

# Crystal Chemistry of $\text{CdIn}_2\text{S}_4$ , $\text{MgIn}_2\text{S}_4$ , and $\text{MnIn}_2\text{S}_4$ Thiospinels under High Pressure

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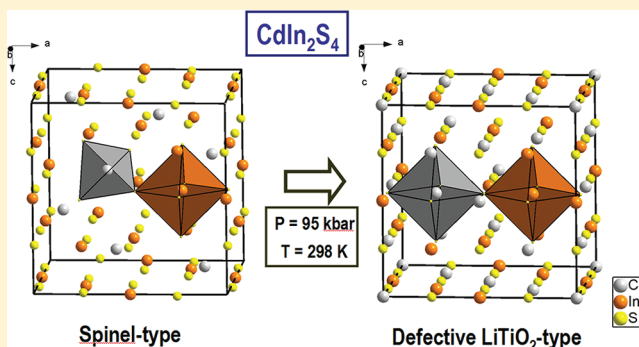
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**ABSTRACT:** We report X-ray diffraction measurements in  $\text{CdIn}_2\text{S}_4$ ,  $\text{MgIn}_2\text{S}_4$ , and  $\text{MnIn}_2\text{S}_4$  thiospinels at room temperature and high pressures. The pressure dependences of the structural parameters have been determined and compared to those from theoretical calculations. It is found that the three thiospinels have similar bulk moduli ( $B_0$ ) between 75 and 80 GPa ( $B_0' \sim 3$ ). The degree of inversion of these thiospinels has also been determined. The three thiospinels undergo a phase transition toward a defect  $\text{LiTiO}_2$ -type structure above 9.5, 8.3, and 6.8 GPa in  $\text{CdIn}_2\text{S}_4$ ,  $\text{MgIn}_2\text{S}_4$ , and  $\text{MnIn}_2\text{S}_4$ , respectively. Interestingly, the low- and high-pressure phases belong to the same symmetry group ( $Fd-3m$ ), the transition mechanism being associated to the migration of the tetrahedrally coordinated cations to a Wyckoff position of higher multiplicity, where these cations present an octahedral environment. The new postspinel phase exhibits a larger compressibility than the spinel phase for the three compounds, likely due to the presence of stoichiometric vacancies in the unit cell as it occurs for defect chalcopyrites and stannites. The relation between the bulk and the polyhedral compressibilities is discussed as well.



## 1. INTRODUCTION

Indium thiospinels of Cd, Mg, and Mn are semiconductors that crystallize in the cubic spinel structure (space group  $Fd-3m$ , No. 227). The spinel structure is described by three symmetry-independent sites: a tetrahedral site (T) and an octahedral site (O) occupied by cations and a S atom bearing site ( $u,u,u$ ).<sup>1</sup> Therefore, the cubic spinel structure has only two structural variables: the unit-cell parameter  $a$  and the anion internal positional parameter  $u$ . Curiously, the anion sublattice forms a quasi-ideal close-packed fcc structure since the internal parameter  $u$  is slightly larger than 0.25. In  $(A)[\text{In}_2]\text{S}_4$  spinels, the A ( $A = \text{Cd, Mg, Mn}$ ) and In cations are distributed over the T and O sites, respectively (normal spinel), but they can partially interchange their sites (inversion) creating a partial cation disorder. Thus, in the formula unit  $(A_{1-x}\text{In}_x)[\text{A}_x\text{In}_{2-x}]\text{S}_4$ , the ratio of A cations in O sites (Wyckoff position 16d, orange atoms in Figure 1a) may vary between  $x = 0$  for the normal

spinel and  $x = 1$  for the inverse spinel. Consequently, the  $x$  parameter denotes the degree of inversion of the spinel.<sup>2</sup>

In the last decades, there has been an increasing interest in understanding the high-pressure (HP) behavior of compounds belonging to the spinel family, especially since  $\text{MgAl}_2\text{O}_4$  became a technologically important compound.<sup>3</sup> Besides its electronic applications and prototypical character for ceramics,  $\text{MgAl}_2\text{O}_4$  plays a significant role in geophysics as a common constituent of the shallow upper mantle.<sup>4</sup> The thiospinel subfamily forms an interesting group of materials for optoelectronic applications given their nonlinear optical properties.<sup>5</sup> Their partial degree of cation inversion makes them defect semiconductors with a high concentration of antisite defects. The concentration of these defects can be

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