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]

[a]*Institute of Applied Physics, Academy of Sciences of Moldova, 2028 Chisinau, Moldova*
[b]*Laboratory of Low-Dimensional Semiconductor Structures, Technical University of Moldova, 2004 Chisinau, Moldova*
[c]*Departament 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.

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/cm^2 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).

0022-3697/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0022-3697(03)00098-2