theoretical analyses of β - In_2S_3 under compression

S.Gallego-Parra^{1*}, O. Gomis², R. Vilaplana², E. Lora da Silva¹, A. Muñoz³, P. Rodríguez-Hernández³, C. Popescu⁴, D. Martínez-García⁵ and F. J. Manjón¹

¹ Instituto de Diseño para la Fabricación y Producción Automatizada, MALTA Consolider Team, Universitat Politècnica de València, 46022 Valencia, Spain

² Centro de Tecnologías Físicas: Acústica, Materiales y Astrofísica, MALTA Consolider Team, Universitat Politècnica de València, 46022 Valencia, Spain

³ Departamento de Física, Instituto de Materiales y Nanotecnología, MALTA Consolider Team, Universidad de La Laguna, 38205 Tenerife, Spain

⁴ ALBA-CELLS, Cerdanyola, E-08290 Barcelona, Spain

⁵ Departament de Física Aplicada – ICMUV, MALTA Consolider Team, Universitat de València, Burjassot, Spain

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*e-mail: sagalpar@doctor.upv.es

Semiconductors can be considered as one of the main cornerstones of optical, opto-electronic, and photonic functional components. Since the start of the technological age, they most common employed semiconductors were those based mainly on Cd- and Pb elements due to their suitable features, such as chemical stability, reliability, life expectancy and cost, etc [1]. However, inherent toxicity of Cd and Pb has driven research towards compounds free of these atoms, as In-based chalcogenides.

In particular, In-S system have drawn attention of the research community due to the misvalency between In and S atoms arising from different stoichiometries and polymorphisms. In_2S_3 stoichiometry exhibit three well-known phases: the defective spinel β - In_2S_3 at room temperature, and the defective cubic α - In_2S_3 and layered γ - In_2S_3 at 420 and 754 °C, respectively [2]. An additional fourth phase, the ε - In_2S_3 (corundum-type structure) is known to be synthesized at 3.5 GPa and 500 °C [3], although confirmation of this phase is still pending. β - In_2S_3 has been extensively studied when compared to the other phases, mainly due to the tunable band gap, photoluminescence, ferromagnetism, catalytic and photocatalytic activity, among other relevant properties, via rare earth and transition metal doping [4-6].

All phases of In_2S_3 have fractional occupancy on In sites, between In atoms and vacancies, but only β - In_2S_3 can be considered as an ordered-vacancy compound. **Fig. 1** shows the conventional cell of β - In_2S_3 (space group $I4_1/amd$, No. 141, $Z = 16$). As can be observed, the S atoms occupy 16h sites and In atoms are distributed at the octahedral 8c and 16h sites and 2/3 of tetrahedral 8e sites. Finally, 1/3 of tetrahedral 8e sites are occupied by vacancies in a regular fashion.

High-pressure (HP) offers a proper way to modify properties and even discovering pressure-induced phase transitions by reducing interatomic distances and strengthening interatomic interactions, therefore varying the nature of the chemical bonds. In spite of existing HP studies on β - In_2S_3 , there are still several gaps to be reassessed on its HP behavior. Among the HP X-ray diffraction (XRD) studies, the first reported three pressure-induced phase transitions. Those close to 6.6 GPa and 11.1 GPa occurring at room temperature, and at 35.6

GPa by high-temperature annealing [7]. However, crystalline structure of HP phases at \sim 6.6 GPa and \sim 11.1 GPa was not determined HP [7]. In contrast, the most recent HP-XRD study carried out up to 41.3 GPa has not been able to observe any evidences of phases transitions, despite of the emergence and disappearance of some diffraction peaks under compression [8]. Surprisingly, these authors have shown in a later study a reversible semiconductor-to-metal transition at around 6.8 GPa on the β - In_2S_3 structure [9].

Here we report HP-XRD measurements and HP-Raman scattering measurements up to 15 GPa to study the nature of the HP phases observed on earlier studies. We complement this study with *ab initio* simulations. Moreover, we have analyzed the topology of the charge density to understand the pressure behavior of vacancies and lone electron pairs of S atoms.

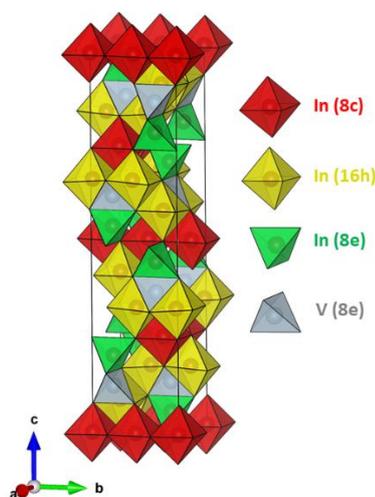


Figure 1. Crystal structure of β - In_2S_3 . Brown, yellow and green balls represent In atoms. Vacancies are represented by grey balls. S atoms are omitted to facilitate the view of the polyhedra. The Wyckoff sites are given in parenthesis.

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