



ELSEVIER

Journal of Physics and Chemistry of Solids 64 (2003) 1603–1607

JOURNAL OF
PHYSICS AND CHEMISTRY
OF SOLIDS

www.elsevier.com/locate/jpcs

Raman scattering study of pressure-induced phase transitions in $A^{II}B_2^{III}C_4^{VI}$ defect chalcopyrites and spinels

I.M. Tiginyanu^{a,b,*}, V.V. Ursaki^a, F.J. Manjón^c, V.E. Tezlevan^a

^aInstitute of Applied Physics, Academy of Sciences of Moldova, 2028 Chisinau, Moldova

^bLaboratory of Low-Dimensional Semiconductor Structures, Technical University of Moldova, 2004 Chisinau, Moldova

^cDepartament de Física Aplicada, Universitat Politècnica de València, EPSA, 03801 Alcoi, Spain

Abstract

$A^{II}B_2^{III}C_4^{VI}$ defect chalcopyrites (DC) and spinels were investigated by Raman scattering spectroscopy under hydrostatic pressure up to 20 GPa. All these compounds were found to undergo a phase transition to a Raman inactive defect NaCl-type structure. The phase transition is reversible for spinels and irreversible for DC. From the analysis of the pressure behavior of Raman-active modes, it was concluded that the phase transition from spinel to NaCl-type structure is direct in $MnIn_2S_4$ and $CdIn_2S_4$, while it occurs via an intermediate $LiVO_2$ -type NaCl superstructure in $MgIn_2S_4$. The observed differences in the pressures and the paths of the pressure-induced phase transitions in $A^{II}B_2^{III}C_4^{VI}$ compounds are discussed.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: A. Semiconductors; D. Phase transitions; C. High pressure

1. Introduction

$A^{II}B_2^{III}C_4^{VI}$ compounds reveal a large variety of physical properties according to the individual composition. These compounds are obtained in different crystal structures and therefore are ideal to investigate the role of structure and composition in a response on external fields such as heat, pressure, electricity, magnetism, etc.

Most of the $A^{II}B_2^{III}C_4^{VI}$ compounds crystallize in the defect chalcopyrite (DC) and spinel structures [1]. Pressure induced phase transitions including order–disorder effects in tetrahedrally coordinated $A^{II}B_2^{III}C_4^{VI}$ compounds have been recently investigated experimentally by Raman scattering [2] and X-ray diffraction [3] as well as theoretically [4,5]

Investigations of spinels under pressure have important geophysical implications. The hypothesis of the layering of the earth's mantle is mainly explained by the phase transitions of olivine-like compounds to the intermediate

stage of spinel structure and finally to the perovskite-like structure as pressure and temperature increase with depth [6, 7]. Nevertheless, a limited number of high-pressure studies have been performed on $A^{II}B_2^{III}C_4^{VI}$ spinels up to now [8–11]. The goal of this work is to perform a comparative study of pressure induced phase transitions in $A^{II}B_2^{III}C_4^{VI}$ compounds with initial DC and spinel structure.

2. Experimental details

DC and spinel-type $A^{II}B_2^{III}C_4^{VI}$ single crystals were grown by chemical vapor transport using iodine as a transport agent [12]. For the optical measurements under pressure, the samples were loaded into a diamond anvil cell with methanol–ethanol pressure medium. The ruby luminescence method [13] was used for pressure calibration. Raman experiments were performed in backscattering geometry using 647.1 nm line of a Kr^{+} -ion laser at an intensity of less than 100 W/cm² on the sample. The scattered light was analyzed by a Jobin-Yvon T64000 triple spectrometer in combination with a multichannel CCD detector.

* Corresponding author. Institute of Applied Physics, Academy of Sciences of Moldova, 2028 Chisinau, Moldova.

E-mail address: tiginyanu@yahoo.com (I.M. Tiginyanu).

