Structural behaviour of β -Cu_{2- δ} Se ($\delta = 0, 0.15, 0.25$) in dependence on temperature studied by synchrotron powder diffraction

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Abstract

Superionic β -copper selenide, β -Cu_{2- δ} Se ($\delta = 0, 0.15, 0.25$), has been studied by synchrotron powder diffraction and calorimetric methods in the range 293 K < T < 823 K. Cu_{1.75}Se exists in the superionic phase at room temperature and remains stable in air up to 600 K. Cu_{1.85}Se exists at room temperature as a mixture of β and α phases, $\beta + \alpha \rightarrow \beta$ phase transition is not detected in DCS experiment, however, pure β -phase was observed in diffraction pattern of Cu_{1.85}Se at 353 K; Cu_{1.85}Se remains stable in air up to 600 K. A copper release process starts in Cu₂Se at a temperature below the superionic–non-superionic phase transition. At $T > 543$ K the composition is close to Cu_{1.95}Se and remains stable up to 573 K. Time average structure of β -Cu_{2- δ} Se has been analysed in the whole temperature range of existence in air. A face centred cubic unit cell (space group $Fm\bar{3}m$) is formed by the selenium anions with copper cations distributed over tetrahedral 8(c) and 32(f) (x, x, x) split positions within the octahedral voids ($1/3 < x < 1/2$). The copper occupancy of the 32(f) sites increases with temperature with a simultaneous decrease in the 8(c) sites. Besides, the copper occupancy of the 32(f) lattice site also increases with the total copper content $2 - \delta$. A diffusion pathway of mobile Cu ions along the tetrahedral sites, in “skewed” $\langle 100 \rangle$ directions through the peripheries of octahedral cavities is proposed.

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1. Introduction

Copper selenide Cu_{2- δ} Se ($\delta = 0$ –0.25) is a mixed ionic–electronic conductor and exists in two modifications: the low-temperature α -phase and the high-temperature superionic β -phase with high mobility of the copper cations. The self-diffusion coefficient D_i of the copper cations in β -Cu_{2- δ} Se ($\delta = 0.01$ –0.20) reaches $5.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ at $T = 673$ K [1], and the ionic conductivity is $\sigma_i \sim 1.9 \Omega^{-1} \text{ cm}^{-1}$ [2]. Therefore, many investigations were devoted to the nature of the ionic disorder.

Previous investigations revealed a face centred cubic (fcc) lattice for the selenium atoms with the copper ions distributed on the different interstitial sites within the tetrahedral and octahedral voids [3–13]. Tetrahedral and octahedral voids in the fcc lattice share faces, whereas similar “octahedron–octahedron”

and “tetrahedron–tetrahedron” voids are connected by common edges. According to molecular dynamics simulations [14], the minimum energy diffusion pathway in the anti-fluorite structure passes alternately tetrahedral and octahedral voids through the octahedral 4(b) site at $(1/2, 1/2, 1/2)$. Most structure determinations, however, did not reveal any occupation of copper ions in the centre of the octahedron [6–9,12,13]. Some publications, however, report intensity changes of reflections as a function of temperature and unusual thermal expansion in β -Cu_{2- δ} Se ($\delta = 0$ –0.25) [4,15,16]. Thus, the lattice parameter of β -Cu_{2- δ} Se ($\delta = 0$ –0.25) increases most rapidly at the beginning of the heating then, slows down with increasing temperature and becomes linear at temperatures above 573 K. This behaviour corresponds to a continuous change of intensity of certain diffraction lines between room temperature and about 573 K. These effects have been observed first by Borchert [4] and later by Tonejc et al. [16] and were explained by a redistribution of copper ions during heating up to 573 K. In this paper, the divergent results on the structure of the superionic β -Cu_{2- δ} Se were explained by the existence of different structural modifications, whereas Heyd-

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ing and Murray [6] related the intensity changes to the history of sample preparation or trace impurity.

In order to clarify the variety of results we launched structural studies of β - $\text{Cu}_{2-\delta}\text{Se}$ with different composition ($\delta = 0, 0.15, 0.25$) in a broad range of temperatures. Most results reported previously concern only studies on specific samples with particular stoichiometry and at particular temperatures. Synchrotron powder diffraction has been chosen for structural investigations because of the high intensity of synchrotron radiation and difficulties to synthesize high-quality single crystals. In several recent publications on “single” crystal studies [11,17] multiple twinning and smearing out of reflections was reported. The main focus of the present work is a clarification of the temperature dependence of the average structure in β - $\text{Cu}_{2-\delta}\text{Se}$. Special attention was devoted to the determination of stability of the samples in air at high temperatures.

