ELSEVIER

Journal of Crystal Growth 237–239 (2002) 2014–2018

JOURNAL OF CRYSTAL GROWTH

www.elsevier.com/locate/jcrysgro

Lattice dynamics of the chalcopyrite and defect stannite phases in the Cu–(In, Ga)–Se system

Shigetaka Nomura*, Saburo Endo

Department of Electrical Engineering, Faculty of Engineering, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Abstract

Raman spectra observed for bulk crystals of defect stannite phases in the Cu–(In, Ga)–Se system are analyzed mainly by the dispersion curve calculations with a superposed lattice model, assuming four fundamental structures. The calculations are performed on the basis of the Keating model, solving dynamical matrix of 24×24. Vacancy induced modifications on force interactions between nearest atoms are also discussed with effective bond overlap population and effective charges determined by the DV-Xα calculations for unit cell clusters. Apparently, invariable Raman profiles with respect to the In to Ga molar ratios through the alloy systems are explained by the superposed lattice model.

PACS: 63.20.Dj; 78.30.−j

Keywords: A1. Computer simulation; A1. Crystal structure; A1. Defects; A1. Dispersion curve calculation; A1. DV-Xα calculation; A1. Raman spectra; B1. Alloys; B2. Semiconducting ternary compounds

1. Introduction

The defect stannite phases in the Cu–(In, Ga)–Se system have been known to have a non-stoichiometric structure that cannot be represented by a simple unit cell. Only the averaged structure was known to belong to a space group $I\bar{4}2m$ from the convergent electron beam diffraction study [1], categorized to the 'defect stannite'.

The authors have investigated these materials on the structural properties in view of the lattice dynamics [2,3]. In this work, Raman spectra observed on these materials are analyzed by the dispersion curve calculations assuming superposed lattice model where the defect stannite structure consists of four kinds of fundamental structures in atomic occupation. The bond properties are also discussed with the effective charges and effective bond overlap populations estimated by the molecular orbital calculations using the DV-Xα method for a unit cell cluster.

2. Experimental procedure

Bulk crystals in the alloy systems of the $Cu(In_{1-x}Ga_x)_3Se_5$ were prepared by the normal

*Corresponding author. Tel.: +81-3-3260-4272x3397; fax: +81-3-5261-4805.

E-mail address: stnomura@da2.so-net.ne.jp (S. Nomura).

0022-0248/02/$ - see front matter
PII: S0022-0248(01)02246-1

freezing method. Single phase formations of these crystals were confirmed by the X-ray diffraction analysis, and the compositions were analyzed by the energy dispersive X-ray microanalysis (EDX). Raman spectra measurements were performed for these crystals in air at room temperature with the Ar^+ ion laser as an excitation light source.

3. Calculations

Dispersion curve calculations of the chalcopyrite and the defect stannite phases in the Cu–(In, Ga)–Se system were made by solving the respective dynamical matrices of 24×24 ranks which consist of force constants, atomic masses, tetragonal distortion parameter *c/a* and anion displacement parameters.

Phonon branches were calculated between the main symmetrical points and assigned in reference to the group theory. From the factor group analysis, the 24 eigen modes are expressed as $1\Gamma_1 + 2\Gamma_2 + 3\Gamma_3 + 4\Gamma_4 + 7\Gamma_5$ for the chalcopyrite type and $2\Gamma_1 + \Gamma_2 + 2\Gamma_3 + 5\Gamma_4 + 7\Gamma_5$ for the stannite one, where only the Γ_2 mode is silent, or both Raman and infrared inactive, and only the Γ_5 is doubly degenerated.

Effective charges and effective bond overlap populations for the constituent elements were estimated by the molecular orbital calculations with the DV-Xα method using SCAT [4] on a unit cell cluster for each crystal structure concerned here. Defect induced modifications on the bond properties are discussed.

4. Results and discussion

Fig. 1 illustrates unit cells of the tetragonal chalcopyrite ($I\bar{4}2d$) and the possible four types of (defect) stannite structures ($I\bar{4}2m$) in the Cu–(In, Ga)–Se system. For the stannite structure, unoccupied site is limited to the 2b (or 2a, both of them are equivalent) site, as structural types (a) or (b) in Fig. 1. For example, the combination of 60%, 20% and 20% of the structural types of (a), (b) and (d), respectively, satisfies the composition of $Cu(In, Ga)_3Se_5$.

Fig. 2 shows a lineup of X-ray diffraction profiles for bulk crystals of the $Cu(In_{1-x}Ga_x)_3Se_5$ system. All these profiles satisfy the tetragonal symmetry, showing characteristic peaks of the defect stannite structure such as (1 1 0), (2 0 2) and (1 1 4). Lattice constants are very close to the corresponding chalcopyrite structure: $a = 0.5757$, $c = 1.1534$ nm for $CuIn_3Se_5$ with $a = 0.5782$, $c = 1.1620$ nm for $CuInSe_2$, and $a = 0.5503$, $c = 1.0974$ nm for $CuGa_3Se_5$ with $a = 0.5596$, $c = 1.1003$ nm for $CuGaSe_2$.

The composition rates of $CuIn_3Se_5$ and $CuGa_3Se_5$ were Cu:In:Se = 15.4:29.7:55.3 and Cu:Ga:Se = 13.5:33.4:53.1, respectively. There was a

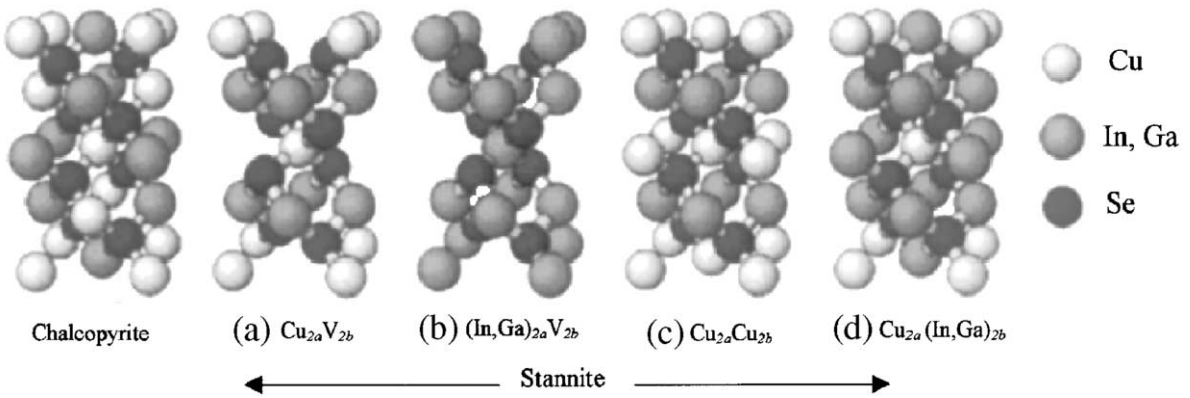

Fig. 1. Unit cells of the tetragonal chalcopyrite ($I\bar{4}2d$) and the possible four types (different in atomic occupation at 2a and 2b sites) of stannite structures ($I\bar{4}2m$) in the Cu–(In, Ga)–Se system, where V denotes vacancies.