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Room temperature formation of Cu_3Se_2 by solid-state reaction between α-Cu_2Se and α-CuSe

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Abstract

Upon being brought into contact with each other, α-Cu_2Se and α-CuSe pellets reacted entirely forming Cu_3Se_2 at room temperature. After 10 days, the reaction was almost completed. Weight measurements revealed that copper atoms migrated from α-Cu_2Se to α-CuSe. Solid-state reactions were also observed in the (α-Cu_2Se + Cu_3Se_2) and (α-Cu_2Se + CuS) systems, but not in the (Cu_3Se_2 + α-CuSe), (Cu_2S + CuS) and (α-CuSe + Cu_2S) systems. Therefore, the high ionic conductivity of copper ions in α- and β-Cu_2Se is considered to be responsible for the solid-state reactions observed in these systems.

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Keywords: Solid-state reaction; Cu_2Se; CuSe; Cu_3Se_2; EPMA; Room temperature reaction

1. Introduction

It is well known that elemental copper and silver are highly reactive with chalcogen (S, Se, Te) [1–3]. A number of copper and silver chalcogenides were previously prepared from elemental mixtures using a mechanical alloying method with a ball mill [4,5]. In addition, sonochemical synthesis of $Cu_{1.96}S$, Cu_3Se_2, α-Cu_2Se and Ag_2Se by irradiating elemental mixtures immersed in methanol with an ultrasound at 28 kHz at room temperature was successful [6]. These observations prompted the consideration that the reaction may occur between the different copper chalcogenides by simply making contact between the selenides. In the present work, the solid-state reaction between copper chalcogenides at room temperature was investigated by focusing on the (α-Cu_2Se and α-CuSe) system.

Fig. 1 shows a phase relation of Cu_2Se, Cu_3Se_2 and CuSe, based on the phase diagram reported by Glazov et al. [7]. Similar phase diagram was early reported by Heyding [8]. Stoichiometric Cu_2Se has α and β phase below and above ca. 396 K, respectively. At room temperature, the α phase is stable in the region between 33.3 and 33.8 at% of Se, and the β phase in the region between ca. 35.3 and 36.4 at% of Se [7,9]. The structures of the α and β phases are both basically of an antifluorite structure, where Cu atoms occupy tetrahedral positions in the face-centered cubic (fcc) Se sublattice [10]. Statistically distributed Cu atoms in the $Cu_{1.75}Se$ (β phase) showed ordering at about 250 K, forming a superstructure of $2a \times 2a \times 2a$ [11,12]. The Cu_3Se_2 phase (umangite) is stable only at a stoichiometric composition below 408 K. This phase has a tetragonal unit cell (space group $P42_1m$), primarily composed of a tetrahedral network of Cu atoms, with Se atoms situated at atypical positions coordinated by six Cu atoms [10,13]. The α-CuSe phase (klockmannite) with a covellite structure is also line phase stable below 326 K. This phase has a hexagonal cell based on $P6_3/mmc$ [14], where the atomic arrangement consists of alternative packing of hexagonal close-packed layers of

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[CuSe] and [Cu_2Se_2] in the *c* direction; Cu atoms in the [CuSe] layers are triangularly coordinated by Se atoms, and Cu atoms in the [Cu_2Se_2] layers are surrounded by four tetrahedrally arranged Se atoms. It should be noted that there is no obvious similarity in the crystal structures of these three compounds.

Folmer and Jellinek found in X-ray photoelectron spectroscopy (XPS) measurements that the copper is monovalent in these three selenides as well as many other copper chalcogenides [15]. All these compounds show a metallic conductivity [16]. It is well known that both α- and β-Cu_2Se phases have a high ionic conductivity for Cu^+ ions; β-$Cu_{1.75}Se$ has an ionic conductivity of $3 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ at room temperature [17].

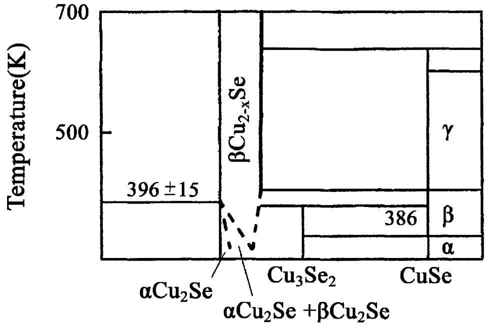

Fig. 1. Partial phase diagram of the Cu–Se system based on the report by Glazov et al. [7].