2. Experimental

The samples ($\text{Cu}_{1.75}\text{Se}$, $\text{Cu}_{1.85}\text{Se}$ and Cu_2Se) were prepared by solid-state reactions. Copper and selenium powders of high purity (Chempur, >99.99%) were weighed in appropriate ratios, ground and pressed in pellets. The pellets were sealed in silica tubes at 10^{-5} mbar pressure and heated up to 720 K over 100 h with subsequent annealing for 48 h at 520 K.

X-ray diffraction (XRD) experiments were performed with a conventional powder diffractometer STOE STADIP (Cu $K\alpha_1$ radiation, curved Ge monochromator, transmission mode, step 0.03° (2θ) linear PSD counter).

Simultaneous thermal analysis (STA), which combined thermogravimetry (TG) and differential scanning calorimetry (DSC), has been carried out using a Netzsch STA 429 device. Calorimetric heating experiments have been performed in air with different rates (from 10 to 20 K/min) in the temperature range of 293–823 K.

High-resolution powder diffraction experiments at elevated temperatures have been performed at the beam-line B2 at HASYLAB/DESY with wavelength of $\lambda = 0.509702 \text{ \AA}$ from Si(1 1 1) double crystal monochromator [18,19]. The powdered samples were filled into capillaries of 0.3 mm diameter with an empty 0.1 mm capillary inside to reduce absorption. The sealed capillary was mounted inside a STOE furnace in Debye–Scherrer geometry equipped with a Eurotherm temperature controller and capillary spinner. Diffraction patterns for Cu_2Se , $\text{Cu}_{1.85}\text{Se}$ and $\text{Cu}_{1.75}\text{Se}$ compounds have been collected in the 2θ -range 10 – 35° (step 0.004°) with temperature intervals of 10, 20 and 25 K, correspondingly. Data analyses was performed using the program package “FULLPROF” [20]: lattice parameter, zero shift, background and profile shape parameters were determined by whole-pattern decomposition procedure and time average structure has been analysed by the full-profile Rietveld method.

3. Results and discussion

3.1. Stability of $\text{Cu}_{2-\delta}\text{Se}$ ($\delta = 0, 0.15, 0.25$) at elevated temperatures in air

Preliminary XRD measurements at room temperature confirm the superionic β -phase for $\text{Cu}_{1.75}\text{Se}$, α -phase for Cu_2Se , whereas $\text{Cu}_{1.85}\text{Se}$ consists of a mixture of α - Cu_2Se (PDF-2 card [27–1131]) and β - $\text{Cu}_{1.8}\text{Se}$ (PDF-2 card [71–44]) in a ratio corresponding to a stoichiometry of 1.85 (Fig. 1). The results of XRD measurements are in agreement to the phase diagram published in [16,21].

STA measurements on $\text{Cu}_{1.75}\text{Se}$ and $\text{Cu}_{1.85}\text{Se}$ are shown in Fig. 2. The results look similar for both samples: DSC-curves do not show thermal effects up to 650 K; several consecutive ther-

Fig. 1. XRD patterns of studied samples at room temperature, $\lambda = 1.540562 \text{ \AA}$.

mal effects observed above 650 K are most probably connected with the formation of copper and selenium oxides. These effects correlate to a strong increase of the samples weight observed in TG-curves at that temperature. It should be noted that the $\beta + \alpha \rightarrow \beta$ phase transition in $\text{Cu}_{1.85}\text{Se}$ is not detected in a DSC experiment, however, pure β -phase was observed in diffraction pattern of $\text{Cu}_{1.85}\text{Se}$ at 353 K.

