High-pressure effects on the optical-absorption edge of $CdIn_2S_4$, $MgIn_2S_4$, and $MnIn_2S_4$ thiospinels

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The effect of pressure on the optical-absorption edge of $CdIn_2S_4$, $MgIn_2S_4$, and $MnIn_2S_4$ thiospinels at room temperature is investigated up to 20 GPa. The pressure dependence of their band gaps has been analyzed using Urbach's rule. We have found that, within the pressure range of stability of the low-pressure spinel phase, the band gaps of $CdIn_2S_4$ and $MgIn_2S_4$ exhibit a linear blueshift with pressure, whereas the band gap of $MnIn_2S_4$ exhibits a pronounced nonlinear shift. In addition, an abrupt decrease of the band-gap energies occurs in the three compounds at pressures of 10, 8.5, and 7.2 GPa, respectively. Beyond these pressures, the optical-absorption edge redshifts upon compression for the three studied thiospinels. All these results are discussed in terms of the electronic structure of each compound and their reported structural changes. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2887992]

INTRODUCTION

Many AB_2X_4 compounds with $A=Cd, Mg, Mn, Zn$; $B=Al, Ga, In$; and $X=O, S$ are semiconductors that crystallize in the cubic-spinel structure (space group: $Fd\bar{3}m$, No.: 227). In this structure, the A and B atoms occupy tetrahedral and octahedral sites, respectively.[1] In the last few decades, there has been an increasing interest in understanding the high-pressure behavior of ternary compounds belonging to the cubic-spinel family, in particular, since $MgAl_2O_4$ became a technologically important compound.[2] Besides the electronic applications of oxide spinels as transparent conducting oxides in solar cells and other devices, $MgAl_2O_4$ is a prototypical ceramic that plays a significant role in geophysics as a common constituent of the shallow upper mantle.[3] The elastic behavior of its polymorphs can be used to predict seismic velocities, and some of its high-pressure forms have been proposed as constituents of shock-metamorphosed meteorites.

Regarding the sulfide spinel or thiospinel subfamily of cubic spinels, they are interesting materials for optoelectronic applications given their nonlinear optical properties, e.g., nonlinear optical susceptibility and birefringence.[4] Usually, spinels present some degree of inversion, i.e., the cations can partially interchange their sites in the crystal structure, which makes them defect semiconductors with high concentration of antisite defects. The concentration of these defects can be tuned by means of pressure application, making the thiospinels as interesting materials for defect engineering applications.[5] Raman[6] and x-ray diffraction (XRD) experiments[7] as well as pseudopotential calculations[8,9] have been performed in order to study the pressure effects on the crystal structure of AIn_2S_4 compounds with $A=Cd, Mg, Mn$. However, no information currently exists on how the electronic band structure of $MnIn_2S_4$ and $MgIn_2S_4$ is affected by pressure, existing only limited information for $CdIn_2S_4$ up to 4 GPa.[10] It is the aim of this work to contribute to the understanding of the high-pressure behavior of cubic spinels and, in particular, of the effect of pressure on the electronic and optical properties. In order to address this issue, we have carried out a systematic characterization of the pressure effects on the absorption edge of three different indium thiospinels up to 20 GPa. The obtained results are analyzed on the light of previous structural studies in these compounds and its comparison with other isostructural compounds.

EXPERIMENTAL DETAILS

High-pressure optical-absorption measurements have been performed in spinel-type $CdIn_2S_4$, $MgIn_2S_4$, and $MnIn_2S_4$ at room temperature up to 20 GPa using a diamond-anvil cell (DAC). The samples used for these measurements were cleaved from single crystals grown by chemical vapor transport using iodine as a transport agent.[11] XRD patterns obtained at ambient conditions confirmed the spinel-type structure of these crystals. For the reported experiments, samples of about $20-30$ μm thickness and 100×100 μm^2 in size were loaded together with a ruby chip in a 250-μm-diameter hole drilled in 45-μm-thick Inconel gasket and inserted between the diamonds of a membrane-type DAC. A methanol-ethanol-water (16:3:1) mixture was used as a pressure transmitting medium and the pressure was determined by the ruby fluorescence technique.[12] The optical-absorption spectra were obtained from the transmittance spectra of the samples which were measured using the

