Preparation and structural analysis of ordered vacancy compounds in the Cu-In-Se system

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The possibility of forming the OVC structure has been investigated for a variety of compositions not only on the Cu_2Se-In_2Se_3 binary tie line but also in the vicinity of the tie line. The authors attempted to obtain OVC crystals both by quenching and by normal freezing method. Each sample crystal phase and the homogeneity are checked using the x-ray diffraction measurement and the electron probe microanalysis. These experimental results reveal that the OVC phase allows a variety of compositions around the starting one such as $CuIn_2Se_{3.5}$. This can be explained by assuming $Cu+In+\square$ site for the ordered vacancy formation.

1. INTRODUCTION

It has been found that the ordered vacancy chalcopyrite (OVC) compound, $CuIn_3Se_5$, forms a surface layer of indium-rich $CuInSe_2$ thin films [1]. This suggests that the OVC phase would play an important role in the homo and/or hetero-junction devices including $CuInSe_2$ layer. However, little has been known about the fundamental properties, because single crystals of the OVC phases have not been successfully obtained except for some thin-film synthesis [2]. Only two phases, $CuIn_3Se_5$ and $CuIn_2Se_{3.5}$, are known as the possible OVC phases, both of which exist on the Cu_2Se-In_2Se_3 binary tie line.

Hönle et al [3] gave the detailed crystal structure for one example of the OVC (β) phase, which was informative for a possible atomic arrangement of the OVC phase. However, the OVC structure was observed to be flexible in composition, showing various compositions even out of the binary tie line in our experimental results. There has not been detailed discussion on the mechanism allowing the compositional variety.

In this work, the possible OVC structures allowing the compositional variation are proposed in view of the simulation of the x-ray diffraction intensity in comparison with the experimental results.

2. EXPERIMENTAL

2.1 Sample Preparation

We attempted to synthesize two possible OVC phases of $CuIn_3Se_5$ and $CuIn_2Se_{3.5}$. Compositional elements of the respective 6N purity were used for the sample preparation. These elements were sealed in a quartz tube (16 $\phi \times 120mm$) under a vacuum of $\sim 10^{-6}$ Torr ($\sim 10^{-4}$ Pa), heated up to 1100°C, using an electric furnace, held for 8 hours, and then gradually (0.1deg/min) cooled down to the temperatures forming the respective OVC phases. After holding the temperature for 3-5 days, the last step of crystallization was performed both with quenching from the temperatures (normally 700-900°C) and with gradual cooling (0.1deg/min) down to room temperature.

Table 1. Atomic positions (x, y) of A, B, and C sublattices of the tetragonal chalcopyrite structure, u=0.224 for CuInSe₂ [5].

z (n/8)	site	site
7	C₇(1/4, 1/2-u)	C₈(3/4, 1/2+u)
6	A₄ (0, 1/2)	B₄ (1/2, 0)
5	C₅(1-u, 1/4)	C₆(u, 3/4)
4	A₃ (0, 0)	B₃ (1/2, 1/2)
3	C₃(1/4, u)	C₄(3/4, 1-u)
2	A₂ (1/2, 0)	B₂ (0, 1/2)
1	C₁(1/2+u, 1/4)	C₂(1/2-u, 3/4)
0	A₁ (1/2, 1/2)	B₁ (0, 0)

2.2 EPMA measurement and x-ray diffraction

Sample compositions were analyzed by the EPMA (Electron Probe Microscope Analysis) measurement. Powder x-ray (Cu-K α) diffraction (XRD) was used to determine crystal phases and the lattice constants and to measure diffraction intensity of each diffraction line for the comparison with the calculated results. In order to measure both the diffraction angle and the intensity precisely, the diffraction angle 2θ was scanned at a rate of 1/32 deg/min.

3. CALCULATION OF DIFFRACTION INTENSITY

Relative x-ray diffraction intensity was calculated for the respective diffraction lines assuming possible OVC structures, using the following equation [4]:

$$I = |F(h)|^2 \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot m \qquad (1)$$

where $F(h)$ is the crystal structure factor followed by its correction factors as a function of diffraction angle θ relating to

both the polarization of an x-ray photon and the divergence of an incident x-ray, and m is the multiplicity of diffraction. The crystal structure factor $F(h)$ can be determined by the atomic scattering factor $f_j(h)$, Miller indices $h=(hkl)$ and the coordinates of atoms (x_j, y_j, z_j) for the j-th atom as follows:

$$F(h) = \sum_j f_j(h) \exp\left\{2\pi i (hx_j + ky_j + lz_j)\right\} \qquad (2)$$

Atomic coordinates of the tetragonal chalcopyrite structure are listed in Table 1.