A qualitative overview of the behaviour of the diffraction pattern of Cu_2Se with increasing temperature is shown in Fig. 3. At $T = 423 \text{ K}$ diffraction patterns of Cu_2Se correspond to the superionic β -phase (PDF-2 card [79–1841]). Superionic $\alpha \rightarrow \beta$ phase transition was observed in the DSC-curve at $T \sim 414 \text{ K}$ in good agreement with other authors [21–24] (see Fig. 4). Simultaneously with the $\alpha \rightarrow \beta$ phase transition a release of copper occurs [25] which already starts before the phase transition. A slight increase of the sample weight of Cu_2Se has been observed by TG measurements at temperatures higher than 450 K (Fig. 4). This is connected to an oxidation of free copper. Oxidation of Cu during heating is not yet fully understood [26,27]. The process of releasing copper from Cu_2Se and oxidation of free copper can be analysed on the basis of STA results (Fig. 4)

Fig. 2. TG/DSC results for $\text{Cu}_{1.75}\text{Se}$ and $\text{Cu}_{1.85}\text{Se}$ at heating rate 10 K/min. Solid and dashed lines correspond to DSC-curves $\text{Cu}_{1.75}\text{Se}$ and $\text{Cu}_{1.85}\text{Se}$; closed and open circles correspond to TG-curves for $\text{Cu}_{1.75}\text{Se}$ and $\text{Cu}_{1.85}\text{Se}$.

Fig. 3. Low angle region of some synchrotron powder diffraction patterns ($\lambda = 0.509702 \text{ \AA}$) from Cu_2Se . The changes in diffraction patterns at the $\alpha \rightarrow \beta$ phase transition and appearance of weak diffraction line from Cu_2O can be clearly seen.

and temperature dependence of the lattice parameter in $\beta\text{-Cu}_2\text{Se}$ (Fig. 5).

The temperature dependence of the lattice parameter of $\beta\text{-Cu}_2\text{Se}$ is shown in Fig. 5. Diffraction measurements show a decrease of the lattice parameter in Cu_2Se during heating in the temperature range between $423 < T < 543 \text{ K}$ under two competitive processes: thermal lattice expansion and decrease of copper content. In the consecutive temperature range $543 < T < 573 \text{ K}$ the lattice parameter increases linearly. According to our results copper releasing finishes at about 543 K when the initial composition of Cu_2Se is $\text{Cu}_{1.95}\text{Se}$ and does not change up to 573 K . The composition of $\text{Cu}_{1.95}\text{Se}$ in this temperature range was determined by comparison of the measured lattice parameter with results on $a(T, \delta)$ in $\text{Cu}_{2-\delta}\text{Se}$ published in [21]. At $T = 583 \text{ K}$ a sudden change in the temperature dependence of the lattice parameter occurs, which correlate with a peak in the DSC-curve at $T = 600 \text{ K}$. The peak in the DSC-curve is most probably con-

Fig. 4. TG/DSC results for Cu_2Se at a heating rate 10 K/min . $T_{\alpha 1}$ and $T_{\alpha 2}$ mark changes of slope in TG-curve; $T_{\alpha-\beta}$ marks temperature of the superionic phase transition.

Fig. 5. Temperature dependence of the lattice parameter in $\beta\text{-Cu}_2\text{Se}$ sample (heating). The following temperature ranges are marked on the picture: 1—change of lattice parameter under two competitive processes: thermal lattice expansion and decrease of the copper content; 2—change of lattice parameter, which corresponds to the composition $\beta\text{-Cu}_{1.95}\text{Se}$; 3—change of lattice parameter under further oxidation of the sample.

nected to a formation of Cu_2O ; the first traces of Cu_2O appear in diffraction patterns at $T > 600 \text{ K}$ (Fig. 3). According to [27] CuO and Cu_2O are formed at the heating of bulk copper in dry air at the 458 and 650 K . At $T > 650 \text{ K}$ both copper oxides, Cu_2O and CuO , form a binary film at the surface of bulk copper. At higher temperatures CuO gradually disappears whereas more and more Cu_2O is formed [27]. It should be noted that no diffraction peaks of Cu and CuO have been observed between room temperature and 573 K .

Above 600 K the slope in the TG-curve becomes steeper; the DSC-curve displays several consecutive thermal effects, which can be related to the formation of oxides of selenium and copper (Fig. 4). X-ray diffraction performed on $\text{Cu}_{2-\delta}\text{Se}$ ($\delta = 0, 0.15, 0.25$) samples at room temperature after STA measurements up to 823 K in air, indicate a decomposition to copper oxide CuO (PDF-2 card [45–937]) and copper oxide selenite $\text{Cu}_2\text{O}(\text{SeO}_3)$ (PDF-2 card [46–793]) (see Fig. 6).

