

Structural study of Cu_{2-x}Se alloys produced by mechanical alloying

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The crystalline structures of the superionic high-temperature copper selenides Cu_{2-x}Se ($0 < x < 0.25$) produced using mechanical alloying were investigated using X-ray diffraction (XRD). The measured XRD patterns showed the presence of peaks corresponding to the crystalline superionic high-temperature $\alpha\text{-Cu}_2\text{Se}$ phase in the as-milled sample, and its structural data were determined by means of a Rietveld refinement procedure. After heat treatment in argon at 473 K for 90 h, this phase transforms to the superionic high-temperature $\alpha\text{-Cu}_{1.8}\text{Se}$ phase, whose structural data were also determined by Rietveld refinement. In this phase, a very low occupation of the trigonal $32(f)$ sites ($\sim 3\%$) by Cu ions is found. In order to explain the evolution of the phases in the samples, two possible mechanisms are suggested: (i) the high mobility of Cu ions in superionic phases and (ii) the important diffusive processes in the interfacial component of samples produced by mechanical alloying.

1. Introduction

Owing to their physical and chemical characteristics, selenium-based alloys are very important from a technological and scientific point of view, especially those alloys containing germanium, zinc or copper because of their very interesting optical properties. Recently, cation-deficient copper selenide, Cu_{2-x}Se , which is a mixed ionic–electronic superionic conductor with a homogeneity range of $0 \leq x \leq 0.25$, has been extensively studied because of its interesting properties and potential application in solar cells (Lakshmikumar & Rastogi, 1994), window materials (Haram *et al.*, 1992), optical filters (Toyaji & Hiroshi, 1990), superionic conductors (Chen *et al.*, 1985), electro-optical devices (Kainthla *et al.*, 1980) and thermoelectric converters (Rau, 1967), and also as a precursor for the preparation of copper indium diselenide, CuInSe_2 (CIDS; Ueno *et al.*, 1989). The superionic transition from the β -phase (low temperature) to the α -phase (high temperature) occurs at 414 K for Cu_2Se and decreases with increasing deviation from this 2:1 stoichiometry. At room temperature, the superionic α -phase is stable for $0.15 \leq x \leq 0.25$ (Abrikosov *et al.*, 1983). Cu_{2-x}Se films are typically materials with *p*-type activity, highly conducting and semitransparent, with a band gap between 1.1 and 1.4 eV, and are very suitable for solar energy conversion. A solar cell (Schottky type) employing a semi-transparent layer of Cu_{2-x}Se as the window material on an *n*-type semiconductor is estimated to have excellent photovoltaic properties and a conversion efficiency

of around 9% (Okimura *et al.*, 1980). Many preparation methods of Cu_{2-x}Se alloys have been reported, including sonochemical synthesis (Xu *et al.*, 2002; Xie *et al.*, 2002), chemical bath deposition (Garcia *et al.*, 1999; Clement *et al.*, 1997; Pathan *et al.*, 2003), the photochemical route (Yan *et al.*, 2003), γ -irradiation (Qiao *et al.*, 2000), solid-state reaction (Danilkin *et al.*, 2003), microwave-assisted heating (Zhu *et al.*, 2000), a hydrothermal method (Wang *et al.*, 1999), electro-deposition (Lippkow & Strehblow, 1998; Battacharya *et al.*, 1996) and mechanical alloying (MA; Ohtani *et al.*, 1995).

The crystalline structure of Cu_{2-x}Se has been studied several times (Danilkin *et al.*, 2003; Rahlfs, 1936; Borchert, 1945; Heyding & Murray, 1976; Oliveria *et al.*, 1988; Boyce *et al.*, 1981; Yamamoto & Kashida, 1991; de Montreuil, 1975; Milat *et al.*, 1987), but the precise distribution of the Cu ions and the structure itself are still under discussion and diverse crystallographic data can be found in the literature. Rahlfs (1936) described the α - Cu_{2-x}Se phase using $F23$ symmetry and Borchert (1945) proposed a structural model for α - Cu_{2-x}Se consisting of a cage of $F\bar{4}3m$ symmetry, built by Se atoms in 4(*a*) sites and Cu ions in 4(*c*) sites, and a mobile cation subsystem formed by the remaining Cu ions distributed over the interstitial sites [tetrahedral 4(*d*), octahedral 4(*b*) and trigonal 16(*e*) sites]. Heyding & Murray (1976) considered an f.c.c. (face-centered cubic) cage formed with Se atoms only and a mobile subsystem formed by Cu ions in tetrahedral 8(*c*) and trigonal 32(*f*) sites, with an overall symmetry of $Fm\bar{3}m$. Neutron diffraction results (Oliveria *et al.*, 1988), on the other hand, suggest that Cu ions are distributed over the trigonal 32(*f*) sites, leaving the octahedral sites empty. The β - Cu_{2-x}Se phases are either described as monoclinic or tetragonal (de Montreuil, 1975; Milat *et al.*, 1987). The ordering of Cu ions in the β -phase results in a complicated superstructure which is very sensitive to the composition and preparation technique.