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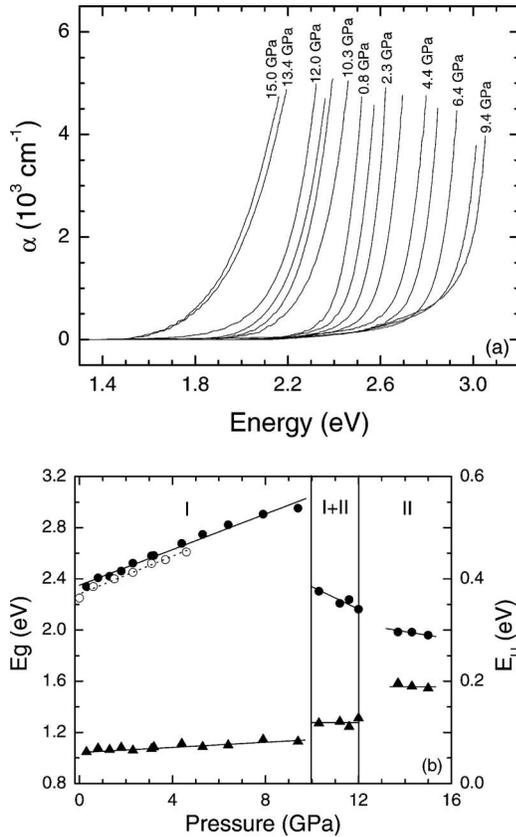
FIG. 1. (a) Room temperature optical-absorption spectra of $CdIn_2S_4$ at different pressures of up to 15 GPa. (b) Pressure dependence of band-gap energy (circles) and Urbach's energy (triangles) in $CdIn_2S_4$. Solid (empty) symbols: This work (Ref. [10]). The solid vertical lines indicate the onset and completion of the phase transition. I (II) indicates the pressure range of stability of the low—(high-)pressure phase. I+II is the region of phase coexistence.

FIG. 2. Same as Fig. 1 but for $MgIn_2S_4$ up to 19.9 GPa. The inset of (a) shows the spectra measured up to 7.3 GPa to avoid the overlap with the spectra measured at higher pressures.

sample-in sample-out method in an optical setup similar to that described in Ref. [13]. At least two independent runs were carried out for each compound in order to check the reproducibility of the obtained results.

RESULTS AND DISCUSSION

The absorption coefficients (α) of the three studied compounds, obtained at several pressures of up to 20 GPa, are shown in Figs. 1(a), 2(a), and 3(a). Given the thickness of the studied samples and the stray light level of our spectroscopic system, the highest measurable value of the absorption coefficient is of the order of 5000 cm^{-1}, which is a typical value for the low-energy tails of direct absorption edges. The absorption spectra of the three compounds at every pressure exhibit a steep absorption, characteristic of a direct band gap, plus a low-energy absorption band which overlaps partially with the fundamental absorption. This low-energy absorption band has been observed in related compounds and seems to be related to the presence of defects or impurities. [14] On the other hand, the steep absorption edge exhibits an exponential dependence on the photon energy following Urbach's law. [15] This dependence is typical of the low-energy tails of direct absorption edges with excitonic effects and has been attributed to the dissociation of excitons in the electric fields of polar phonons or impurities. For α values of below 50 cm^{-1},