4. Results and Discussion

4.1 Phase formation

Homogeneous single phase was easily obtained from the starting composition of Cu:In:Se=1:2:3.5 even on the crystallization with slow cooling rate (0.1deg/min). On the other hand, homogeneous synthesis was not attained from the starting composition of Cu:In:Se=1:3:5 even by quenching at temperatures (700-900℃) expected to form the OVC phase [6]. The resultant crystals were inevitably followed by a copper-deficient layer phase. However, it was easy to distinguish the layer phase material from OVC crystals. Figure 1 shows the x-ray diffraction profiles of (a) CuIn₂Se₃.₅ and (b) CuIn₃Se₅ crystals. Although these diffraction profiles are quit similar to that of CuInSe₂, small but definite three diffraction lines, i.e. (110), (202), and (114), characteristic of OVC phase are seen. The lattice constants of these two phases were determined as a=0.5756 nm, c=1.1525 nm for CuIn₂Se₃.₅ and a=0.5757 nm, c=1.1534 nm for CuIn₃Se₅. Composition rates Cu:In:Se of these powdered samples used for the XRD measurement were determined by the EPMA as 15.35:29.47:55.18 for CuIn₂Se₃.₅ and 11.28:33.69:55.03 for CuIn₃Se₅.
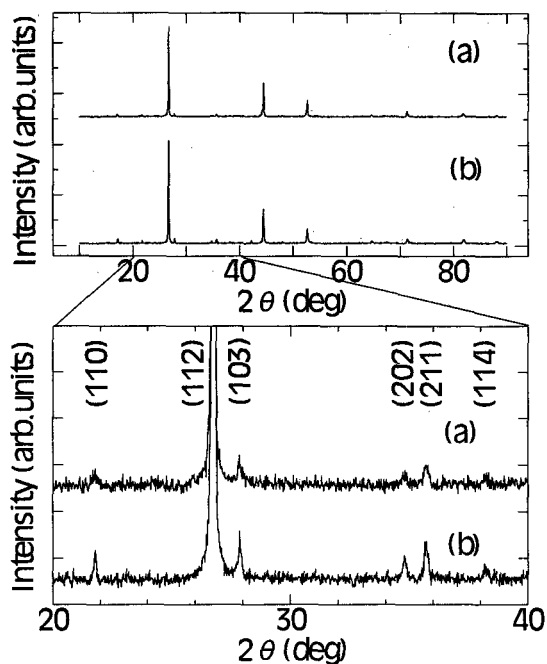
Figure 1. X-ray diffraction profiles of two OVC phases of (a) $CuIn_2Se_{3.5}$ and (b) $CuIn_3Se_5$.
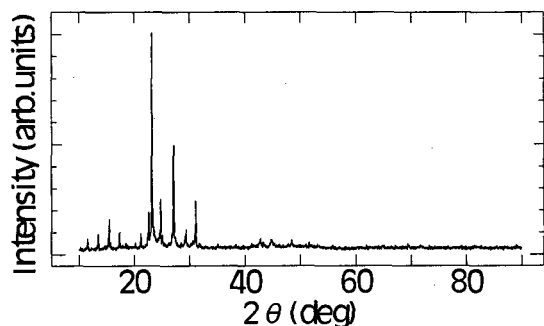
Figure 2. A layer copper-deficient phase found additional to $CuIn_3Se_5$ crystals.

Figure 2 shows a diffraction profile of the copper-deficient layer material found being segregated from $CuIn_3Se_5$ crystals. The phase separation was remarkable when the quenching temperature was 900℃. The average composition of this substance is $Cu:In:Se = 8.57:34.50:56.93$, approximately 1:4:6.5 which corresponds to Cu_2Se (20%) + In_2Se_3 (80%) on the binary tie line. Copper-deficient ternary phases were reported as

ε, ζ, and η in ref.4. These phases are richer in In_2Se_3 composition than the layer phase found in our samples.

4.2 OVC structure model

In the case of $CuInSe_2$, Three sublattices, A, B, and C-site listed in Table 1 are fully occupied by Cu, In, and Se atoms, respectively. The unit cell has $4ABC_2$ atoms. A general expression of composition, $Cu_xIn_ySe_z$, can be equally replaced in the form of $A_4B_4C_8$ with:$Cu_{8x/z}In_{8y/z}\square_{8[1-(x+y)/z]}Se_8$, where the symbol $\square$ expresses vacancies. Vacancies in anion (Se) site have not been considered in this work. The atomic portions of Cu and In atoms are $Cu:In:\square=2:4:1$ for $CuIn_2Se_{3.5}$ and 1:3:1 for $CuIn_3Se_5$.

Figure 3 shows the relationship between Cu/Se and In/Se molar ratios detected by the EPMA spot data for the crystal growth surface of OVC samples. The data points distribute around $Cu_2Se-In_2Se_3$ binary tie line. The expected OVC region is $1/2 < x/z + y/z < 1$, which is shown by dotted lines in Fig.3. The range of distribution is wider along the In/Se axis. The respective data distributions of $CuIn_2Se_{3.5}$ and $CuIn_3Se_5$ clearly share the neighboring regions along the Cu/Se axis.