3. Results and discussion

$\text{CdM}_2^{\text{III}}\text{Se}_4$ ($\text{M}^{\text{III}} = \text{Ga}, \text{Al}$) defect chalcopyrites (DC) and MIn_2S_4 ($\text{M} = \text{Mn}, \text{Cd}, \text{Mg}$) spinels were investigated up to pressures of 20 GPa.

The first order RS spectra of the thiogallate structure consists of 13 Raman-active optical modes at the center of the Brillouin zone: $3A + 5B + 5E$, of which B and E modes are also IR active [14,15]. The nonpolar A-symmetry modes correspond to oscillations of the anion; the lowest-energy A^1 mode, the so-called ‘breathing’ mode, is connected to symmetric oscillations of the anions surrounding a stoichiometric vacancy [16]. The polar B- and E-symmetry modes exhibit LO–TO splitting.

Fig. 1 presents the measured pressure dependence of the Raman shift for all the modes in CdGa_2Se_4 as compared with the results of recent theoretical analysis [5]. This figure demonstrates a good agreement between experiment and theory. Fig. 2 shows the same dependence for CdAl_2Se_4 . The intensity of one B-symmetry mode was very low in this compound for a reliable plot. The full lines in Fig. 2 show the calculated pressure dependence of the phonon frequencies reproduced from Ref. [4]. It can be seen from Fig. 2 that the agreement between theory and experiment is excellent for the $E^1 - E^3$, $B^1 - B^3$, $A^1 - A^2$ modes and it is satisfactory for the other modes if one take the TO-component. The calculated slope is outstanding for all the modes.

The behavior of CdGa_2Se_4 and CdAl_2Se_4 in up-ward pressure run is typical for $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{C}_4^{\text{VI}}$ compounds with the tetrahedrally coordinated structure. The disappearance of RS signal at high pressures is caused by a phase transition to a denser rocksalt-type structure. The formation of a disordered rocksalt-type phase at high-pressure was recently confirmed in CdGa_2Se_4 compound by powder X-ray

diffraction analysis [3]. The pressure of the transition from the DC to the rocksalt-type structure was established to exhibit a dependence on bond ionicity and bond length [2]. The higher is the ionicity of the material the lower is the pressure of phase transition.

The structure of the initially tetrahedrally coordinated $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{C}_4^{\text{VI}}$ materials after decompression depends on many factors, including the pressure dependence of the potential barrier between the low- and high-pressure phase [2] and the difference in the parameters of anions and cations [17]. A metastable disordered NaCl-type structure, an amorphous phase, or a disordered ZnS-type material is obtained [2,3].

The first order RS spectra of the spinel structure consists of five Raman-active optical modes at the center of the Brillouin zone: $A_{1g} + E_g + 3F_{2g}$. A common feature of the Raman spectra of $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{C}_4^{\text{VI}}$ spinels is the non-elementary character of the A_{1g} mode consisting of two bands. This is a consequence of the disorder in the cation sublattice. In an ideal spinel structure, A^{II} atoms are located on tetrahedral sites of T_d symmetry and B^{III} atoms on octahedral sites of D_{3d} symmetry; whereas C atoms occupy C_{3v} sites [1]. In real spinel structures, the distribution of the cations is not ideal, and the cations are sometimes disordered on their sites. The disordering of cations is described by means of the normality index, X. This parameter leads to a more general formula $\text{A}_X\text{B}_{1-X}(\text{A}_{1-X}\text{B}_{1+X})$ which describes the occupation of the tetrahedral (octahedral) positions in the lattice. The value of $X = 1$ describes an ideal spinel structure, while $X = 0$ corresponds to an inverse spinel structure. An ideal stochastic distribution is obtained with the value $X = 1/3$. It is well known that the A_{1g} breathing mode corresponds to the vibrations of the anions towards the center of the tetrahedron [18]. Since in the partially inverse spinels tetrahedra are occupied by both A and B atoms, the A_{1g}