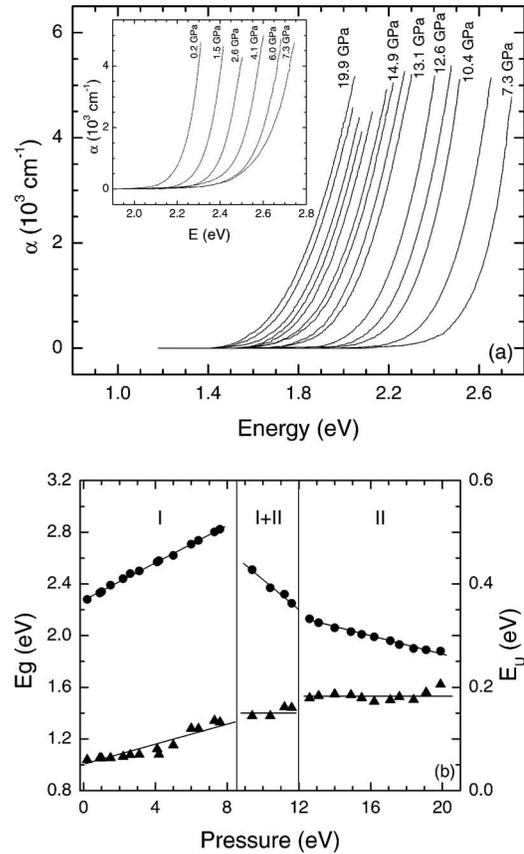the photon energy dependence of the absorption coefficient is not exponential but approximately follows a potential law. This has led some authors to propose an indirect character for the fundamental gap of $CdIn_2S_4$. [9] $MnIn_2S_4$ and $MgIn_2S_4$ are known to have direct band gaps of 1.95 and 2.28 eV, [6,8,16,17] respectively. However, according to Meloni and Mula, [9] $CdIn_2S_4$ has an indirect band gap of 2.2 eV. Our measurements undoubtedly indicate that the three studied compounds are direct band-gap semiconductors, where the determined band gaps at ambient pressure (10^{-4} GPa) are in good agreement with the literature for $MnIn_2S_4$ (1.95 eV) and $MgIn_2S_4$ (2.28 eV). In the case of $CdIn_2S_4$, we have found the band gap to be 2.35 eV. The differences observed between our work and previous results for $CdIn_2S_4$ could be explained by the fact that previously, the presence of Urbach's tail in the absorption edge was neglected. [9] Therefore, the exponential tail of the direct absorption edge could have been considered as a part of the fundamental absorption, leading to a different characterization of the band gap and an underestimation of its energy. Recently, Betancourt *et al.* have studied the optical properties of $Cd_{1-x}Mn_xIn_2S_4$ alloys for different samples with $x < 0.2$, [16] where all the studied samples are direct band-gap materials. An extrapolation of the band-gap energies (E_g) reported in Ref. [16] to $x=0$ (i.e., for $CdIn_2S_4$) yields $E_g = 2.45$ eV, which confirms our conclusions giving additional support to the hypothesis that E_g was underestimated in Ref. [9].
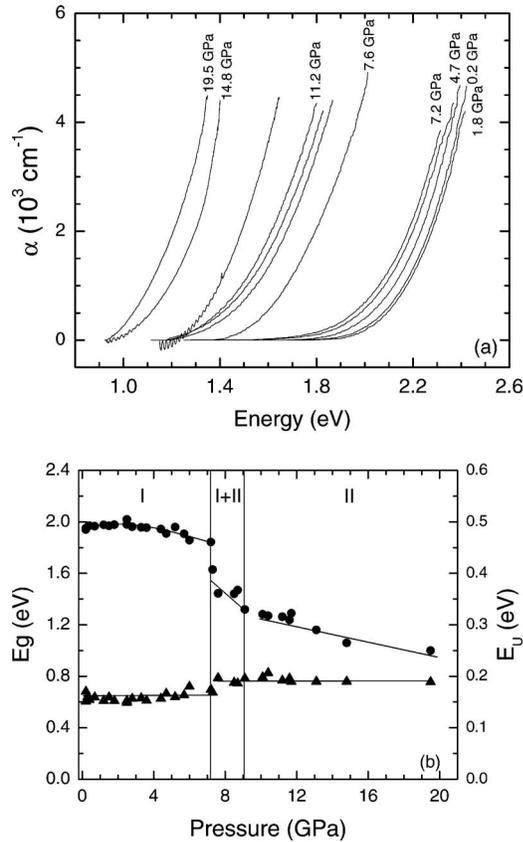
In Figs. 1(a) and 2(a), it can be seen that the absorption

FIG. 3. Same as Fig. 1 but for MnIn$_2$S$_4$ up to 19.5 GPa.

spectra of the spinel phase of CdIn$_2$S$_4$ and MgIn$_2$S$_4$ move toward higher energies under compression up to near 10 and 8.5 GPa, respectively. However, in Fig. 3(a), it can be observed that spinel MnIn$_2$S$_4$ shows an absorption edge that slightly moves toward higher energies only up to near 3 GPa and beyond this pressure, it starts to move toward lower energies up to 7.2 GPa. A sudden redshift jump of the absorption edge is observed in the three compounds at 10 GPa (CdIn$_2$S$_4$), 8.5 GPa (MgIn$_2$S$_4$), and 7.2 GPa (MnIn$_2$S$_4$). This jump in the absorption edge occurs together with a color change of the samples, suggesting the occurrence of a pressure-induced band-gap collapse which could be indicative of a pressure-induced phase transition.

