# Structural and Vibrational Study of Pseudocubic $CdIn_2Se_4$ under Compression

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**ABSTRACT**

We report a comprehensive experimental and theoretical study of the structural and vibrational properties of α-$CdIn_2Se_4$ under compression. Angle-dispersive synchrotron x-ray diffraction and Raman spectroscopy evidence that this ordered-vacancy compound with pseudocubic structure undergoes a phase transition (7 GPa) towards a disordered rocksalt structure as observed in many other ordered-vacancy compounds. The equation of state and the pressure dependence of the Raman-active modes of this semiconductor have been determined and compared both to *ab initio* total-energy and lattice dynamics calculations and to related compounds. Interestingly, on decreasing pressure, at ~ 2 GPa, $CdIn_2Se_4$ transforms into a spinel structure which, according to calculations, is energetically competitive with the initial pseudocubic phase. The phase behaviour of this compound under compression and the structural and compressibility trends in $AB_2Se_4$ selenides are discussed.

KEYWORDS: ordered vacancy compounds, phase transition, high pressure, pseudocubic, X-ray diffraction, Raman, ab initio calculations

## INTRODUCTION

Ternary adamantine $A^{II}B^{III}{}_2X_4$ semiconductors have been extensively investigated in the last 30 years mainly because they are tetrahedrally-coordinated ordered-vacancy compounds (OVCs) derived from the zincblende (ZB) structure whose behaviour locates them as a bridge between crystal and impurity physics[1]. In these OVCs, only three quarters of the ZB cation sites are filled

leaving one vacant site per formula unit. This stoichiometric atomic-vacancy arrangement leads to tetragonal structures instead of cubic ones that provide to these compounds interesting optical and structural properties such as nonlinear-optic characteristics and order-disorder transitions[1-3]. Particularly, studies of structural transformations of these semiconductors at high-pressure (HP) conditions have received increasing attention in the last years[4-31], leading to systematics in compressibility and pressure - composition phase boundaries. It has been found that these semiconductors usually crystallize in tetragonal structures like defect chalcopyrite (DC) [space group (S.G.) *I-4,* No. 82, *Z*=2] and defect stannite (DS) [S.G. *I-42m,* No. 121, *Z*=2]. The behaviour of these structures at high pressures has been reviewed in several chapters[32-34] of a recent monograph.

$CdIn_2Se_4$ is an OVC whose structural and vibrational properties have been thoroughly studied at ambient conditions. X-ray diffraction (XRD) measurements have evidenced that $CdIn_2Se_4$ shows structural polytypism as its tetragonal cell has been reported with at least three different *c/a* values of 1, 2 and 4, which correspond to the α, β and γ phases, respectively[1, 35-38]. The different modifications can be obtained depending upon transport conditions during the crystal growth[36]. The common α phase crystallizes in a tetragonal pseudocubic (PS) structure; therefore, α-$CdIn_2Se_4$ will be hereon noted as PS-$CdIn_2Se_4$. The structures of the β and γ phases are still unknown despite a structure similar to the DC phase has been proposed for the β phase[38]. On the other hand, the vibrational properties of PS-$CdIn_2Se_4$ at ambient conditions have been studied by means of Raman scattering and Infrared spectroscopy and many similarities with the vibrational modes of the ZB structure have been found[39-42].

The structural relationship between the ZB (**Fig. 1a**) and PS (**Fig. 1b**) structures of $CdIn_2Se_4$ can be easily illustrated using a simple Bärnighausen-tree[43] (see **Fig. 2**). One starts with the