Crystal structure of $HgGa_2Se_4$ under compression

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Abstract

We report on high-pressure x-ray diffraction measurements up to 17.2 GPa in mercury digallium selenide ($HgGa_2Se_4$). The equation of state and the axial compressibilities for the low-pressure tetragonal phase have been determined and compared to related compounds. $HgGa_2Se_4$ exhibits a phase transition on upstroke towards a disordered rock-salt structure beyond 17 GPa, while on downstroke it undergoes a phase transition below 2.1 GPa to a phase that could be assigned to a metastable zinc-blende structure with a total cation-vacancy disorder. Thermal annealing at low- and high-pressure shows that kinetics plays an important role on pressure-driven transitions.

Keywords:

A. Chalcogénides

C. High-pressure

C. X-ray diffraction

D. Crystal structure

D. Phase transitions

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1. Introduction

Mercury digallium selenide ($HgGa_2Se_4$) is one of the less studied adamantine-type $A^{II}B_2^{III}X_4^{VI}$ ordered-vacancy compounds (OVCs). It crystallizes in the tetragonal defect-chalcopyrite (DC) structure with space group (SG) I-4, Z=2 [see **Fig. 1(a)**]. Adamantine OVCs are tetrahedrally-coordinated semiconductors which have an unoccupied cationic site **[1, 2]**. The presence of vacancies results in a complex physics and explains why OVCs have been scarcely studied. A common feature of them is that they have several non-equivalent tetrahedrally-coordinated cations resulting in a distortion of the crystal lattice from the cubic symmetry. This fact, their anisotropy, and their band-gap energies make them suitable for many technological applications **[3, 4].**

High-pressure (HP) studies on $A^{II}B_2^{III}X_4^{VI}$ compounds are receiving increasing attention in the last years **[3-20]**. In particular, ternary selenide compounds have been recently studied **[3, 4, 6 - 10, 12 - 20]**. However, to our knowledge, only one work has been devoted to $HgGa_2Se_4$ **[3]**, being focused on optical properties. In order to improve the knowledge of the HP behaviour of AGa_2Se_4 compounds, we report here synchrotron XRD measurements in $HgGa_2Se_4$. In particular, we show evidence of the presence of two new phases. They can be probably assigned to a disordered rock-salt (DR) structure (SG: Fm-3m, Z=1) [see **Fig. 1(b)**] and a disorder zinc-blende (DZ) structure (SG: F-43m, Z=1) [see **Fig. 1(c)**].

2. Experimental section

Single crystals of DC-$HgGa_2Se_4$ have been grown from its constituents HgSe and Ga_2Se_3 by chemical vapor transport method using iodine as a transport agent **[21]**. Chemical and structural analyses have shown the stoichiometric composition of the