The measured absorption spectra of the three spinels have been analyzed assuming that the band gap is of direct type and that the absorption edge obeys Urbach's rule $\alpha = A_0 e^{-(E_g - h\nu)/E_U}$.[15] In this equation, E_U is Urbach's energy, which is related to the steepness of the absorption tail, and $A_0 = k\sqrt{E_U}$ for a direct band gap,[15] where k is a characteristic parameter of each material. In order to simplify the interpretation of our experimental results, we assumed k to be pressure independent and determined it at the lowest pressure of our experiments. Applying this analysis to our experimental results, we have obtained the pressure dependence for E_g and E_U. Figures 1(b), 2(b), and 3(b) show the obtained results. In CdIn$_2$S$_4$ and MgIn$_2$S$_4$, E_g increases linearly upon compression up to 10 and 8.5 GPa, respectively, with a pressure coefficient close to $dE_g/dP = 70$ meV/GPa in good agreement with previous measurements up to 4 GPa in CdIn$_2$S$_4$ [see empty symbols in Fig. 1(b)].[10] In contrast, in MnIn$_2$S$_4$, E_g

presents a nonlinear evolution with pressure of up to 7.2 GPa, showing a maximum at around 3 GPa and a pressure coefficient of 20 meV/GPa at ambient pressure. From the analysis of the measured optical absorption spectra, an accused band-gap collapses of around 0.65 eV in CdIn$_2$S$_4$ at 10 GPa, of around 0.3 eV in MgIn$_2$S$_4$ at 8.5 GPa, and of around 0.3 eV in MnIn$_2$S$_4$ at 7.2 GPa have been found. Additionally, abrupt changes in the pressure dependence of E_g are observed at 12, 12, and 9 GPa for CdIn$_2$S$_4$, MgIn$_2$S$_4$, and MnIn$_2$S$_4$, respectively. The above described changes in the band-gap energies and their pressure coefficients for the three compounds suggest either the presence of two phase transitions or that the phase transition taking place in the three compounds is rather slow and there is a coexistence of two phases between 10 and 12 GPa, between 8 and 12 GPa, and between 7.2 and 9 GPa in CdIn$_2$S$_4$, MgIn$_2$S$_4$, and MnIn$_2$S$_4$, respectively.

The occurrence of the described changes correlates quite well with previous high-pressure structural studies.[6,7,18] Raman spectroscopy measurements under pressure performed in the three spinels found the onset of a phase transition from the spinel structure to a non-Raman-active phase at 9.3, 10, and 7.2 GPa in CdIn$_2$S$_4$, MgIn$_2$S$_4$, and MnIn$_2$S$_4$, respectively.[6] This transition seems to have a martensitic character[19] and is not completed up to 12 GPa in the case of MgIn$_2$S$_4$. Recently, XRD measurements under pressure have detected the same phase transition and assigned the high-pressure phase to a double NaCl-type structure of the LiTiO$_2$-type.[7,18] XRD measurements located the onset and completion of the phase transition at slightly different pressures from Raman experiments, where the pressure values for the starting and finishing points of the transition are 7.7 and 12 GPa for CdIn$_2$S$_4$, 8 and 17 GPa for MgIn$_2$S$_4$, and 6 and 9 GPa for MnIn$_2$S$_4$.[7,18] XRD measurements show that within these pressure ranges, the low- and high-pressure phases coexist. Consequently, the important structural changes taking place during the phase transition could cause the collapse of E_g and the changes in the pressure coefficient of E_g observed in the three spinels, in agreement with what has been previously found in other ternary semiconductors.[20]

We would like to comment now on the similarities and differences observed in the values of the E_g and the pressure coefficient in the three studied compounds within the pressure range of stability of the spinel phase on the light of previous studies. In the three ternary indium thiospinels, the band-gap energy is very similar to that of the spinel β-In$_2$S$_3$ (around 2.1 eV),[21] which is a defective spinel structure crystallizing above 330 °C with In atoms occupying both tetrahedral and octahedral sites.[22] In fact, β-In$_2$S$_3$ samples show a dark red color similar to that of our ternary thiospinels. X-ray photoelectron spectroscopy measurements evidenced that the topmost valence band in CdIn$_2$S$_4$ was similar to that of β-In$_2$S$_3$ and mainly contributed by S $3p$ states.[23] The electronic states contributing to the valence band in thiospinels have not been confirmed by theoretical calculations but are supported by band-structure calculations in spinel CdIn$_2$O$_4$ and CdGa$_2$O$_4$ that confirm that the topmost valence band in CdIn$_2$O$_4$ is due to O $2p$ states.[24] Calculations yield a direct band gap for CdIn$_2$O$_4$ (CdGa$_2$O$_4$) of around 1.18 eV

