Pressure induced phase transition in defect chalcopyrite compounds

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Abstract The large band gap semiconducting compounds of the type $A^{II}B^{III}C_{4}^{VI}$ crystallizing in the defect chalcopyrite (DCP) tetragonal structure are of great technological interest and have potential applications in non linear optical and photovoltaic devices. These compounds contain a crystallographically ordered array of vacancies (stoichiometric voids) in the cation sublattice and exhibit several interesting physical and chemical properties. The presence of the vacancies facilitates the doping of these compounds by impurities and has stimulated investigations about occurrence of order–disorder effects in the cation sublattice. In this presentation our recent experimental results on the high pressure investigations on some of the defect chalcopyrite compounds would be discussed.

1. Introduction
The large band gap ternary chalcopyrite compounds have attracted considerable attention from fundamental and application point of view as a new generation of semiconducting materials. Their crystal structure is common to compounds of chemical formula $A^{III}B^{II}C_{2}^{VI}$ and $A^{II}B^{IV}C_{2}^{VI}$. These can be thought of as being derived from the parent III-V and II-VI compounds respectively, by replacing the group-III element by alternating a group-II and group-IV element or the group II by a group-I and group-III element. The presence of nonequivalent tetrahedrally coordinated cations in these compounds because of the displacement of the anion from the sphalerite-like position results in a distortion of the crystal lattice from the cubic to tetragonal symmetry.

Another class of tetrahedrally bonded materials, known as the defect chalcopyrites can be derived by successive substitution from the sphalerite (zinc blende) structure. For instance, the formula unit of the $A^{II}B^{III}C_{4}^{VI}$ compound may be doubled and subsequently one of the group-I elements could be removed, thus creating a vacancy. In order to maintain the valency the other group I element could be replaced by a group-II element thus forming the $A^{III}B^{II}C_{4}^{VI}$ compound. Most of the $A^{III}B^{II}C_{4}^{VI}$ semiconductors crystallize in the thiogalate structure, also called defect chalcopyrite (DCP), $\{SG:\ I\ 4\};$ while some of them crystallize in the defect famatinite (DF), also known as defect stannite, with higher symmetry $\{SG:\ I\ 4\ 2m\}$. The difference between the two structures according to the partial cation ordering model lies in a partial disordering between the A and B cations for the $I\ 4\ 2m$ structure. Table 1 and Table 2 summarizes the structural parameters for a representative of both the DCP and DF structures respectively [1].
Table 1. Atomic positions and site occupancy for CdGa$_2$S$_4$ [1] in the defect-chalcopyrite structure, \{SG: $I \bar{4}$, \(Z=2\} at ambient pressure.

| Atom | Site | \(x\) | \(y\) | \(z\) | site occupancy |
|------|------|------|------|------|----------------|
| Cd   | 2a   | 0    | 0    | 0    | 1              |
| Ga(1) | 2b   | 0    | 0    | 0.5  | 1              |
| Ga(2) | 2c   | 0    | 0.5  | 0.25 | 1              |
| Vacancy | 2d   | 0    | 0.5  | 0.75 | 0              |
| S    | 8g   | 0.271(8) | 0.261(8) | 0.140(4) | 1 |

Table 2. Atomic positions and site occupancy for ZnGa$_2$Se$_4$ [1] in the defect-stannite structure, \{SG: $I \bar{4} 2m$, \(Z=2\} at ambient pressure.

| Atom | Site | \(x\) | \(y\) | \(z\) | site occupancy |
|------|------|------|------|------|----------------|
| Zn   | 4d   | 0    | 0.5  | 0.25 | 0.5            |
| Ga(1) | 4d   | 0    | 0.5  | 0.25 | 0.5            |
| Ga(2) | 2a   | 0    | 0    | 0    | 1              |
| Vacancy | 2b  | 0    | 0    | 0.5  | 0              |
| S    | 8i   | 0.264(8) | 0.264(8) | 0.117(4) | 1 |