Fig. 6. Powder diffraction pattern from mixed phase CuO and $\text{Cu}_2\text{O}(\text{SeO}_3)$ measured on $\text{Cu}_{1.85}\text{Se}$ sample after STA measurements, $\lambda = 1.540562 \text{ \AA}$. Points are experimental data, the line through points is the refined profile and lower plot is the difference between the experimental and refined profiles. The tick marks show the calculated positions of CuO (lower) and $\text{Cu}_2\text{O}(\text{SeO}_3)$ (upper) peaks.

Fig. 7. Synchrotron powder diffraction patterns of β -Cu_{1.75}Se at 293 (a) and 573 K (b); β -Cu_{1.85}Se at 353 (c) and 573 K (d); β -Cu₂Se at 423 (e) and β -Cu_{1.95}Se at 573 K (f) ($\lambda = 0.509702 \text{ \AA}$); points are experimental data, the line through the points is the refined profile, and the lower plot is the difference between the experimental and refined profiles. Tick marks show the calculated positions of β -Cu_{2- δ} Se peaks.

Because of the instability of Cu₂Se, the structure of Cu₂Se has only been analysed between 423–473 K and 553–573 K (with composition Cu_{1.95}Se). Due to oxidation of the samples the maximum temperature in the diffraction measurements on Cu_{1.75}Se,

Cu_{1.85}Se and Cu_{1.95}Se was restricted to 573 K. To verify the phase composition of our samples after synchrotron diffraction, diffraction patterns for all compounds were collected after heating at the lowest initial experimental temperatures.

Fig. 8. Fragment of the synchrotron powder diffraction patterns of $\beta\text{-Cu}_{1.75}\text{Se}$ (a) and $\beta\text{-Cu}_{1.85}\text{Se}$ (b) showing the thermal evolution of the (200) reflection ($\lambda = 0.509702 \text{ \AA}$).

3.2. Structural results

3.2.1. Intensity changes of specific diffraction lines as a function of temperature and thermal expansion

The diffraction patterns of $\beta\text{-Cu}_{1.75}\text{Se}$ ($T = 293$ and 573 K), $\beta\text{-Cu}_{1.85}\text{Se}$ ($T = 353$ and 573 K), $\beta\text{-Cu}_2\text{Se}$ ($T = 423$) and $\beta\text{-Cu}_{1.95}\text{Se}$ ($T = 573 \text{ K}$) are shown in Fig. 7. The continuous decrease of the (200) Bragg reflection at higher temperatures is clearly observed in the diffraction patterns of $\beta\text{-Cu}_{1.75}\text{Se}$ and $\beta\text{-Cu}_{1.85}\text{Se}$ (Fig. 8). Variation of the reflection intensity was attributed to the existence of the low- and high-temperature structure modifications characterized by redistribution and absence of redistribution of copper ions with temperature [4,16].

The temperature dependences of the lattice parameters for $\beta\text{-Cu}_{1.75}\text{Se}$ at $298 < T < 573 \text{ K}$ and $\beta\text{-Cu}_{1.85}\text{Se}$ at $353 < T < 573 \text{ K}$ show weak deviations from linearity and were fitted by a second order polynomial function. Results are shown in Fig. 9. Change of the order polynomial function from the first to second one results in a reduction of the χ^2 to half its value. The

Fig. 9. The unit cell parameter of $\beta\text{-Cu}_{2-\delta}\text{Se}$ ($\delta = 0.05, 0.15, 0.25$) as a function of temperature determined from powder synchrotron diffraction. The lines correspond to approximating functions fitted to experimental points as it is described in the text. The errors on the values are comparable with the size of the symbols.

thermal expansion coefficient defined by $\alpha(T) = \frac{1}{a(T)} \frac{da(T)}{dT}$ was calculated by differentiating the approximating function (see Fig. 10). There were too few experimental points to establish any deviation from linearity in dependence of $a(T)$ for $\text{Cu}_{1.95}\text{Se}$. Under the assumption of linearity for $\text{Cu}_{1.95}\text{Se}$ $\alpha(T)$ is equal to $1.63 \times 10^{-5} \text{ K}^{-1}$. A non-linear increase of the lattice parameter with temperature in the superionic β -phase was reported by Borchert [4]. Tonejc confirmed Borchert's finding [16]; it was stated there that $\alpha(T)$ does not depend on the stoichiometric composition but depends on temperature. However, a linear dependence of $a(T)$ in $\text{Cu}_{1.75-2.00}\text{Se}$ has been reported in [21] that contradicts to [16] and our results. As it can be seen from Fig. 10, the thermal expansion coefficient decreases with temperature and increasing copper content. Borchert and Tonejc tried to explain the abnormal behaviour of $\alpha(T)$ by a redistribution of Cu ions in the selenium fcc rigid cage during heating [4,16]. Since there is no accurate analysis of copper ions distribution in those papers, such an analysis will be presented in the next section of this work.

