

Structural and Vibrational Properties of CdAl₂S₄ under High Pressure: Experimental and Theoretical Approach

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ABSTRACT The behavior of defect chalcopyrite CdAl_2S_4 at high pressures and ambient temperature has been studied from a joint experimental and theoretical point of view. High-pressure x-ray diffraction and Raman scattering measurements have been complemented with theoretical *ab initio* calculations. The equation of state and pressure dependences of the structural parameters of CdAl_2S_4 have been determined and compared to those of other AB_2X_4 ordered-vacancy compounds. The pressure dependence of the Raman-active mode frequencies has been reported as well as the theoretical phonon dispersion curves and phonon density of states at 1 atm. Our measurements suggest that defect chalcopyrite CdAl_2S_4 undergoes a phase transition above 15 GPa to a disordered-rocksalt structure, whose equation of state has also been obtained up to 25 GPa. In downstroke from 25 GPa to 1 atm, our measurements evidence that CdAl_2S_4 does not return to the defect chalcopyrite phase; it partially retains the disordered-rocksalt phase and partially transforms to the spinel structure. The nature of the spinel structure is confirmed by the good agreement of our experimental results with our theoretical calculations. All in all, our experimental and theoretical results provide evidence that the spinel and defect chalcopyrite phases of CdAl_2S_4 are competitive at 1 atm. This result opens the way to the synthesis of spinel-type CdAl_2S_4 near ambient conditions.

KEYWORDS defect chalcopyrite, spinel, ordered vacancy compounds, high-pressure, x-ray diffraction, Raman

INTRODUCTION

There is a vast number of compounds with AB_2X_4 stoichiometry, where A and B refer to cations and X corresponds to the anion, depending on the cation and anion valences to fit the octet rule. All the families of AB_2X_4 compounds have one thing in common; i.e, they have an unbalanced number of cations (3) and anions (4) per formula unit. Therefore, from the point of view of structural phase transitions at different temperatures or pressures, these compounds are prone to suffer order-disorder processes where cations may get mixed with vacancies at cation sites to fulfill the requirements of highly-coordinated structures.

Chalcogenides with $A^{II}B_2^{III}X_4^{VI}$ stoichiometry constitute a vast family of compounds crystallizing at ambient conditions in a great variety of structures. However, they can be classified into three main groups: i) compounds crystallizing in the spinel or related structures; ii) compounds crystallizing in tetrahedrally-coordinated structures, derived from the diamond and zincblende structures with ordered vacancies in the unit cell and known as adamantine-type ordered-vacancy compounds (OVCs); and iii) compounds crystallizing in structures not related to those of spinel or to those of OVCs, e.g. layered materials. Usually, oxides belong to the first group, selenides and tellurides to the second group, and sulphides belong either to the first, to the second, or to the third group.

Adamantine OVCs crystallize in tetragonal structures resulting from the doubling of the cubic zincblende unit cell along the c axis. These tetragonal structures, mainly with defect chalcopyrite (DC) structure [space group (S.G.) I-4, No. 82, $Z=2$, Fig. 1(a)] or defect stannite (DS) structure [S.G. I-42m, No.121, $Z=2$], confers to the OVCs special properties not present in cubic zincblende-type compounds. Consequently, adamantine OVC have important applications in optoelectronics, solar cells, and non-linear optics that have attracted considerable attention in the