Structural and elastic properties of defect chalcopyrite $HgGa_2S_4$ under high pressure

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Abstract

In this work, we focus on the study of the structural and elastic properties of mercury digallium sulfide ($HgGa_2S_4$) at high pressures. This compound belongs to the family of AB_2X_4 ordered-vacancy compounds and exhibits a tetragonal defect chalcopyrite structure. X-ray diffraction measurements at room temperature have been performed under compression up to 15.1 GPa in a diamond anvil cell. Our measurements have been complemented and compared with *ab initio* total energy calculations. The axial compressibility and the equation of state of the low-pressure phase of $HgGa_2S_4$ have been experimentally and theoretically determined and compared to other related ordered-vacancy compounds. The pressure dependence of the theoretical cation-anion and vacancy-anion distances and compressibilities in $HgGa_2S_4$ are reported and discussed in comparison to other related ordered-vacancy compounds. Finally, the pressure dependence of the theoretical elastic constants and elastic moduli of $HgGa_2S_4$ has been studied. Our calculations indicate that the low-pressure phase of $HgGa_2S_4$ becomes mechanically unstable above 13.8 GPa.

Keywords:

A. Semiconductors

C. Equation of state

C. Elasticity

C. Mechanical properties

D. High-pressure

D. X-ray diffraction

1. Introduction

Mercury digallium sulfide ($HgGa_2S_4$) is a tetrahedrally-coordinated semiconductor of the $A^{II}B_2^{III}X_4^{VI}$ family which crystallizes at ambient conditions in the tetragonal defect chalcopyrite (DC) structure (S.G. I-4, No. 82, Z=2) **[1-3]**. The unbalanced number of cations (A and B) and anions (X) in tetrahedrally-coordinated $A^{II}B_2^{III}X_4^{VI}$ semiconductors results in inequivalent tetrahedrally-coordinated A and B cations (located in different Wyckoff sites) and in the occupation of a cation site by a vacancy in an ordered and stoichiometric fashion. For this reason, these semiconductors are classified as ordered-vacancy compounds (OVCs). The lack of cubic symmetry and the rather strong anisotropy make OVCs suitable for many technological applications **[4–7].**

$HgGa_2S_4$ is of considerable interest because it combines nonlinear optical properties in the mid-infrared range, high non-linear susceptibility coefficients, birefringence, and a wide transparency range from 0.5 to 13 μm **[8-11].** This compound can be used for frequency doubling, optical parametric oscillator, and optical parametric amplifier in the wavelength range from 1.0 to 10 μm because the high values of laser damage threshold and conversion efficiency are combined with a suitable thermal conductivity and high specific heat capacity **[11, 12].** In fact, the combined properties of $HgGa_2S_4$ crystals make this compound to potentially occupy a leading position among the crystals used in non-linear optical devices **[11].**

Several high-pressure (HP) studies on $A^{II}B_2^{III}X_4^{VI}$ compounds have been carried out in the last years **[13-34]**. In particular, HP X-ray diffraction (XRD) measurements have been performed on $CdGa_2Se_4$ **[18]**, $MnGa_2Se_4$ **[24]**, $ZnGa_2Se_4$ **[26]**, $CdGa_2S_4$ **[26]**, $CdAl_2Se_4$ **[25]**, $HgAl_2Se_4$ **[27]**, $CdAl_2S_4$ **[27]**, and $HgGa_2Se_4$ **[32, 33]**. However, to the best of our knowledge, there is no study published on the structural and elastic