2. Experimental

Copper selenide of α-Cu_2Se was prepared by heating elemental mixture of Cu (Katayama Chemical Ind.; 99.9% in purity; 300 mesh) and Se (Rare Metallic Co., Ltd; 99.9999% in purity; shots) with the stoichiometric ratio in evacuated silica tubes for 10 days at 573 K. The Se shots were used after being ground into powder. The samples of α-CuSe were also prepared in the same way at 373 K. Although the reaction temperature of 373 K is below the melting temperatures of both Cu and Se, the reaction of α-CuSe was entirely completed after 10 days. Equimolar ratios of powdered α-Cu_2Se and α-CuSe samples (1.3×10^{-3} mol) were separately pressed into pellets (approximately of 15 mm × 5 mm × 0.6 mm) under a pressure of 4×10^3 kg/cm^2. The α-Cu_2Se and α-CuSe pellets were brought into contact through their rectangular (15 mm × 5 mm) faces under a pressure of 10.0 kg/cm^2, and allowed to react for the periods as long as 30 days at room temperature. The chemical composition of the lateral face (15 mm × 0.6 mm) of each pellet was analyzed by an electronprobe microanalyzer (EPMA), at certain intervals of the reaction. The pellets were subsequently ground into powder, and identified by the powder X-ray diffraction (XRD) method using a diffractometer with monochromatic Cu*K*α radiation. The same procedure was used for the reaction between the (α-Cu_2Se + Cu_3Se_2), (α-Cu_2Se + CuS), (Cu_3Se_2 + α-CuSe), (Cu_2S + CuS) and (α-CuSe + Cu_2S) systems.

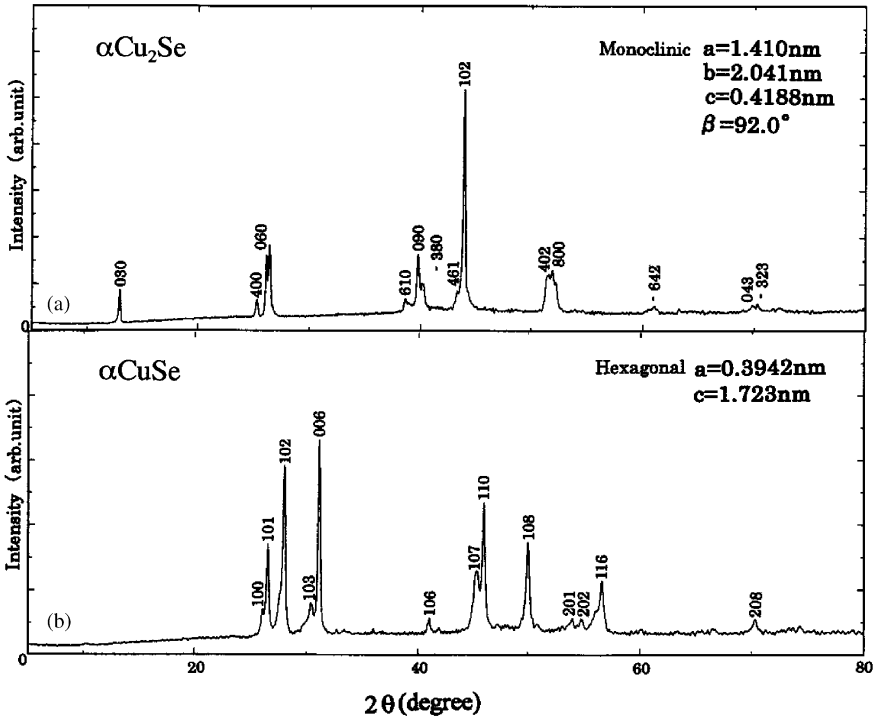

Fig. 2. XRD patterns of the starting materials; α-Cu_2Se (a) and α-CuSe (b).