Fig. 10. Thermal expansion coefficient in $\beta\text{-Cu}_{1.75}\text{Se}$ (solid line), $\beta\text{-Cu}_{1.85}\text{Se}$ (dashed line) and $\beta\text{-Cu}_{1.95}\text{Se}$ (triangles). Empty circles—averaged values for $\beta\text{-Cu}_{2-\delta}\text{Se}$ ($\delta = 0.14-0.28$) [16].

Table 1

Structural models of β -Cu_{1.75}Se at $T = 298$ K; space group $Fm\bar{3}m$, lattice parameter $a = 5.7550(2)$ Å; refined parameters: isotropic thermal displacement B_{Se} , B_{Cu_1} and B_{Cu_2} , copper positional parameters x_{Cu_1} and x_{Cu_2} , copper site occupancies $SITE_{Cu_1}$ and $SITE_{Cu_2}$; parameter constraints: $B_{Cu_1} = B_{Cu_2}$, $SITE_{Cu_2} = 7.00 - SITE_{Cu_1}$

Structural model	$R_B/R_F/\chi^2$	B_{Se} (Å ²)	B_{Cu_1} (Å ²)	x_{Cu_1}	x_{Cu_2}	$SITE_{Cu_1}$, ions per unit cell
1. Cu ₁ in 8c (1/4, 1/4, 1/4)	4.69/3.53/1.55	1.2(1)	3.6(1)			7.00(0)
2. Cu ₁ in 32(f ₁) (x_{Cu_1} , x_{Cu_1} , x_{Cu_1}), 1/4 < x_{Cu_1} < 1/3	3.30/2.61/1.50	1.1(1)	1.4(4)	0.278(2)		7.00(0)
3. Cu ₁ in 8(c) (1/4, 1/4, 1/4); Cu ₂ in 4(b) (1/2, 1/2, 1/2)	3.72/3.73/1.48	1.4(1)	3.4(1)			6.87(4)
4. Cu ₁ in 8(c) (1/4, 1/4, 1/4); Cu ₂ in 32(f ₂) (x_{Cu_2} , x_{Cu_2} , x_{Cu_2}), 1/3 < x_{Cu_2} < 1/2	1.88/1.41/1.51	1.9(2)	2.4(2)		0.386(6)	6.3(1)
5. Cu ₁ in 32(f ₁) (x_{Cu_1} , x_{Cu_1} , x_{Cu_1}), 1/4 < x_{Cu_1} < 1/3; Cu ₂ in 32(f ₂) (x_{Cu_2} , x_{Cu_2} , x_{Cu_2}), 1/3 < x_{Cu_2} < 1/2	1.87/1.58/1.41	2.3(2)	0.1(6)	0.230(3)	0.377(4)	6.3(1)

3.2.2. Time averaged structure

The copper ion distribution has been analysed by different structural models in which the fcc lattice array is formed by selenium atoms and copper cations are distributed over different interstitial sites with overall symmetry $Fm\bar{3}m$. Great care was taken to ensure that data have not been overinterpreted by models with an inappropriately large number of structural parameters. This quite simple analysis allows us to establish differences in the time average distribution of copper related to different stoichiometric compositions of the copper selenide β -Cu_{2- δ} Se and its temperature dependence.

We used the so-called “split-site” model (SSM) to introduce a disorder in β -Cu_{2- δ} Se. For instance, in the frame of the SSM each of the 8(c) and 4(b) sites (space group $Fm\bar{3}m$) are split into four 32(f₁) sites at (x , x , x) with 1/4 < x < 1/3 and 32(f₂) at (x , x , x) with 1/3 < x < 1/2. Occupation of the 32(f) positions results in $\langle 111 \rangle$ as preferred direction for the motion; whereas a distribution of ions over 48(g) sites at (x , 1/4, 1/4) results in $\langle 100 \rangle$ as preferred direction of motion. Attempts to apply anisotropic atomic displacement parameters in conjunction with SSM have been performed also. The deviations from the average lattice site are mimicked by the thermal displacement. Examples of experimental and calculated diffraction pattern for Cu_{1.75}Se, Cu_{1.85}Se and Cu₂Se with the most reliable structure model are shown in Fig. 7.