It may be noted that these structures contain a crystallographically ordered array of vacancies (stoichiometric voids or vacancies) in the cation sublattice and hence they can be considered as ordered vacancy compounds [2]. The crystal structure of a typical DCP compound is shown in Figure 1. The vacancy in these compounds is an ordered defect and various attempts to completely fill up the vacancy are unsuccessful indicating that the defect is an inherent one. Hence this class of compounds form a natural bridge between the impurity physics and crystal physics and they can help to understand the role played by vacancies in the physical and chemical properties of solids. The tetrahedral coordination of atoms and the stoichiometric vacancies also result in a low packing efficiency in the crystal lattice. This facilitates considerably the doping of the DCP compound by impurities and also the formation of solid solution and the occurrence of order-disorder effects in the cation sublattice [3, 4]. Furthermore, this family of semiconductors are of great technological interest and are promising optoelectronic materials due to their high nonlinearity, intense luminescence and high photosensitivity [5]. In particular, tunable filters of CdGa$_2$S$_4$ and UV photodetectors of CdAl$_2$S$_4$ are already used as devices [5, 6].

High pressure investigation of the DCP compound could be of great interest for establishing the general systematics of phase transitions in these ternary compounds. Furthermore, the understanding of the role played by the vacancies in bonding and in pressure induced phase transition is of current theoretical and experimental interest. The knowledge of these data is also important from material design consideration.
Several $A^{II}B^{VI}C^{IV}$ compounds have been extensively investigated both theoretically and experimentally for their high pressure behaviour \([1,7-14]\). High pressure angle dispersive X-ray diffraction (ADXRD) on CdGa$_2$Se$_4$ by Gresechnik et al \([9]\) has shown an order-disorder phase transition at 21 GPa to the rock-salt (SG: $Fm\bar{3}m$, $Z=4$) structure which upon decompression transforms into disordered zinc-blende (SG: $F4\bar{3}m$, $Z=4$). High pressure Raman studies on CdGa$_2$Se$_4$ \([8, 9]\) has indicated an irreversible disappearance of Raman signal around 20.9 GPa due to transition to the Raman inactive rock salt phase. High pressure ADXRD measurements on ZnGa$_2$Se$_4$ and CdGa$_2$S$_4$ \([1]\) have revealed a pressure induced phase transition from the defect tetragonal to a defect cubic NaCl type structure around 15.5 GPa and 17 GPa respectively. Marquina et al \([7]\) have observed a tetragonal to cubic NaCl type structure at about 14 GPa with a two phase region (defect tetragonal + NaCl type) between 12 and 14 GPa in MnGa$_2$Se$_4$.

In view of these interesting results we have carried out high pressure angle dispersive X-ray diffraction and Raman investigation of the DCP compounds AAl$_2$Se$_4$ ($A = Cd, Zn, Hg$) and CdAl$_2$S$_4$ to investigate their structural evolution and vibrational properties under compression. In this paper the results of some of these would be reviewed.

### 2. Experimental Details

The DCP compounds for the study were grown using the chemical vapour transport (CVT) with iodine as transporting agent \([15]\). High pressure ADXRD measurements were carried out at the synchrotron radiation source at Elettra, Trieste, Italy using a Mao-Bell type of diamond anvil cell (DAC) with diamonds of culet size 400 µm. A 150 µm hole in a hardened stainless steel gasket pre-indented to a thickness of ~50 µm constituted the sample chamber. Silver or platinum was used as the internal pressure calibrant. The experimental station was based on an image plate area detector (Marresearch). The sample to image plate distance and wavelength were calibrated using LaB$_6$ as standard. The scanned two-dimensional diffraction patterns were corrected for image plate tilt and converted to intensity vs 2$\theta$ through radial integration using FIT2D software \([16]\). The lattice parameters of the sample and pressure calibrant were determined by carrying out full profile refinement using GSAS software \([17]\). The pressure was then determined from the equation of state of the pressure calibrant.
The Raman studies at high pressure were carried out using a 0.25 m Czerny-Turner spectrometer (SpectraPro 275, Acton Res. Corp.) in backscattering geometry with pressure calibration using ruby fluorescence technique [15]. For all the experiments 4:1 methanol: ethanol served as pressure transmitter except in the case of chemically reactive HgAl\(_2\)Se\(_4\), where paraffin oil was used as the pressure medium.