3. Results and discussion

Fig. 2 shows the XRD patterns of the starting materials; α-Cu_2Se (a), and α-CuSe (b). The patterns of α-Cu_2Se and α-CuSe were identified on the basis of the monoclinic structure [10] and the hexagonal structure [14], respectively. The calculated lattice parameters of α-Cu_2Se were $a = 1.410(7)$ nm, $b = 2.041(5)$ nm, $c = 0.4188(3)$ nm, and $\beta = 92°$, and those of α-CuSe are $a = 0.3942(4)$ nm and $c = 1.723(2)$ nm. These results are in good agreement with the published data [10,14].

Fig. 3 shows the XRD patterns of the samples after being allowed to react for 60 min at room temperature; the α-Cu_2Se pellet (a), and the α-CuSe pellet (b). Pattern (a) was identified as the β-Cu_2Se phase. The lattice parameter of this sample was calculated to be $a = 0.5757(2)$ nm, well identical with the reference data in JCPDS file No. 71-0044 [18]. This observation indicates that the α-Cu_2Se phase was transformed into the β-Cu_2Se phase with less amount of copper atoms compared with the α phase. Pattern (b) shows a two-phase mixture of α-CuSe and Cu_3Se_2, indicative of the increased copper composition in the α-CuSe pellet. After the system was allowed to react further, the α-Cu_2Se pellet was composed of a mixed state, consisting of β-Cu_2Se and Cu_3Se_2 phases, and the amount of Cu_3Se_2 phase in the α-CuSe pellet continuously increased with reaction time. These observations clearly indicate that the composition of each pellet was gradually brought close together to Cu_3Se_2, which lies in at the intermediate between α-Cu_2Se and α-CuSe [7,8]. After 10 days, both the α-Cu_2Se and α-CuSe pellets entirely reacted to forming the Cu_3Se_2 phase, shown in Fig. 4.

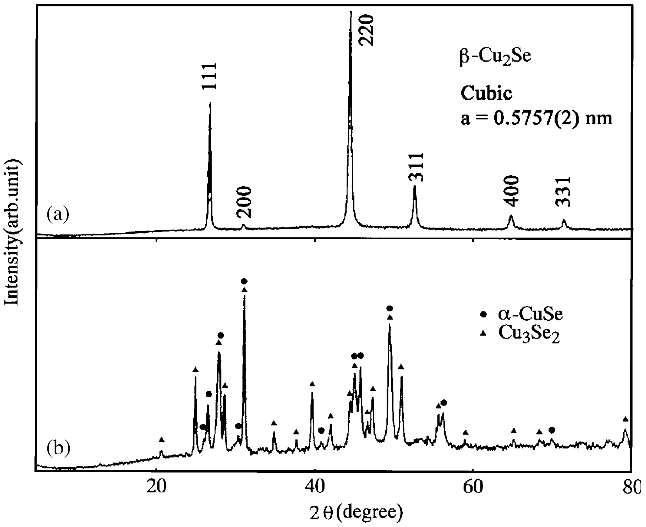

Fig. 3. XRD patterns of samples obtained after the system was allowed to react for 60 min at room temperature; the α-Cu_2Se pellet (a) and the α-CuSe pellet (b).

Fig. 5 shows the chemical compositions of the lateral faces (15.0 mm × 0.6 mm) of both α-Cu_2Se and α-CuSe pellets after allowed to react for 10, 60 and 240 min. The distance from the end of the α-Cu_2Se pellet is plotted in the abscissa (x-axis), and the chemical composition x in Cu_xSe_2 in the ordinate (y-axis). The surface was scanned in a direction normal to the plane of contact of the α-Cu_2Se and α-CuSe pellets. Each of five scans were made in increments of 0.125 mm. The Cu composition of both pellets scarcely varied after the reaction ran for 10 min. After a reaction time of 60 min, the Cu composition x in Cu_xSe_2 decreased from 4.0 to ~3.5 in the α-Cu_2Se (Cu_4Se_2) pellet, and slightly increased in the α-CuSe (Cu_2Se_2) pellet from 2.0 to ~2.1. After allowed to react for 240 min, the composition changed similar to that of Cu_3Se_2 in both pellets. Fig. 6 shows the distribution map of Se obtained by EPMA for the lateral faces of both α-Cu_2Se and α-CuSe pellets after the reaction progressed for 10 (a), 60 (b) and 240 min (c); the upper and lower figures correspond to pellets of α-CuSe and α-Cu_2Se, respectively. As the reaction proceeded, the Se composition in the pellets became closer to each other. It is noteworthy that the lateral faces scarcely showed the compositional gradient during the reaction, suggesting the high mobility of Cu or/and Se ions in the pellets.

