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

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Abstract: 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 the Urbach's rule. We have found that, within the pressure-range of stability of the low-pressure spinel phase, the band-gap of $CdIn_2S_4$ and $MgIn_2S_4$ exhibits a linear blue-shift with pressure, whereas the band-gap of $MnIn_2S_4$ exhibits a pronounced non-linear shift. In addition, an abrupt decrease of the band-gap energies occurs in the three compounds at pressures of 10 GPa, 8.5 GPa, and 7.2 GPa, respectively. Beyond these pressures, the optical-absorption edge red-shifts 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.

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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 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 (TCO) 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 interesting materials for defect engineering applications [5]. Raman [6] and x-ray diffraction (XRD) experiments [7] as well as pseudo-potential 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