$HgGa_2Se_4$ under high pressure: an optical absorption study

O. Gomis,[1,*] R. Vilaplana,[1] F.J. Manjón,[2] J. Ruiz-Fuertes,[3,4] E. Pérez-González,[5] J. López-Solano,[5] E. Bandiello,[6,4] D. Errandonea,[4] A. Segura[4], P. Rodríguez-Hernández,[5] A. Muñoz,[5] V. V. Ursaki,[7] and I. M. Tiginyanu[7]

[1]*Centro de Tecnologías Físicas: Acústica, Materiales y Astrofísica, MALTA Consolider Team, Universitat Politècnica de València, 46022 València, Spain*
[2]*Instituto de Diseño para la Fabricación y Producción Automatizada, MALTA Consolider Team, Universitat Politècnica de València, 46022 València, Spain*
[3]*Geowissenschaften, Goethe-Universität, Altenhöferallee 1, 60438 Frankfurt am Main, Germany*
[4]*Departamento de Física Aplicada-ICMUV, MALTA Consolider Team, Universidad de Valencia, Edificio de Investigación, C/Dr. Moliner 50, Burjassot, 46100 Valencia, Spain*
[5]*Departamento de Física, Instituto de Materiales y Nanotecnología, MALTA Consolider Team, Universidad de La Laguna, 38205 La Laguna, Tenerife, Spain*
[6]*Instituto de Ciencia Molecular, Universidad de Valencia, Paterna, 46980 Valencia, Spain*
[7]*Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, 2028 Chisinau, Moldova*

Abstract

High-pressure optical absorption measurements have been performed in defect chalcopyrite $HgGa_2Se_4$ to investigate the influence of pressure on the bandgap energy and its relation with the pressure-induced order-disorder processes that occur in this ordered-vacancy compound. Two different experiments have been carried out in which the sample undergoes either a partial or a total pressure-induced disorder process at 15.4 and 30.8 GPa, respectively. It has been found that the direct bandgap energies of the recovered samples at 1 GPa were around 0.15 and 0.23 eV smaller than that of the original sample, respectively, and that both recovered samples have different pressure coefficients of the direct bandgap than the original sample. A comprehensive explanation for these results on the basis of pressure-induced order-disorder processes is provided.

PACS numbers: 62.50.-p, 71.20.Nr, 78.40.Fy

Keywords: defect chalcopyrite, high pressure, order–disorder transitions, optical properties, bandgap energy

* Corresponding author, email: osgohi@fis.upv.es

1. Introduction

$HgGa_2Se_4$ is an adamantine-type $A^{II}B_2^{III}X_4^{VI}$ ordered-vacancy compound (OVC) which crystallizes in the tetragonal defect-chalcopyrite (DC) structure whose space group (S.G.) is *I*-4, No. 82. A feature of OVCs is that they are tetrahedrally-coordinated semiconductors that have a vacant cationic site in an ordered and stoichiometric fashion; i.e., a stoichiometric vacancy located at a fixed Wyckoff position in the unit cell **[1]**. The presence of a stoichiometric vacancy in the unit cell leads to a more complex physics in OVCs than in common semiconductors and explains why OVCs have been less studied than common binary and ternary chalcogenide semiconductors.

OVCs are interesting compounds to study the order-disorder phase transitions occurring in tetrahedrally-coordinated semiconductors and the influence of cation disorder in the physico-chemical properties of semiconductors. A common trend in all adamantine OVCs is that they have several non-equivalent tetrahedrally-coordinated cations and a vacancy in the unit cell which results in a distortion of the crystal lattice from the cubic symmetry. The lack of cubic symmetry of OVCs, their anisotropy, and their wide range of bandgap energies provides special properties to this family of semiconductors with important technological applications in optoelectronics, solar cells, and non-linear optics that have been the subject of several reviews **[1-4]**.

High-pressure studies of OVCs with $A^{II}B_2^{III}X_4^{VI}$ stoichiometry are receiving increasing attention in the last years **[5-36].** The vast majority of these works have been focused on the study of the structural and vibrational properties of $A^{II}B_2^{III}X_4^{VI}$ compounds. In particular, three high-pressure works have recently reported the structural and vibrational properties of DC-$HgGa_2Se_4$ under pressure where pressure-induced phase transitions have been observed **[24,25,28]**. The disordered stannite (DS) structure and the disordered rocksalt (DR) structure have been proposed as the high-pressure phases of DC-$HgGa_2Se_4$ **[24,25,28]**. In addition, the DR phase of $HgGa_2Se_4$ on downstroke undergoes a phase transition below 2.1 GPa to a phase assigned to a disordered zincblende (DZ) structure **[24,28]**. However, to the best of our knowledge, only three works have been devoted to the experimental high-pressure study of the optical absorption of the OVC family **[6, 21, 23]**. In this respect, the pressure dependence of the direct bandgap energy of semimagnetic $MnGa_2Se_4$ **[6]**, and of DC-$CdGa_2Se_4$ and DC-$HgGa_2Se_4$ **[21]** were reported. This last work was focused on the explanation of the strong non-linear pressure dependence of the direct bandgap energy