

High-pressure Raman scattering study of defect chalcopyrite and defect stannite ZnGa_2Se_4

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High-pressure Raman scattering measurements have been carried out in ZnGa_2Se_4 for both tetragonal defect chalcopyrite and defect stannite structures. Experimental results have been compared with theoretical lattice dynamics *ab initio* calculations and confirm that both phases exhibit different Raman-active phonons with slightly different pressure dependence. A pressure-induced phase transition to a Raman-inactive phase occurs for both phases; however, the sample with defect chalcopyrite structure requires slightly higher pressures than the sample with defect stannite structure to fully transform into the Raman-inactive phase. On downstroke, the Raman-inactive phase transforms into a phase that could be attributed to a disordered zincblende structure for both original phases; however, the sample with original defect chalcopyrite structure compressed just above 20 GPa, where the transformation to the Raman-inactive phase is not completed, returns on downstroke mainly to its original structure but shows a new peak that does not correspond to the defect chalcopyrite phase. The pressure dependence of the Raman spectra with this new peak and those of the disordered zincblende phase is also reported and discussed. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4810854>]

I. INTRODUCTION

Zinc digallium selenide (ZnGa_2Se_4) is a tetrahedrally coordinated semiconductor of the adamantine-type $A^{II}B_2^{III}X_4^{VI}$ family of ordered-vacancy compounds (OVCs). The lack of cubic symmetry provides special properties to this family of semiconductors with important applications in optoelectronics, solar cells, and non-linear optics that has been considerably reviewed.^{1–4} In particular, ZnGa_2Se_4 has a high photosensitivity and strong luminescence,² can be used for phase change memories,⁵ and has been proposed as a candidate for electronic device applications forming part of heterojunction diodes.⁶

The properties of ZnGa_2Se_4 have been characterized by x-ray diffraction (XRD),^{7,8} neutron and electron diffraction,^{9–12} extended x-ray absorption fine structure,¹³ infrared (IR),^{14,15} Raman spectroscopy,^{15–24} and magnetic²⁵ measurements. To this respect, while some authors claim that ZnGa_2Se_4 crystallizes in the tetragonal ordered defect chalcopyrite (DC) structure with space group (SG) I–4 [see Fig. 1(a)] where cations and vacancies are completely ordered,^{7,13,15,16,22} other authors

report that ZnGa_2Se_4 crystallizes in the partially disordered tetragonal defect stannite (DS) structure, also known as defect famatinite, with SG I–42m and higher symmetry than the DC phase^{8–12,21,26} [see Fig. 1(b)]. In this compound, Zn and Ga atoms have similar x-ray scattering factors and both SG I–4 and I–42m have the same crystallographic extinctions. Therefore, the structure of ZnGa_2Se_4 at ambient conditions is difficult to identify by XRD so neutron scattering measurements are more suitable to determine its crystalline structure. However, the main reason to this discrepancy seems to be related to the growth process and the annealing treatment of the sample since phase diagram studies reveal that several order-disorder transitions at relatively low temperatures are present in ZnGa_2Se_4 .^{16,25,27} It is also well known that details of crystal growth and sample preparation, like the maximum temperature reached in the post-growth annealing treatment and the rate of decrease of temperature during the growth process, are crucial to understand the final structure of this compound at ambient conditions (see Refs. 24 and 25). To this respect, we have shown in a recent work²⁸ that DC- ZnGa_2Se_4 can be grown from original DS- ZnGa_2Se_4 by a thermal annealing at 400 °C during 10 h followed by a slow cooling to ambient temperature at a rate of 1 °C/min. In fact, the DC sample we use in the present study is obtained from DS- ZnGa_2Se_4 in the way described in Ref. 28.

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