In this paper we report on the results obtained for Cu_{2-x}Se alloys produced by the MA (mechanical alloying) technique (Suryanarayana, 2001). MA has been used for almost two decades to produce many unique materials. These include, for instance, nanostructured alloys, amorphous compounds, and unstable and metastable phases (de Lima *et al.*, 2003; Weeber & Bakker, 1988; Mukhopadhyay *et al.*, 1994; Yavari *et al.*, 1992; Campos *et al.*, 2002; Machado *et al.*, 2002, 2003). This method has several intrinsic advantages, such as low-temperature processing, easy control of the composition, no need for expensive equipment and the possibility of scaling up. Although the MA technique is relatively simple, the physical mechanisms involved are not yet fully understood. In order to make use of this technique in industrial applications, a better understanding of these physical mechanisms is desirable.

2. Experimental

A binary mixture of high-purity elemental powders of copper (Vetec 99.5%, particle size < 10 μm) and selenium (Alfa Aesar 99.999% purity, particle size < 150 μm), with the nominal composition Cu_2Se , was sealed together with several steel balls in a cylindrical steel vial under an argon atmosphere. The

ball-to-powder weight ratio was 5:1. A Spex Mixer/Mill model 8000 was used to perform MA at room temperature. The mixture was continuously milled for 72 h. A ventilation system was used to keep the vial temperature close to room temperature. For this sample an X-ray diffraction (XRD) measurement was performed, after which the sample was heat treated at 473 K for 90 h in a quartz capsule containing argon and a new XRD measurement was collected. All XRD measurements were recorded on a Siemens diffractometer with a graphite monochromator in the diffracted beam, using the Cu $K\alpha$ line ($\lambda = 1.5418 \text{ \AA}$).

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern taken for the as-milled (AM) sample (AM- Cu_{2-x}Se). A comparison of this pattern with JCPDS cards [Powder Diffraction File Search Manual (ICDD, Pennsylvania, USA, 1981)] indicated the presence of the Cu_2Se phase in the $F23$ structure given by the JCPDS card 76-0136. The main peaks of this phase are seen at *ca* $2\theta = 26.4, 44.0, 52.1$ and 80.9° , which is in very good agreement with that card. This is the high-temperature α -phase of the Cu_{2-x}Se system, indicating that MA performed at room temperature can produce these phases. The pattern shown in Fig. 1 was simulated using the Rietveld procedure (Young *et al.*, 1995). Garcia *et al.* (1999), using a chemical bath deposition method, obtained the $\text{Cu}_{1.85}\text{Se}$ phase corresponding to the mineral berzelianite (JCPDS card 06-0680). Danilkin *et al.* (2003) produced the low-temperature monoclinic β - Cu_2Se phase using solid-state reactions. We also investigated these possibilities but Rietveld refinements using



Figure 1
XRD pattern for AM- Cu_{2-x}Se and its Rietveld simulation, formed by the three phases α - Cu_2Se , Cu_2O and CuO .

Table 1

Rietveld refinement results for α -Cu₂Se, space group *F23*, JCPDS card 76-0136.

The B_{iso} thermal parameter was set to 0 for all sites and for all phases. For this refinement, we found $R_p = 0.0375$.

Atom	Site	Position	Occupation (%)
Cu	4(c)	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	100
Cu	4(a)	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	42 ± 1
Cu	16(e)	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	8 ± 0.7
Cu	16(e)	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	8 ± 0.7
Se	4(a)	0, 0, 0	100

these structures did not produce good results. The lattice parameters obtained for the α -Cu₂Se phase were $a = b = c = 5.8164 \pm 0.01$ Å. The occupation of the sites was also refined and these data are given in Table 1.¹