3. Results and Discussion

High pressure ADXRD measurements on AA\(_2\)Se\(_4\) (A = Cd, Zn, Hg) and CdAl\(_2\)S\(_4\) indicated a structural phase transition from the ambient tetragonal (\(SG: I \bar{4}\)) structure [15, 18, 19]. Table 3 lists the phase transition pressures for all these compounds. The high pressure phase was characterized by a broadening of the diffraction peaks in addition to the appearance of new diffraction peaks and could be fitted to a disordered NaCl type (\(SG: Fm \bar{3}m\)) structure using full profile refinement. The typical \(R_p\) and \(wR_p\) factor of the fit was about 2.8% and 4.3% respectively. The disordered NaCl phase was stable up to the highest pressure of the current measurements. Furthermore, a mixed phase region where the sharp lines of the tetragonal phase coexist with the broad lines of the NaCl phase was observed in the case of CdAl\(_2\)S\(_4\). The structural evolution for CdAl\(_2\)Se\(_4\) is shown in Figure 2 as a typical case. Upon unloading, the diffraction pattern in all the four compounds was different from that of the initial phase as well as from the high-pressure phase implying that the structural phase transition is irreversible. This pattern with broad diffraction lines could be fitted to a disordered zinc blende (\(SG: F 43m\)) structure. A second order Birch-Murnaghan equation of state [20] fit to the pressure-volume (P-V) data yielded a bulk modulus and volume discontinuity as indicated in Table 3. The presence of a volume discontinuity reaffirms the first order nature of the structural transition.

High pressure Raman measurements for these compounds indicated a decreasing intensity of the spectra with pressure and an irreversible vanishing of the spectrum above a certain transition pressure [15]. This pressure correlates with the structural phase transition pressure to the Raman inactive rock salt structure observed in the X-ray measurements. Table 3 lists the transition pressure for all the four compounds investigated. In addition, the line widths of the Raman peaks was found to change at intermediate pressures between 4 and 6 GPa. This is attributable to the pressure induced two stage order–disorder transition proposed by Bernard et al [2]. According to this model in the first stage A and B cations substitute each other leading to a partially cation disordered phase. In the second stage, mutual disorder of both cations and vacancies is established, resulting in a disordered zinc blende phase. If pressure is increased further, this structure transforms to a high symmetry rock salt type structure.

| Compound  | X-ray transition pressure (GPa) | Raman transition pressure (GPa) | Bulk Modulus (GPa) | Volume discontinuity (%) |
|-----------|---------------------------------|---------------------------------|-------------------|--------------------------|
| CdAl\(_2\)Se\(_4\) | 9.1                             | 9.6                             | 52.1              | 10.0                     |
| ZnAl\(_2\)Se\(_4\) | 10.6                            | 14.4                            | 43.7              | 7.6                      |
| HgAl\(_2\)Se\(_4\) | 13.0                            | 12.7                            | 66.0              | 2.1                      |
| CdAl\(_2\)S\(_4\) | 14.4                            | 13.5                            | 44.6              | 7                         |
The phase transition from the defect chalcopyrite to the disordered NaCl type structure implies an increase in the symmetry and increase in the coordination from tetrahedral to octahedral. Interestingly, a similar pressure induced phase transition to the cubic rock salt type structure has also been observed in the normal cubic zinc-blende and chalcopyrite (AIBIIIC2VI) compounds [21-23]. The similitude between the high-pressure behaviour of defect chalcopyrite and pure chalcopyrite and II-VI semiconductors is not surprising since the DCP structure could be considered to be derived from the zinc-blende (ZnSe) structure with the unit cell nearly doubled along [001] axis. On comparing the bulk modulus of the DCP compounds with the pure chalcopyrite and the II-VI compounds it is noted that the DCP compounds are more compressible than the latter.

