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Thermally activated cation ordering in $ZnGa_2Se_4$ single crystals studied by Raman scattering, optical absorption, and *ab initio* calculations

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Abstract
Order–disorder phase transitions induced by thermal annealing have been studied in the ordered-vacancy compound $ZnGa_2Se_4$ by means of Raman scattering and optical absorption measurements. The partially disordered as-grown sample with tetragonal defect stannite (DS) structure and $I\bar{4}2m$ space group has been subjected to controlled heating and cooling cycles. *In situ* Raman scattering measurements carried out during the whole annealing cycle show that annealing the sample to 400 °C results in a cation ordering in the sample, leading to the crystallization of the ordered tetragonal defect chalcopyrite (DC) structure with $I\bar{4}$ space group. On decreasing temperature the ordered cation scheme of the DC phase can be retained at ambient conditions. The symmetry of the Raman-active modes in both DS and DC phases is discussed and the similarities and differences between the Raman spectra of the two phases emphasized. The ordered structure of annealed samples is confirmed by optical absorption measurements and *ab initio* calculations, that show that the direct bandgap of DC-$ZnGa_2Se_4$ is larger than that of DS-$ZnGa_2Se_4$.

(Some figures may appear in colour only in the online journal)

1. Introduction

Zinc digallium selenide ($ZnGa_2Se_4$) is one of the most studied, and probably one of the most controversial, semiconductors of the adamantine-type tetrahedrally coordinated $A^{II}B_2^{III}X_4^{VI}$ family of ordered-vacancy compounds (OVCs). OVCs derive from the diamond and the zincblende or sphalerite ($F\bar{4}3m$) structure and have a vacant cationic site in an ordered and stoichiometric fashion; i.e., a stoichiometric vacancy is located at a fixed Wyckoff position in the unit cell [1]. A common trend in all adamantine OVCs is that

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