In addition to the peaks of the α -Cu₂Se phase, other peaks were found in the XRD pattern of AM-Cu_{2-x}Se, which were identified as belonging to the oxides Cu₂O (JCPDS card 78-2076) and CuO (JCPDS card 80-1917). Although the sample was kept under argon atmosphere during the milling, it was probably contaminated by oxygen during its preparation and also during the XRD measurement. Approximately 73% of the crystalline phases present in this sample are in the α -Cu₂Se phase, whereas the contaminant phases are responsible for 18 (Cu₂O) and 9% (CuO), respectively. The contribution of the three phases to the XRD pattern of AM-Cu_{2-x}Se is also shown in Fig. 1. It should be noted that the strong diffuse scattering seen in Fig. 1 is a well established characteristic of the α -Cu₂Se phase, owing to the large number of vacancies in the Cu-atom sublattice (Sakuma *et al.*, 1995). Thus, we did not consider it to be an amorphous part in the Rietveld refinement. The refined lattice parameters of the oxides are $a = b = c = 4.3108 \pm 0.00$ Å for Cu₂O (space group *Pn $\bar{3}$ m*) and $a = 4.6888 \pm 0.01$, $b = 3.4201 \pm 0.00$, $c = 5.1342 \pm 0.01$ Å and $\beta = 99.66^\circ$ (space group *Cc*). The average crystallite sizes found using the Scherrer formula (Klug & Alexander, 1974) for α -Cu₂Se, Cu₂O and CuO are 60, 78 and 50 Å, respectively, showing that all of them are in nanometric form.

To study the stability of the α -Cu₂Se phase, a heat treatment was made at 473 K for 90 h. The XRD pattern of the heat-treated Cu_{2-x}Se sample (HT-Cu_{2-x}Se) is shown in Fig. 2. A comparison with Fig. 1 indicates the presence of a phase different from those found in AM-Cu_{2-x}Se. The peaks at $\sim 2\theta = 26.5, 44.3, 52.3, 64$ and 81.7° are the most intense of the superionic high-temperature α -Cu_{1.8}Se-phase given in JCPDS card 71-0044, which corresponds to one of the forms of the mineral berzelianite. This phase belongs to the space group *Fm $\bar{3}$ m* and its refined lattice parameters are $a = b = c = 5.7762 \pm 0.00$ Å. The Rietveld refinement indicated that the Cu ions are found mainly in the tetrahedral 8(c) sites. The trigonal 32(f) sites are almost unoccupied. In addition, the refined position of the trigonal 32(f) sites agrees with those given in the ICSD card 238, as can be seen in Table 2, which gives the

refined data of this phase. Danilkin *et al.* (2003) have also studied this phase, but they found the trigonal 32(f) sites in a different position and with a different occupation. Our results agree with the neutron diffraction study of Oliveria *et al.* (1988), which did not give any indication of octahedral occupation. It should be noted that we tried to make refinements of the XRD pattern shown in Fig. 1 considering this phase in addition to those found in AM-Cu_{2-x}Se, but the results indicated that it was not present.

In addition to the α -Cu_{1.8}Se phase, the HT-Cu_{2-x}Se sample contains the two oxides already seen in AM-Cu_{2-x}Se and a small quantity of the tetragonal Cu₃Se₂ phase known as umangite, given in JCPDS as card 47-1745 (space group *P4 $\bar{2}$ 1m*). Approximately 75% of the crystalline phases found in HT-Cu_{2-x}Se are given by the α -Cu_{1.8}Se phase and the contributions of the other phases are 6% for Cu₂O, 16% for CuO and 3% for Cu₃Se₂. The refined lattice parameters obtained for the contaminant phases are $a = b = c = 4.2850 \pm 0.01$ Å for Cu₂O, $a = 4.6826 \pm 0.04$, $b = 3.4163 \pm 0.02$, $c = 5.1570 \pm 0.04$ Å and $\beta = 99.732^\circ$ for CuO, and $a = b = 6.3835 \pm 0.03$ and $c = 4.2596 \pm 0.07$ Å for Cu₃Se₂.

With the heat treatment at 473 K, the α -Cu₂Se phase changes to the α -Cu_{1.8}Se phase and the Cu₂O phase decreases while CuO increases. These processes could be explained by a