(1.98 eV). However, the experimentally determined direct gaps in $CdIn_2O_4$ and $MgIn_2O_4$ are similar (around 3 eV),[25,26] similar to the direct gaps in our three thiospinels, thus, indicating that the energy of the direct gap in AB_2X_4 spinels is mainly due to the $B-X$ hybridization rather than to the $A-X$ hybridization. This result is reasonable since in the normal spinel, each anion X is bonded to three B cations (at octahedral sites) and with only one A cation (at tetrahedral sites); therefore, the band structure is mainly formed by the hybridization of the B cation and the X anion.

Band-structure calculations in spinel $CdIn_2O_4$ and $CdGa_2O_4$ also show that the lowest conduction band in $CdIn_2O_4$ consists mostly of hybridized In $5s$ states and Cd $5s$ states, while in $CdGa_2O_4$, it consists mostly of hybridized Ga $4s$ states and Cd $5s$ states.[24] This result agrees with those previously obtained by Kawazoe and Ueda, who discussed that the exact value of the direct gap in spinels depends very much on the cation A–cation B interaction because much of the dispersion of the conduction band comes from this interaction.[27] These authors evidenced that metal cations with no d or f states or with filled d and f states would form an extended conduction band. This is the case in spinel-type In_2S_3, $CdIn_2S_4$, and $MgIn_2S_4$, so we expect a similar electronic structure with similar band gaps (around 2.2 eV) and pressure coefficients (around 70 meV/GPa) in the three compounds since the formation of the band gap is mainly due to the In–S hybridization, as commented before. Consequently, the linear increase of the band gap is coherent with this interpretation as it reflects the energy shift up of the conduction band (antibonding In $5s$ character) due to the increase of the bonding-antibonding splitting as the In distances decrease under pressure. It seems relevant to notice that our result concerning the band-gap pressure coefficient of thiospinels is consistent with the fact that the calculated pressure coefficients of the band gap of spinel oxides are also very close to each other (around 30 meV/GPa).[24] The lower absolute value of the pressure coefficient in spinel oxides is most probably related to the lower compressibility of oxides with respect to sulfides.

The importance of the cation A–cation B interaction for the conduction band in AB_2X_4 spinels and the nature of the states involved in the lowest conduction band has been confirmed by recent x-ray absorption spectroscopy (XAS) measurements in β-In_2S_3 and by band-structure calculations in $CdIn_2O_4$ and $CdGa_2O_4$. XAS measurements have shown that the lowest conduction band in this compound is mainly due to the hybridized In $5s$ orbitals that in β-In_2S_3 are contributed from In atoms at both tetrahedral and octahedral sites of the defect-spinel structure.[28] On the other hand, electronic density of states calculations in the oxide spinels have confirmed that the lowest conduction band is mainly due to Cd $5s$ and In $5s$ and to Cd $5s$ and Ga $4s$ in $CdIn_2O_4$ and $CdGa_2O_4$, respectively.[24]

Kawazoe and Ueda also concluded that metal cations having open shell d or f electronic configurations would cause a different conduction band with intrashell transitions in the visible. Therefore, we expect, in such cases, smaller band gaps and smaller pressure coefficients, as we have observed in $MnIn_2S_4$ ($E_g=1.95$ eV, $dE_g/dP=20$ meV/GPa).

This result is reasonable since magnetic-effect interactions could be important in $MnIn_2S_4$,[29] and the Mn^{3+} ions are Jahn-Teller active.[30] Under compression, the spin state of Mn^{3+} can be modified and the cooperative interactions of Mn^{3+} ions could influence the band structure of $MnIn_2S_4$, which could originate the strongly nonlinear behavior observed for E_g in $MnIn_2S_4$. This hypothesis is supported by low-temperature studies, which have shown that in $MnIn_2S_4$, E_g, is much less temperature dependent than in the rest of the thiospinels.[16] However, high-pressure band-structure calculations are needed for $MnIn_2S_4$ in order to better understand the nonlinear behavior of its band gap.