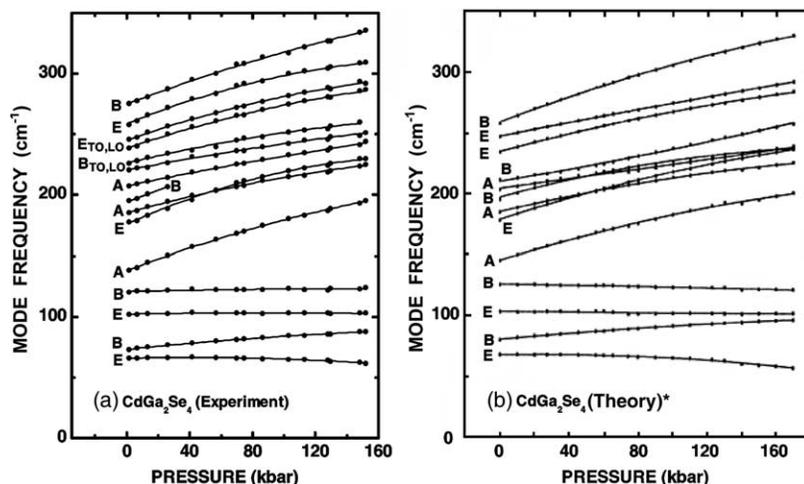


Fig. 1. Measured (a) and calculated (b) pressure dependence of the Raman active modes in CdGa_2Se_4 . *Theoretical results are reproduced from Ref. [5].

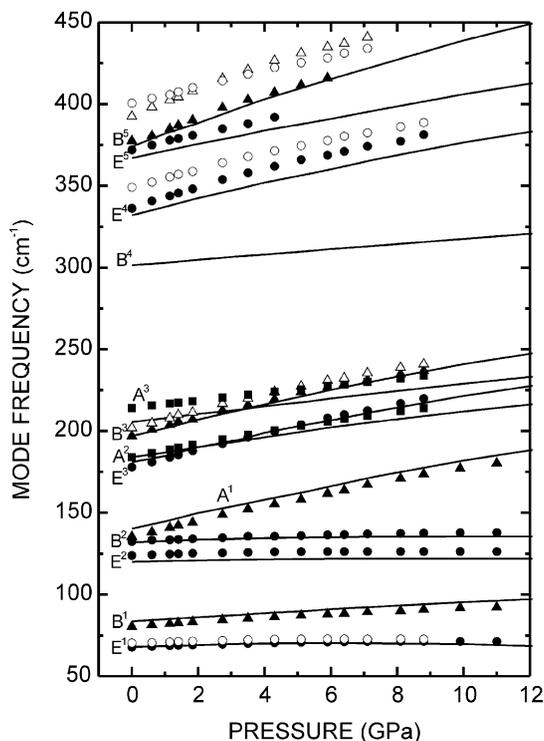


Fig. 2. Pressure dependence of the Raman active modes in CdAl_2Se_4 . Full (open) symbols are for the TO (LO) components, respectively. Solid lines present the result of calculation reproduced from Ref. [4].

mode is formed by two bands, corresponding to the vibration of AS_4 and BS_4 tetrahedral units.

One of the methods of obtaining an estimation of the normality index of a spinel compound is provided by the relative Raman intensity of the $A_{1g}(\text{MS}_4)/A_{1g}(\text{InS}_4)$ bands which should be equal to $X/(1-X)$. In this sense, we have estimated the normality index in our spinels from the knowledge of the frequencies and intensities of the A_{1g} modes at different pressures.

