Jpn. J. Appl. Phys. Vol. 37 (1998) pp. 135–140
Part 1, No. 1, January 1998

Pressure Induced Phase Transitions in Spinel and Wurtzite Phases of $ZnAl_2S_4$ Compound

Veacheslav V. URSAKI[1], Igor I. BURLAKOV[1], Ivan M. TIGINYANU[1], Yannis S. RAPTIS[2], Evangelos ANASTASSAKIS[2], Igor AKSENOV[3] and Katsuaki SATO[4,*]

[1] *Institute of Applied Physics, Academy of Sciences of Moldova, Kishinev 2028, Moldova*
[2] *Physics Department, National Technical University, 15780 Athens, Greece*
[3] *Joint Research Center for Atom Technology, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan*
[4] *Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan*

(Received July 14, 1997; accepted for publication October 20, 1997)

$ZnAl_2S_4$ single crystals with spinel (α-phase) and wurtzite (w-phase) structures have been studied by Raman spectroscopy under hydrostatic pressures of up to 300 kbar. Significant changes in the phonon spectrum of the α-phase have been observed at the critical pressure of 230 kbar, which are attributed to a reversible phase transition to a denser high-pressure phase, having a similar structure to that of calcium ferrite. In the pressure interval of 180 to 230 kbar, the two phases coexist. The irreversible disappearance of the Raman signal of w-$ZnAl_2S_4$ doped by Cd at pressures above 90 kbar was attributed to a phase transition to a rocksalt-type structure. This critical pressure is 40 kbar lower than that in undoped w-$ZnAl_2S_4$ and is explained on the basis of crystal structure quality. Different structures were realized upon removing the pressure, depending on the highest pressure previously reached, such as a mixture of wurtzite and spinel phases, a spinel quasi-crystalline structure, or a pressure-induced amorphous phase. The behavior of the quasi-crystalline spinel structure upon repeating the pressure cycle was found to be different from that of the α-phase single crystal.

KEYWORDS: $ZnAl_2S_4$, spinel, wurtzite, high-pressure, Raman spectroscopy, phase transitions, pressure-induced amorphization

1. Introduction

Structural studies of semiconductors have become a fundamental problem of high-pressure science since the discovery of pressure-induced phase transitions. A systematic structural study of the standard II–VI, III–V and group IV semiconductors has been undertaken over the past few years.[1–3] While considerable efforts were put on the study of pressure-induced phase transitions in I–III–VI_2 chalcopyrites,[4–6] only a single high-pressure study has been reported on II–III_2–VI_4 ordered vacancy compounds.[7] Since these materials crystallize in different structures, depending on the growth conditions,[8–10] their behavior under hydrostatic pressure appears to be an interesting problem. One of the most important materials in this regard is $ZnAl_2S_4$ which can be obtained as different structural modifications, depending on growth temperature.[11,12] Three phases exist in the region of low-growth temperatures (700–900°C), namely, the spinel structure (α-phase), the wurtzite-type structure with a statistical distribution of the cations, called w-phase, and the layered structure with a hexagonal lattice, called the L- or γ'-phase. At high-growth temperatures (1050–1100°C) an orthorhombic β-phase and a rhombohedral γ-phase can be obtained. Furthermore, quaternary solid solutions $ZnAl_{2(1-x)}Ga_{2x}S_4$ (obtained by adding gallium atoms to the Zn–Al–S system) crystallize in a defect chalcopyrite (DC) structure.[13] In this work, we present the results of a structural study of α- and w-type phases of $ZnAl_2S_4$ under hydrostatic pressure of up to 300 kbar.

2. Experimental

The α- and w-phase $ZnAl_2S_4$ crystals were grown by the chemical transport technique, with iodine used as the transport agent. The initial elements Zn, Al and S (total mass 2–2.5 g) were loaded in quartz ampoules (15 mm in diameter, 15 cm in length). For the α-phase, the temperatures at the charge and growth zones were 850 and 750°C, respectively. The spinel structure of the single crystals was confirmed through X-ray analysis, with a lattice parameter of 10.01 Å; w-phase crystals were obtained when the growth temperature was 50°C lower than that for the α-phase. Two types of w-$ZnAl_2S_4$ crystals were grown, one with full stoichiometry and a second one with about 10 % of the Zn atoms substituted by Cd atoms. According to the X-ray analysis, both types of w-$ZnAl_2S_4$ crystals possess a random distribution of cations and stoichiometric vacancies among the possible tetrahedral sites of the lattice, with unit cell parameters of $a = 3.76$ Å and $c = 6.15$ Å.[14]

Unpolarized Raman spectra were taken in a diamond anvil cell at ambient temperature. The pressure was calibrated to within 0.1 kbar using the ruby luminescence lines. The Raman spectra were measured with a double spectrometer in nearly back-scattering geometry. The 514.5 nm line of an argon laser was used at power levels of approximately 30 mW. The laser spot on the sample was 50 μm and the resolution was better than 1 cm^{-1}.

3. Results and Discussion

3.1 α-phase of $ZnAl_2S_4$

The α-$ZnAl_2S_4$ exhibits a normal spinel structure (space group Fd3m) with two formula units per unit cell. The ideal spinel structure consists of a cubic closed array of anions in which one-third of the cations (Zn) are on tetrahedrally coordinated sites and two-thirds of the anions (Al) are on octahedrally coordinated sites. The presence of vacancies in the crystal structure results in distortions in the anion sublattice. This effect is usually quantified by the so-called internal distortion parameter u, the value of which is 3/8 for the ideal fcc structure. In the case of α-$ZnAl_2S_4$ it is equal to 0.385.

Forty-two normal vibrations are expected in a normal spinel structure at $k = 0$.[15] These vibrations are described by the following reduction into the irreducible representations of the point group,

*To whom reprint requests should be addressed.
E-mail: satokats@cc.tuat.ac.jp