These results can be explained by assuming the flexible atomic occupation of cation site. Assuming that Cu/Se is nearly constant for the respective $CuIn_2Se_{3.5}$ and $CuIn_3Se_5$ phases, the portion of vacancies v has the following relation with In/Cu ratio, i.e. y/x,

$$v = 8\left[1 - Const.(1 + y/x)\right]. \tag{3}$$

The constant parameter is 2/7 for $CuIn_2Se_{3.5}$, and 1/5 for $CuIn_3Se_5$. The OVC structures are flexible for In/Cu ratio with changing the portion of vacancies v. This suggests that vacancies unlikely exist as independently unoccupied sites, but exist such as $Cu+\square$, $In+\square$, or $Cu+In+\square$ site.

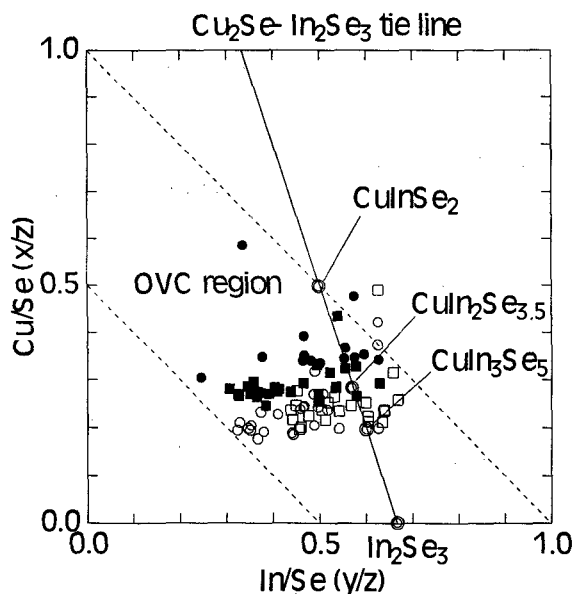Figure 3. Relationship between Cu/Se and In/Se molar ratios. Symbols denote: ● q-$CuIn_2Se_{3.5}$, ○q-$CuIn_3Se_5$, ■ nf- $CuIn_2Se_{3.5}$, □ nf-$CuIn_3Se_5$ (q:quenched, nf:normal freezing).
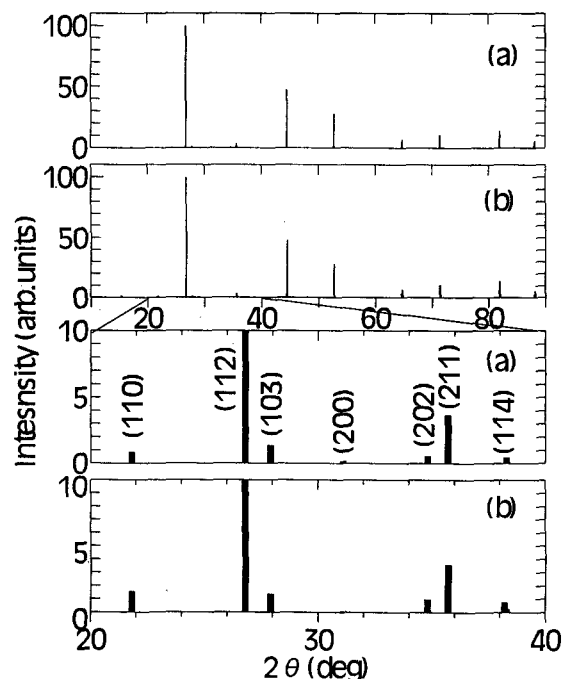

Figure 4. Diffraction profiles of (a) $CuIn_2Se_{3.5}$ and (b) $CuIn_3Se_5$ simulated according to the site occupation listed in Table 2.

Taking tetragonal symmetry into account, each site occupation is proposed as listed in Table 2. Difference between the two OVC phases is that atomic sites fully occupied by Cu exist in $CuIn_2Se_{3.5}$. Figure 4 shows the calculated diffraction patterns for $CuIn_2Se_{3.5}$ and $CuIn_3Se_5$ assuming the site occupation listed in Table 2. The results of simulation successfully reproduce the experimental diffraction profiles.

Table 2
Proposed site occupation for the two OVC phases.

Site	$CuIn_2Se_{3.5}$	$CuIn_3Se_5$
A_3, B_1	Cu	$Cu_{0.8}\square_{0.2}$
A_2, B_4	In	In
A_1, A_4, B_2, B_3	$Cu_{0.071}In_{0.643}\square_{0.286}$	$In_{0.7}\square_{0.3}$

5. Summary

Two OVC phases in the Cu-In-Se system, $CuIn_2Se_{3.5}$ and $CuIn_3Se_5$, were investigated. Crystal structures allowing the compositional variety were proposed using the simulation of x-ray diffraction in comparison with the experimental results, assuming Cu+In+ $\square$ site for ordered vacancy formation.

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