

Raman scattering study of pressure-induced phase transitions in $M\text{In}_2\text{S}_4$ spinels

V V Ursaki¹, F J Manjón^{2,4}, I M Tiginyanu^{1,3} and V E Tezlevan¹

¹ Institute of Applied Physics, Academy of Sciences of Moldova, 2028 Chisinau, Moldova

² Departament de Física Aplicada, Universitat Politècnica de València, EPSA, 03801 Alcoi, Spain

³ Laboratory of Low-Dimensional Semiconductor Structures, Technical University of Moldova, 2004 Chisinau, Moldova

E-mail: fmanjon@fis.upv.es

Received 8 April 2002, in final form 5 June 2002

Published 28 June 2002

Online at stacks.iop.org/JPhysCM/14/6801

Abstract

$M\text{In}_2\text{S}_4$ ($M = \text{Mn}, \text{Cd}, \text{Mg}$) spinels were investigated by Raman scattering spectroscopy under hydrostatic pressure up to 20 GPa. These compounds were found to undergo a reversible phase transition to a Raman-inactive defect NaCl-type structure. Transition pressures of 7.2, 9.3, and 12 GPa were found for $M = \text{Mn}, \text{Cd},$ and Mg , respectively. From the analysis of the pressure behaviour 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 pressure and path of the pressure-induced phase transition between these indium sulphide spinels are discussed.

1. Introduction

$A^{\text{II}}B_2^{\text{III}}C_4^{\text{VI}}$ compounds exhibit a variety of physical properties and some of them have proved to be promising for optoelectronics applications [1, 2]. Since these compounds can be grown in different crystalline structures, they are uniquely suited for use in investigating the role of structure and composition in the response of matter to external excitations such as heat, pressure, and electromagnetic fields. In view of this, systematic studies of the influence of hydrostatic pressure on the structure of tetrahedrally coordinated $A^{\text{II}}B_2^{\text{III}}C_4^{\text{VI}}$ [3–5] and $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ [6–9] compounds have been carried out during recent years. These studies have led to the observation of some important trends of pressure-induced phase transitions in zincblende-derived materials.

Most of the $A^{\text{II}}B_2^{\text{III}}C_4^{\text{VI}}$ compounds crystallize in the spinel structure. $A^{\text{II}}B_2^{\text{III}}C_4^{\text{VI}}$ spinels belong to the $O_h^7 (Fd\bar{3}m)$ space group with eight formula units per unit cell [10]. In this structure, the anions form a nearly ideal fcc framework surrounded by tetrahedral and

⁴ Author to whom any correspondence should be addressed.

octahedral sites. Cations occupy only 1/8 of the tetrahedrally coordinated sites and 1/2 of the octahedrally coordinated sites. 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 [10]. 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 A_{*X*}B_{1-*X*}(A_{1-*X*}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.

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 [11, 12]. Nevertheless, a limited number of high-pressure studies have been performed on A^{II}B^{III}₂C₄^{VI} spinels up to now [13–16]. In this work, we investigate the common features in the behaviour of MIn₂S₄ spinels with different M cations and normality indices under hydrostatic pressure.

2. Experimental details

Spinel-type MnIn₂S₄, CdIn₂S₄, and MgIn₂S₄ single crystals were grown by chemical vapour transport using iodine as a transport agent [17]. For the optical measurements under pressure, the samples (100 μm × 100 μm in size and 30 μm thick) were inserted together with a ruby chip in a hole (250 μm in diameter) drilled in an Inconel gasket inside a Syassen–Holzapfel diamond anvil cell (DAC) with diamond culets 0.5 mm in diameter. Pressure was determined by calibration with the ruby luminescence [18], and a 4:1 methanol–ethanol mixture was used as pressure-transmitting medium ensuring hydrostatic conditions up to 10 GPa and quasi-hydrostatic conditions between 10 and 20 GPa [19]. Raman experiments at room temperature were performed in backscattering geometry using a Jobin-Yvon T64000 triple spectrometer in combination with a multi-channel CCD detector. The 647.1 nm line of a Kr⁺-ion laser was used for excitation and the spectral resolution was of the order of 1 cm⁻¹. In order to avoid sample heating due to the focusing of the laser spot to a diameter of ~50 μm, the excitation light power was kept below 5 mW at the entrance of the DAC.

3. Results and discussion

3.1. General considerations

The whole cubic cell of the spinel structure contains 56 atoms and is largely redundant as regards determining the number of vibrations of the lattice from group theoretical considerations since only two octants of the cell, which lie along the main body diagonal, are really different. Taking the reduced cell, which contains only 14 atoms and is equivalent to the smallest Bravais cell, the total number of vibration modes at the centre of the Brillouin zone, described by the irreducible representation of the O_h point group [20], is

$$\Gamma = A_{1g} + E_g + 3F_{2g} + 5F_{1u} + 2A_{2u} + 2E_u + F_{1g} + 2F_{2u}.$$

Five of these modes (A_{1g} + E_g + 3F_{2g}) are Raman active, four F_{1u} modes are infrared active, and the remaining F_{1u} mode is an acoustic phonon. All other modes are silent. Figures 1(a), 2(a), and 3(a) show the Raman scattering (RS) spectra at different pressures of MnIn₂S₄, CdIn₂S₄, and MgIn₂S₄, respectively. The assignment of modes observed in the RS spectra, based on previous polarized measurements [21–23], is shown in table 1.