Regarding the behavior of E_g in the high-pressure phases, it is important to note that beyond the onset of the phase transition from the spinel phase, the band-gap energy has large negative pressure coefficients in the three compounds ($dE_g/dP=-80-110$ meV/GPa) up to the completion of the phase transition. However, once the phase transition is finished in all three compounds, the band gap continues to exhibit a negative linear dependence on pressure but with a smaller pressure coefficient ($dE_g/dP=-20-30$ meV/GPa). On decreasing pressure, the spinel phase is recovered in $MgIn_2S_4$ and $MnIn_2S_4$ with almost not detectable hysteresis. This fact is in agreement with the observations made in Raman experiments.[6] However, previous experiments suggested a similar behavior in the Cd thiospinel, a fact that we have not observed in our samples. This irreversibility observed in the optical measurements in $CdIn_2S_4$ can be explained by the creation of defects in the samples under pressure, likely related to the larger ionic radius of Cd with respect to In.

Let us comment now on the pressure effects on Urbach's energy. As we mentioned above, this parameter is related to the shape of the absorption edge, so it indirectly gives information on the disorder and the appearance of defects in the spinels. In $CdIn_2S_4$ and $MgIn_2S_4$ at ambient pressure, E_U is close to 50 meV, but in $MnIn_2S_4$, it is close to 160 meV, suggesting a higher presence of defects in $MnIn_2S_4$. In $CdIn_2S_4$ and $MgIn_2S_4$, as we increase the pressure, we observed that E_U increases linearly in both compounds up to the onset of the phase transition. Beyond this point, E_U remains practically constant with pressure up to the completion of the phase transition where an additional increase is observed, reaching E_U a value close to 200 meV. This observation agrees with the fact that while samples remain in spinel-type phase, the defect concentration increases with pressure, reaching constant values once the samples have transited to a more ordered doubled NaCl-type phase. Against this hypothesis, it can be argued that the change of the shape in the absorption edge, which causes the increase of E_U, could be the consequence of a pressure-induced direct to indirect band-gap crossover.[31] However, in such a case, the changes of the width of the exponential absorption should be fully reversible, as this is not the present case even for samples where pressure was decreased before reaching the onset of the phase transition. Regarding $MnIn_2S_4$, it can be concluded that E_U remains constant upon compression and close to 160 meV for the low-pressure phase. On the other hand, at the phase transition, E_U apparently increase in

$MnIn_2S_4$ as in the other two spinels, remaining nearly constant and close to 200 meV in the high-pressure phase. The high E_U value determined for $MnIn_2S_4$ in the low-pressure phase indicates that this compound is a highly disordered spinel even at ambient pressure. We think that the origin of the disorder in $MnIn_2S_4$ is related to the fact that Mn and In have nearly the same ionic radii for the same coordination, which leads to a high degree of inversion (i.e., a large number of Mn and In interchange their positions) in $MnIn_2S_4$,[32] where inversion is much less important in $CdIn_2S_4$ and $MgIn_2S_4$.[33]

CONCLUSIONS

In summary, absorption spectra of $CdIn_2S_4$, $MgIn_2S_4$, and $MnIn_2S_4$ were measured as a function of pressure up to 20 GPa. The analysis of the pressure dependence of these spectra permitted us to obtain the evolution of the band gaps up to 20 GPa. We have found that within the range of stability of the spinel structure, $CdIn_2S_4$ and $MgIn_2S_4$ behave in a similar way with a linear increase of E_g with pressure, which is in agreement with their expected similar electronic band structures. On the contrary, a nonlinear dependence for E_g has been observed in $MnIn_2S_4$. This different behavior could be related to the magnetic character of the Mn cation and its partially filled d shells. *Ab initio* band-structure calculations on the three thiospinels, in particular, for $MnIn_2S_4$, are needed to confirm the nature of the electronic band structure suggested in this work and to better understand the nonlinear behavior of the band gap of $MnIn_2S_4$.

Additionally, abrupt changes were observed in the band gaps of $CdIn_2S_4$, $MgIn_2S_4$, and $MnIn_2S_4$ at 10, 8.5, and 7.2 GPa, respectively. These changes have been interpreted as a consequence of structural changes suffered by the compounds, being correlated with phase transitions previously identified by means of XRD and Raman spectroscopy measurements.

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