As mentioned above, the tetrahedrally coordinated $A^{\text{II}}B_2^{\text{III}}C_4^{\text{VI}}$ compounds undergo a phase transition to a Raman-inactive phase of disordered NaCl-type under application of pressure. In this context, MIn_2S_4 spinels are expected to behave in a similar way; i.e. a pressure-induced phase transition to a NaCl-type structure is expected. The transition to the NaCl phase in spinels is coherent with our observation of the disappearance of the Raman signal at pressures of 7.2, 9.3, and 12 GPa for $M = \text{Mn}, \text{Cd},$ and Mg , respectively. The main difference between the spinels and tetrahedrally coordinated compounds is that the phase transition is reversible in spinels unlike in tetrahedrally coordinated compounds, as exemplified by the observation of the E_g mode of the spinel structure plotted in Fig. 3. Furthermore, the phase transition pressure between the spinel and the NaCl-type structure in MIn_2S_4 spinels seems to follow the same rules

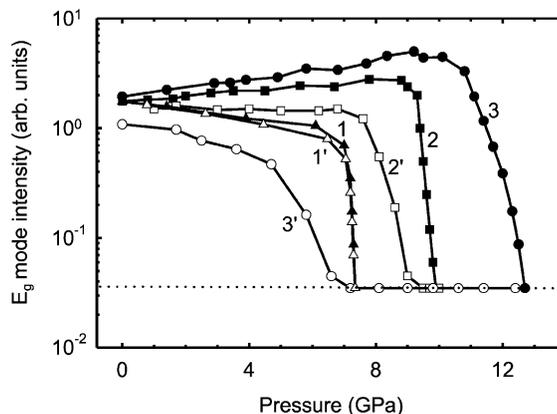


Fig. 3. Pressure dependence of the intensity of E_g mode in MnIn_2S_4 (curve 1, triangles), CdIn_2S_4 (curve 2, squares) and MgIn_2S_4 (curve 3, circles). Full symbols correspond to upstroke and open symbols to downstroke runs. The horizontal line indicates the sensitivity level of the experimental set-up.

established for materials with DC structure; i.e. the lower the ionicity of the compound the higher the pressure of the phase transition. According to Lutz et al. [19], the ionicity of inverse spinels is smaller than that of ideal spinels. This means that the ionicity of MnIn_2S_4 and CdIn_2S_4 should be nearly the same and higher than that of MgIn_2S_4 [19]. This result allows to explain why the phase transition pressure in MgIn_2S_4 is higher than that of the other two compounds. On the other hand, since the normality index of MnIn_2S_4 increases with pressure and that of CdIn_2S_4 decreases (Fig. 4(a)), one can expect the ionicity of CdIn_2S_4 to become lower than that of MnIn_2S_4 . This result allows to explain also why the phase transition pressure in CdIn_2S_4 is higher than that in MnIn_2S_4 . Furthermore, the phase transition in spinels is characterized by a hysteresis cycle that seems to depend on the ionicity of the compound (Fig. 3). In this sense, the phase transition in MnIn_2S_4 (highest ionicity) shows almost no hysteresis, while in CdIn_2S_4 and MgIn_2S_4 (lowest ionicity) the width of the hysteresis cycle is about 2 and 6 GPa, respectively.

In spite of the common features of the phase transition to the defect-NaCl phase in the indium sulfide spinels studied, the character of the transition is different for the three materials under consideration. This different character is indicated by the behavior of the normality index as a function of pressure (Fig. 4(a)). The normality index of MnIn_2S_4 increases with pressure and approaches that of an ideal spinel structure. The normality index of CdIn_2S_4 decreases slowly with pressure and tends to the value 0.33 characteristic of a completely disordered structure. Finally, the normality index of MgIn_2S_4 is constant up to 9 GPa and decreases with further increasing pressure, thus indicating a tendency to a totally inverse spinel structure. Mn, Cd and Mg indium sulfide spinel structures show different behaviors at the phase transition pressure. In