In order to distinguish which type of ion migration is dominant, the weight change was measured for each

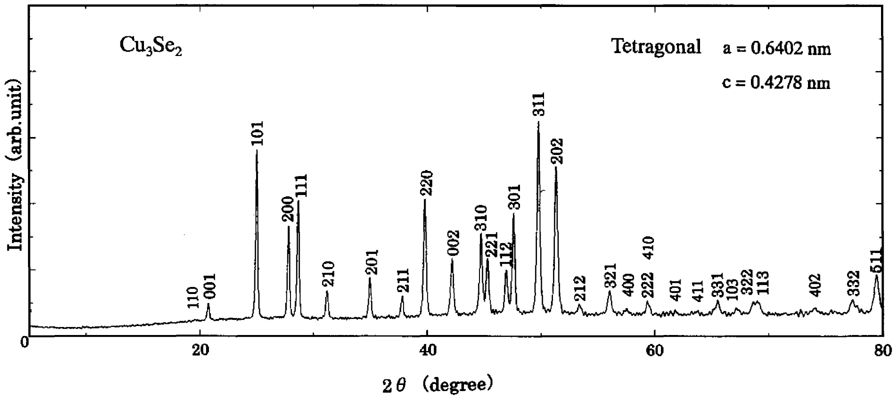

Fig. 4. XRD pattern of Cu_3Se_2 obtained after the reaction progressed for 10 days.

pellet after reaction was completed. The α-Cu_2Se (0.200 g) pellets and α-CuSe (0.200 g) were allowed to react for 20 days. After the reaction, the α-Cu_2Se pellet was found to change entirely to a single Cu_3Se_2 phase with a weight of 0.173 g. The weight loss of the α-Cu_2Se pellet was consistent with the calculated value, assuming that only Cu^+ ions migrate from α-Cu_2Se to α-CuSe pellet. It is considered, thus, that the reaction in the α-Cu_2Se pellet can be represented as α-$Cu_2Se-Cu^+ \rightarrow Cu_3Se_2$, and that in the α-CuSe pellet as α-$CuSe+Cu^+ \rightarrow Cu_3Se_2$.

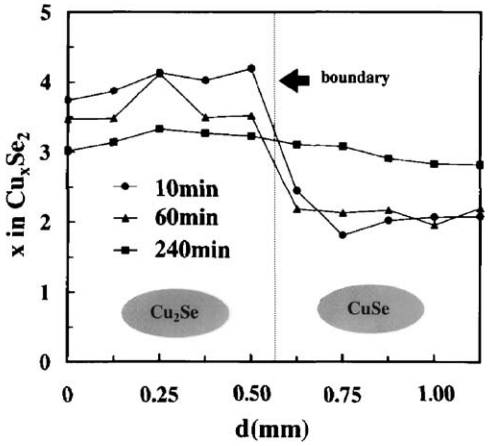

Fig. 5. Chemical composition of the lateral faces (15.0 mm × 0.6 mm) of both α-Cu_2Se and α-CuSe pellets allowed to react for 10, 60 and 240 min.

The electromotive force (EMF) of the α-Cu_2Se | α-CuSe system was measured at 373 K. The value of EMF was observed to be +8.0 μV immediately after contact with the pellets, and continued to decrease with time, consistent with the result that Cu^+ ions migrate from α-Cu_2Se to the α-CuSe pellet. The EMF values of were reversible in charge–discharge cycles.

