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Vibrational study of $HgGa_2S_4$ under high pressure

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In this work, we report on high-pressure Raman scattering measurements in mercury digallium sulfide ($HgGa_2S_4$) with defect chalcopyrite structure that have been complemented with lattice dynamics *ab initio* calculations. Our measurements evidence that this semiconductor exhibits a pressure-induced phase transition from the completely ordered defect chalcopyrite structure to a partially disordered defect stannite structure above 18 GPa which is prior to the transition to the completely disordered rocksalt phase above 23 GPa. Furthermore, a completely disordered zincblende phase is observed below 5 GPa after decreasing pressure from 25 GPa. The disordered zincblende phase undergoes a reversible pressure-induced phase transition to the disordered rocksalt phase above 18 GPa. The sequence of phase transitions here reported for $HgGa_2S_4$ evidence the existence of an intermediate phase with partial cation-vacancy disorder between the ordered defect chalcopyrite and the disordered rocksalt phases and the irreversibility of the pressure-induced order-disorder processes occurring in ordered-vacancy compounds. The pressure dependence of the Raman modes of all phases, except the Raman-inactive disordered rocksalt phase, have been measured and discussed. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4794096]

I. INTRODUCTION

Many compounds of the type $A^{II}B_2^{III}X_4^{VI}$, with A^{II} and B^{III} being divalent and trivalent metals, respectively, crystallize at ambient conditions in tetragonal structures derived from the diamond or zincblende (space group (S.G.) F-43m, No. 216, Z = 2) structure. These compounds contain both *A* and *B* cations in tetrahedral coordination so there is an unbalanced number of cations and anions in the structure which leads to the appearance of vacancies in these structures. In most cases, the vacancies are located in fixed Wyckoff positions of the unit cell and so these compounds are called adamantine ordered-vacancy compounds (OVCs).

Adamantine OVCs constitute a class of semiconductors that exhibit extraordinary and unusual properties. The different number of anions and cations, unlike in the zincblende structure, implies that *A* and *B* cations are usually inequivalent tetrahedrally coordinated cations located in different Wyckoff sites. Consequently, the doubling of the cubic zincblende unit cell along the *c* axis in OVCs results in a tetragonal symmetry which provides them with special properties not present in cubic zincblende-type compounds. In particular, adamantine OVCs have important applications in optoelectronics, solar cells, and non-linear optics that have attracted considerable attention in the last thirty years, as evidenced in several reviews.[1–4]

Mercury digallium sulfide ($HgGa_2S_4$) crystallizes at ambient conditions in the tetragonal defect chalcopyrite (DC) structure (S.G. I-4, No. 82, Z = 2) as shown in Fig. 1(a).[5,6] This semiconductor is of considerable interest because of its nonlinear optical properties in the mid-infrared (IR) spectral range, high nonlinear susceptibility coefficients, fairly good birefringence, and a wide transparency range from 0.5 to 13 μm.[5–8] High values of laser threshold and conversion efficiency allow using this compound as frequency doubling, optical parametric oscillator (OPO), and optical parametric amplifier (OPA) in the wavelength range from 1.0 to 10 μm.[9] The development of the technique of growing mercury thiogallate crystals helped synthesize high-quality optical crystals, which offer the possibility of using them in OPOs pumped by radiation of widespread Nd:YAG lasers. Owing to the combination of their properties, this compound can occupy a leading position among the most promising nonlinear materials. Therefore, the good nonlinear properties and the optical quality of $HgGa_2S_4$ crystal allow this material to compete with $AgGaS_2$, $AgGaSe_2$, $ZnGeP_2$, and GaSe crystals.[10]

Despite the strong interest in the characterization of the properties of $HgGa_2S_4$, there is no study, to our knowledge, of its properties at high pressures probably due to the difficulties found in growing these crystals.[11] On the contrary, there are several measurements of the physical properties of other sulfide-based OVCs ($ZnGa_2S_4$, $CdGa_2S_4$, $CdAl_2S_4$, and $HgAl_2S_4$) under pressure.[12–16] In some of these works it has been shown that sulfide-based adamantine OVCs undergo a pressure-induced phase transition from the DC structure toward the disordered rocksalt (DR) structure, where cations

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