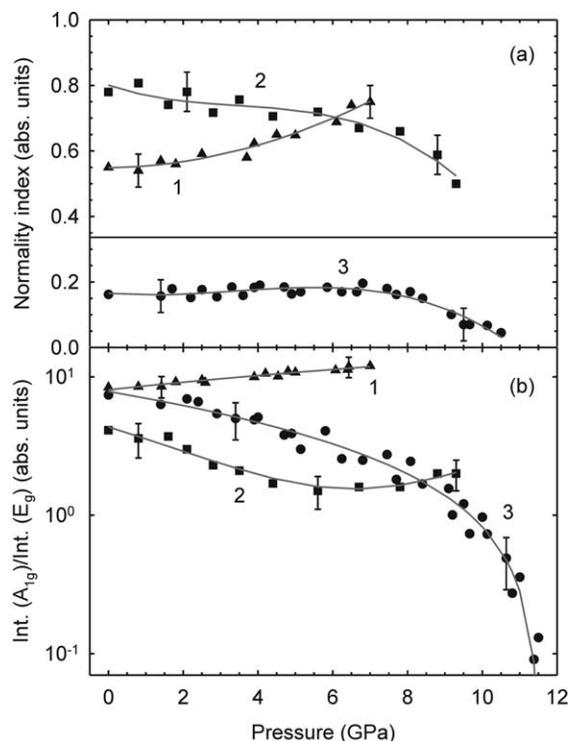


Fig. 4. Pressure dependence of the normality index (a) and of the integral intensity of the A_{1g} mode normalized to the intensity of E_g mode (b) for $MnIn_2S_4$ (curve 1, triangles), $CdIn_2S_4$ (curve 2, squares) and $MgIn_2S_4$ (curve 3, circles). The lines are guides for the eye.

$MnIn_2S_4$ and $CdIn_2S_4$ all Raman modes of the spinel structure disappear sharply at pressures 7.2 and 9.3 GPa, respectively. On the contrary, with increasing pressure above 10 GPa, the lowest energy F_{2g} mode of $MgIn_2S_4$ disappears and the A_{1g} mode intensity decreases sharply (Fig. 4(b)). From these findings one can conclude that the amount of tetrahedrally coordinated metal ions, which give rise to the A_{1g} breathing mode, diminishes with increasing pressure in $MgIn_2S_4$. This means that In atoms migrate from tetrahedral 8a sites to interstitial positions, i.e. to the normally unoccupied octahedral 16c sites. This migration leads to a phase transition to a NaCl superstructure with 1:1 ordering in the octahedral voids ($LiVO_2(cF64)$ -type) [20]. In this structure, one half of In ions occupy half of the octahedral 16c sites and the other half together with Mg ions locate at 16d sites ($LiVO_2$ defect structure). An analogous phase transition to a $LiVO_2$ -type structure has been reported in MLi_2Cl_4 inverse spinel-type compounds with increasing temperature [21].

Group theoretical considerations of the $LiVO_2$ -type NaCl superstructure ($q \approx 0$) give the total number of vibration modes at the center of the Brillouin zone. This results in Raman active modes belonging to

the irreducible representation

$$\Gamma = A_{1g} + E_g + 2F_{2g}[21],$$

i.e. one F_{2g} mode less than in spinel structure.

4. Conclusions

We have performed Raman scattering measurements in $CdM_2^{III}Se_4$ ($M^{III} = Ga, Al$) DC and MIn_2S_4 ($M = Mn, Cd, Mg$) spinels at room temperature up to 20 GPa. The pressure dependence of the frequency of the Raman modes in these compounds is reported and compared with calculated data when available. All these compounds were found to undergo a phase transition to a Raman inactive defect NaCl-type structure. The phase transition is reversible for spinels and irreversible for DC.