![Graph showing structural evolution of CdAl₂Se₄ under compression](image)

**Figure 2.** Structural evolution of CdAl₂Se₄ under compression [15].

### 4. Conclusions

High pressure ADXRD measurements on the defect chalcopyrites AAl₂Se₄ (A = Cd, Zn, Hg) and CdAl₂S₄ indicate an irreversible structural phase transition to a disordered rock salt phase which upon pressure release goes to a disordered zinc blende phase with broad X-ray diffraction lines.

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### References

[1] Errandonea D, Kumar R S, Manjon F J, Ursaki V V and Tiginyanu I M 2008 *J. Appl. Phys.* 104 063524

[2] Bernard J E and Zunger A 1988 *Phys. Rev. B* 37 6835

[3] Kim W T, Cho G J and Kim C S *Phys. Rev. B* 43 14265

[4] Park T Y, Kim C D, Yoon C S, Yang D I, Song H J, Kim W T 1998 *J. Phys. Chem. Solids* 59 645

[5] Radautsan and I.M. Tiginyanu I M 1993 *Jpn. J. Appl. Phys. Suppl.* 32 5

[6] Badikov V V, Matveev I N, Pshenichnikov S M, Rychik O V, Trosenko N K, and Ustinov N D 1981 *Sov. J. Quantum Electron.* 11 548
[7] Marquina J, Power C, Grima P, Moroçoima M, Quintero M, Couzinnet B, Chervin J C, Munsch P and Gonzalez J 2006 J. Appl. Phys. 100 093513

[8] Ursaki V V, Burlakov I I, Tigiynanu I M, Raptis Y S, Anastassakis E and Anedda A 1999 Phys. Rev. B 59 257

[9] Mitani T, Naitou T, Matsuishi K, Onari S, Allakhverdiev K, Gashimzade F and Kerimova T 2003 Phys. Stat. Solids. B, 235 321

[9] Grzechnik A, Ursaki V V, Syassen K, Loa I, Tigiynanu I M and Hanfland M 2001 J. Solid State Chem. 160 205

[11] Allakhverdiev K, Gashimzade F, Kerimova T, Mittani T, Naitou T, Matsuishi K and Onari S 2003 J. Phys. Chem. Solids 64 1597

[12] Ursaki V V, Burlakov I I, Tigiynanu I M, Raptis Y S, Anastassakis E, Aksenov I and Sato K 1998 Jpn. J. Appl. Phys. 37 135

[13] Cabrera M F and Sankey O F 2001 J. Phys. Condens. Matter 13 1669

[14] Waskowska A, Gerward L, Olsen J S, Feliz M, Liusar R, Gracia L, Marques M and Recio J M 2004 J. Phys. Condens. Matter 16 53

[15] Meenakshi S, Vijayakumar V, Godwal B K, Eifler A, Orgzall I, Tkachev S and Hocheimer H D 2006 J. Phys. Chem. Solids 67 1660

[16] Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Hausermann D 1996 High Press. Res. 14 235

[17] Larson A C and Von Dreede R B 1994 General Structure Analysis System (GSAS), Los Alamos National Laboratory LUAR 86 748

[18] Meenakshi S, Vijayakumar V, Eifler A and Hocheimer H D 2010 J. Phys. Chem. Solids 71 832

[19] Meenakshi S, Vijayakumar V, Eifler A and Hocheimer H D 2010 Azerbajian J of Phys. 16 10

[20] Birch F 1978 J. Geophys. Res. 83 1257

[21] McMahon M I and Nelmes R J 1995 J. Phys. Chem. Solids 56 485

[22] Werner A, Hocheimer H D and Jayaraman A 1981 Phys. Rev. B 23 3836

[23] Arora A K, Sakuntala T and Artus L 1993 J. Phys. Chem. Solids 54 381