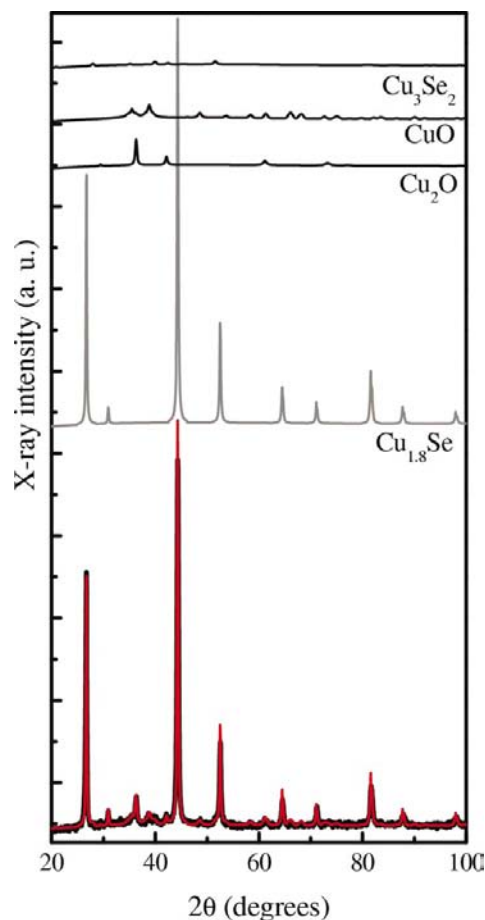


Figure 2
XRD pattern for HT-Cu_{2-x}Se and its Rietveld simulation, formed by the four phases α -Cu_{1.8}Se, Cu₂O, CuO and Cu₃Se₂.

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV5007). Services for accessing these data are described at the back of the journal.

Table 2

Rietveld refinement results for α -Cu_{1.8}Se, space group $Fm\bar{3}m$, JCPDS card 71-0044.

The B_{iso} thermal parameter was set to 0 for all sites of the contaminant phases. For this refinement, we found $R_p = 0.0364$. The error in the position of the trigonal 32(*f*) sites is ± 000002 .

Atom	Site	Position	B_{iso} (\AA^2)	Occupation (%)
Cu	8(<i>c</i>)	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	5.2 ± 0.5	80 ± 2
Cu	32(<i>f</i>)	$\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$	1.7 ± 0.2	3 ± 0.6
Se	4(<i>a</i>)	0, 0, 0	3.6 ± 0.4	100

combination of two factors. First, in the superionic α -phase Cu ions have a very high mobility, which could be explained by the very small activation energy that Cu atoms need in order to jump between sites. Second, it is well known that MA produces materials with two components: the nanocrystalline component, which preserves the crystalline structure of the crystals, and the interfacial region, formed by defect centers. The diffusive processes in the interfacial component can be much more important than they are in the nanocrystalline component, and Cu, Se and O atoms belonging to this region could have reacted during the heat treatment and produced the structural changes seen in the XRD pattern of the heat-treated sample. An indication that these processes really take place in the alloy is the large increase in the average crystallite size of the phases. The values obtained are 39, 225, 113 and 144 \AA , respectively, for α -Cu_{1.8}Se, Cu₂O, CuO and Cu₃Se₂. The crystallinity of all the phases improves during heat treatment, in particular the crystallinity of the α -Cu_{1.8}Se phase, whose average crystallite size increases more than six times.

4. Conclusion

From the results shown above, we conclude that:

(i) The superionic high-temperature α -Cu₂Se-phase can be produced by mechanical alloying at room temperature. It is the majority phase (about 73%) in the as-milled Cu_{2-x}Se sample. During the preparation of the sample some contamination by oxygen occurred and two oxides, Cu₂O and CuO, were formed.

(ii) The α -Cu₂Se-phase present in the as-milled Cu_{2-x}Se sample is found in the space group *F23* and its refined structural parameters, shown in Table 1, are a little different from those seen in the literature. The oxides are also found in nanometric form.

(iii) After heat treatment in argon at 473 K for 90 h, the structure of α -Cu₂Se changes and the superionic high-temperature α -Cu_{1.8}Se-phase is formed. It is found in the space group $Fm\bar{3}m$ and its refined structural parameters are found in Table 2. Almost all the Cu ions are found in tetrahedral 8(*c*) sites and the trigonal 32(*f*) sites have a very small occupation ($\sim 3\%$). There is no indication of octahedral occupation, which is in agreement with the results of Oliveria *et al.* (1988) and Boyce *et al.* (1981). The crystallinity of all the phases is much improved during the heat treatment, in particular the crystallinity of the Cu_{1.8}Se-phase, whose average crystallite size increases by more than six times, from 60 to

390 \AA . There are at least two possible reasons for the structural changes occurring in the sample on heat treatment. First, Cu ions in the superionic phases have a high mobility since their activation energy for jumping is expected to be very small and the heat treatment can produce this energy. Second, atoms in the interfacial component of the sample produced by mechanical alloying also have a very high mobility and the diffusive processes in this component can be very important. A combination of the two processes could explain the structural changes and the crystallinity improvement which occurred during the heat treatment, and also the formation of the superionic phase at room temperature.

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