This phase transition in MIn_2S_4 spinels contrasts with that of spinels present in the earth's mantle, which transform under pressure into a perovskite-like phase [6, 7], and with that of $MgAl_2O_4$ and $ZnAl_2S_4$ spinels, which undergo a phase transition to an amorphous [8,11] or to a calcium ferrite-type structure [9,10]. $MnIn_2S_4$ and $CdIn_2S_4$ compounds, which show a nearly ideal spinel structure at zero pressure, transform directly into a disordered NaCl-type phase. On the other hand, $MgIn_2S_4$, which is an almost inverse spinel, do not transform directly from the spinel to the disordered NaCl-type and this transition proceeds via an intermediate $LiVO_2$ -type NaCl superstructure. This intermediate phase transforms into the disordered NaCl-type structure at higher pressures.

Acknowledgements

The authors want to express their gratitude to K. Syassen at the Max Planck Institut für Festkörperforschung for his help in providing access to experimental set-ups and to W. Dietrich, U. Oelke and U. Engelhardt for technical assistance in experiments. V.V.U. acknowledges financial support from the Deutscher Akademischer Austauschdienst and F.J.M. acknowledges financial support from the European Union through a Marie Curie Fellowship under contract HPMF-CT-1999-00074.

References

- [1] R.W.G. Wyckoff, *Crystal Structures*, 2nd ed., vol. 3, Interscience, New York, 1965.
- [2] V.V. Ursaki, I.I. Burlakov, I.M. Tiginyanu, Y.S. Raptis, E. Anastassakis, A. Anedda, *Phys. Rev. B* 59 (1999) 257.
- [3] A. Grzechnik, V.V. Ursaki, K. Syassen, I. Loa, I.M. Tiginyanu, M. Hanfland, *J. Solid State Chem.* 160 (2001) 205.
- [4] M. Fuentes-Cabrera, O.F. Sankey, *J. Phys. Condens. Matter.* 13 (2001) 1669.

- [5] M. Fuentes-Cabrera, *J. Phys. Condens. Matter.* 13 (2001) 10117.
- [6] B.J. Wood, *Nature (UK)* 341 (1989) 278.
- [7] E. Ito, E Takahashi, *J. Geophys. Res.* 94B (1989) 10637.
- [8] A. Chopelas, A.M. Hofmeister, *Phys. Chem. Min.* 18 (1991) 279.
- [9] T. Irifune, K. Fujino, E. Ohtani, *Nature (UK)* 349 (1991) 409.
- [10] V.V. Ursaki, I. Burlakov, I.M. Tiginyanu, Y.S. Raptis, E. Anastassakis, I. Aksenov, K. Sato, *Jpn. J. Appl. Phys.* 37 (1998) 135.
- [11] J. Wittlinger, S. Werner, H. Schulz, *High Pressure Sci. Technol.* 7 (1998) 49.
- [12] R. Nitsche, *J. Cryst. Growth* 9 (1971) 238.
- [13] G.J. Piermarini, S. Block, J.D. Barnett, R.A. Forman, *J. Appl. Phys.* 46 (1975) 2774.
- [14] H.C. Gupta, M.K. Singh, L.M. Tiwari, *J. Raman Spectrosc.* 31 (2000) 949.
- [15] A. Eifler, J.D. Hecht, G. Lippold, V. Riede, W. Grill, G. Krauss, V. Krammer, *Physica B* 263 (1999) 806.
- [16] A. MacKinnon, *J. Phys. C* 12 (1979) 655.
- [17] K.-J. Range, W. Becker, A. Weiss, *Z. Naturforsch.* 24b (1969) 1654.
- [18] H.D. Lutz, W. Becker, B. Muller, M. Jung, *J. Raman Spectrosc.* 20 (1989) 99.
- [19] H.D. Lutz, G. Waschenbach, G. Kliche, H. Haeuseler, *J. Solid State Chem.* 48 (1983) 196.
- [20] C. Chieh, B.L. Chamberland, A.F. Wells, *Acta Crystallogr. Sect. B* 37 (1981) 1813.
- [21] K. Wussow, H. Haeuseler, P. Kuske, W. Schmidt, H.D. Lutz, *J. Solid State Chem.* 78 (1989) 117.