The solid-state reaction was also observed between α-Cu_2Se and Cu_3Se_2 pellets, when the pellets were placed in contact at room temperature. After 3 days, the α-Cu_2Se pellet partially changed to the Cu_3Se_2 phase, and Cu_3Se_2 pellet partially changed to the β-Cu_2Se phase, indicating that the composition was that of an intermediate between Cu_2Se and Cu_3Se_2. Furthermore, the reaction was observed in the (α-Cu_2Se + CuS) system; α-Cu_2Se entirely changed to Cu_3Se_2 after 7 days. On the other hand, the solid-state reaction was not observed in the (Cu_3Se_2 + α-CuSe), (Cu_2S + CuS)

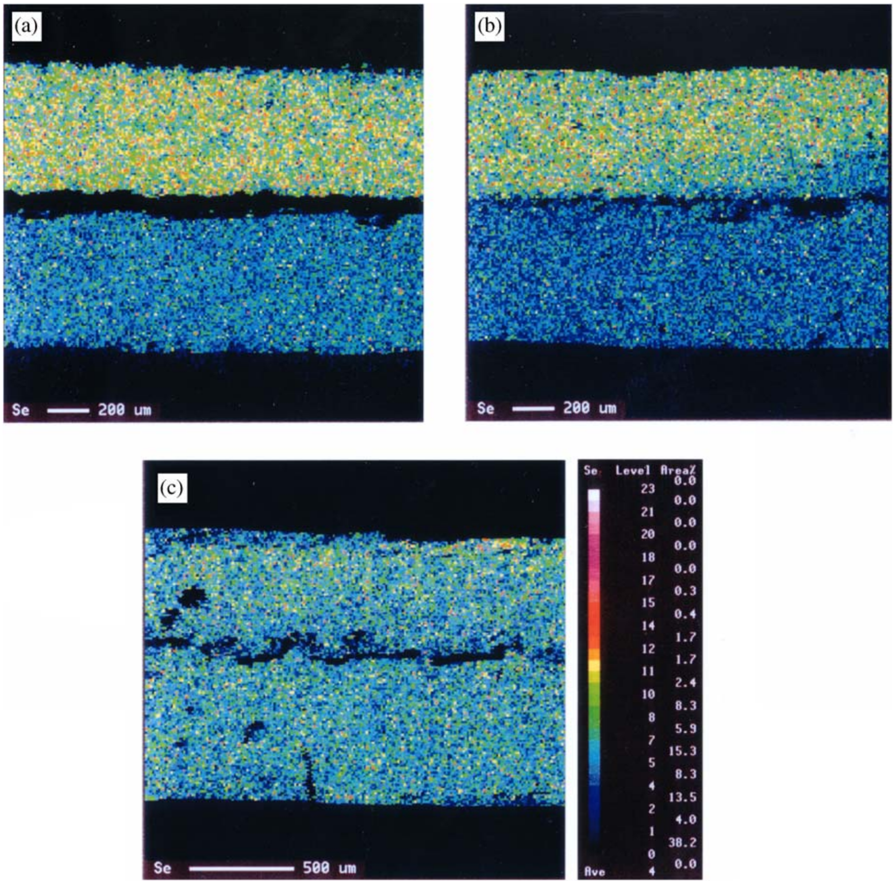

Fig. 6. The distribution map of Se obtained by EPMA for the lateral faces of the α-CuSe (upper) and α-Cu_2Se (lower) pellets after allowed to react for 10 min (a), 60 min (b) and 240 min (c).

and (α-CuSe + Cu_2S) systems. It is important to note that the reaction occurred only in the systems including the α-Cu_2Se phase. This observation indicates that the high ionic conductivity in α-, and β-Cu_2Se is primarily responsible for the solid-state reactions.

4. Conclusion

The pellets of α-Cu_2Se and α-CuSe were entirely reacted into Cu_3Se_2 at room temperature for about 10 days. There is no obvious structural similarity among these three compounds. Some intercalation reactions take place in the solid state at room temperature, where the host lattices in these cases are not altered substantially. It should be noted that the present reactions are accompanied by the structural change. The similar solid state reactions were also observed in the systems of (α-Cu_2Se + Cu_3Se_2) and (α-Cu_2Se + CuS). The reactions were observed to be proceeded by the migration of Cu^+ ions from α-Cu_2Se to α-CuSe. It is most probable, thus, that the present reactions originate from the high ionic conductivity of Cu^+ ions in α-Cu_2Se. The present results will open a new area of solid state reactions.

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