

# High-pressure x-ray diffraction study on the structure and phase transitions of the defect-stannite $\text{ZnGa}_2\text{Se}_4$ and defect-chalcopyrite $\text{CdGa}_2\text{S}_4$

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**Abstract:** X-ray diffraction measurements on the sphalerite-derivatives  $\text{ZnGa}_2\text{Se}_4$  and  $\text{CdGa}_2\text{S}_4$  have been performed upon compression up to 23 GPa in a diamond-anvil cell.  $\text{ZnGa}_2\text{Se}_4$  exhibits a defect tetragonal stannite-type structure ( $I\bar{4}2m$ ) up to 15.5 GPa and in the range from 15.5 GPa to 18.5 GPa the low-pressure phase coexists with a high-pressure phase, which remains stable up to 23 GPa. In  $\text{CdGa}_2\text{S}_4$ , we find the defect

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tetragonal chalcopyrite-type structure ( $I\bar{4}$ ) is stable up to 17 GPa. Beyond this pressure a pressure-induced phase transition takes place. In both materials, the high-pressure phase has been characterized as a defect-cubic NaCl-type structure ( $Fm\bar{3}m$ ). The occurrence of the pressure induced phase transitions is apparently related with an increase of the cation disorder on the semiconductors investigated. In addition, the results allow the evaluation of the axial compressibility and the determination of the equation of state for each compound. The obtained results are compared with those previously reported for isomorphic digallium selenides. Finally, a systematic study of the pressure-induced phase transition in twenty-three different sphalerite-related  $ABX_2$  and  $AB_2X_4$  compounds indicates that the transition pressure increases as the ratio of the cationic radii and anionic radii of the compounds increases.

PACs numbers: 62.50.-p, 61.50.Ks, 61.05.cp, 64.70.kg

## I. Introduction

Zinc digallium selenide ( $\text{ZnGa}_2\text{Se}_4$ ) and cadmium digallium sulphide ( $\text{CdGa}_2\text{S}_4$ ) are tetrahedrally coordinated  $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$  defective compounds the structure of which is still contradictory discussed in the literature. While some studies suggest a defect-chalcopyrite structure ( $\bar{1}\bar{4}$ ) others report a defect-stannite structure ( $\bar{1}\bar{4}2\text{m}$ ) for these compounds. Both structures are tetragonal and structurally related to the cubic sphalerite structure ( $\bar{F}\bar{4}3\text{m}$ ), commonly known as zinc-blende, with only differences arising due to slightly deviations on the atomic positions of the anions. This family of semiconductors are of interest as possible infrared-transmitting windows materials. They are also applied in various nonlinear optical devices and as gyrotropic media in narrow-band optical filters. In addition, these compounds are promising optoelectronic materials due to their high values of nonlinear susceptibility, optical activity, intense luminescence, and high photosensitivity. Some compounds like  $\text{CdGa}_2\text{Se}_4$  and  $\text{CdAl}_2\text{S}_4$  have already found practical applications as tunable filters and ultraviolet photodetectors [1, 2]. High-pressure studies on  $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$  compounds are receiving increasing interest in the last years. In particular, these materials have been extensively studied by Raman spectroscopy [3 – 6] because of pressure-induced phase transitions. However, the structure of the high-pressure phases has been so far characterized only for two compounds,  $\text{CdGa}_2\text{Se}_4$  [7] and  $\text{MnGa}_2\text{Se}_4$  [8]. In both materials the high-pressure phase has been determined as a cubic NaCl-type structure.

In the present work, we report angle dispersive x-ray diffraction (ADXRD) measurements performed on  $\text{ZnGa}_2\text{Se}_4$  and  $\text{CdGa}_2\text{S}_4$  as a function of pressure in a diamond-anvil cell (DAC) at room temperature up to 23 GPa. From these experiments, we have determined the effect of pressure on the lattice parameters and atomic positions, as well as observed pressure-driven structural phase transitions. In both