Tables 1 and 2 show a number of models for the disordered structures of the cations in β -Cu_{2- δ} Se for Cu_{1.75}Se as example.

Model #1 is the ideal anti-fluorite structure formed by the selenium sublattice with copper cations located at the tetrahedral interstices at the 8(c) site. Model #1 can be considered as a starting point, which gave rather good refinement results for all samples. An improved agreement in the refinement was obtained by a variation of the occupancy of the copper sites. A lower copper content than estimated from stoichiometry was then obtained. This is a clear indication of disorder but does not give any information about the actual position.

Model #2 mimics the effect of anharmonicity by splitting the 8(c) (1/4, 1/4, 1/4) cation site into 32(f₁) (x , x , x) sites. Instead of one single copper cation located in the centre of the tetrahedron, the cation is distributed over a set of four symmetry equivalent sites, which are shifted off the centre of the tetrahedra in $\langle 111 \rangle$ direction. In the refinement process the x value of the 32(f₁) site and the isotropic thermal displacement factors for copper and selenium ions were refined. The total content of copper ions in the unit cell was fixed according to stoichiometry. This model gives better fit with respect to the agreement factor than Model #1.

Model #3 contains an additional possible position for the copper ions in the ideal octahedral 4(b) site. This model also produces improvements in the fitting and the isotropic temper-

Table 2

Structural models of β -Cu_{1.75}Se at $T = 573$ K; space group $Fm\bar{3}m$, lattice parameter $a = 5.7981(1)$ Å; refined parameters: isotropic thermal displacement B_{Se} , B_{Cu_1} and B_{Cu_2} , copper positional parameters x_{Cu_1} and x_{Cu_2} , copper site occupancies $SITE_{Cu_1}$ and $SITE_{Cu_2}$; parameter constraints: $B_{Cu_1} = B_{Cu_2}$, $SITE_{Cu_2} = 7.00 - SITE_{Cu_1}$

Structural model	$R_B/R_F/\chi^2$	B_{Se} (Å ²)	B_{Cu_1} (Å ²)	x_{Cu_1}	x_{Cu_2}	$SITE_{Cu_1}$, ions per unit cell
1. Cu ₁ in 8(c) (1/4, 1/4, 1/4)	7.27/3.55/1.79	1.6(2)	8.7(3)			7.00(0)
2. Cu ₁ in 32(f ₁) (x_{Cu_1} , x_{Cu_1} , x_{Cu_1}), 1/4 < x_{Cu_1} < 1/3	5.01/3.21/1.57	1.4(1)	2.6(3)	0.296(1)		7.00(0)
3. Cu ₁ in 8(c) (1/4, 1/4, 1/4); Cu ₂ in 4b (1/2, 1/2, 1/2)	5.93/5.47/1.64	2.4(1)	9.0(3)			6.62(9)
4. Cu ₁ in 8(c) (1/4, 1/4, 1/4); Cu ₂ in 32(f ₂) (x_{Cu_2} , x_{Cu_2} , x_{Cu_2}), 1/3 < x_{Cu_2} < 1/2	2.02/2.60/1.35	3.8(2)	5.3(3)		0.375(3)	5.4(1)
5. Cu ₁ in 32(f ₁) (x_{Cu_1} , x_{Cu_1} , x_{Cu_1}), 1/4 < x_{Cu_1} < 1/3; Cu ₂ in 32(f ₂) (x_{Cu_2} , x_{Cu_2} , x_{Cu_2}), 1/3 < x_{Cu_2} < 1/2	2.09/2.64/1.35	3.8(2)	5(1)	0.25(6)	0.375(4)	5.4(2)

ature factor of the copper ions in the octahedral sites was very large, if no constrain $B_{\text{Cu}_1} = B_{\text{Cu}_2}$ was applied.

Model #4 includes two possible positions for the copper ions: the ideal tetrahedral 8(c) site and the 32(f_2) site ($1/3 < x < 1/2$), where the copper ions are distributed between sites away from $(1/2, 1/2, 1/2)$ in $\langle 111 \rangle$ directions within the octahedral voids.

In Model #5 the 8(c) and 4(b) were splitted simultaneously into 32(f_1) and 32(f_2) sites. In analogy to Models #1–4 the total content of copper ions in the unit cell was fixed. However, correlation between the parameters was rather high for a reliable determination.

Attempts were made to refine data with a splitting of 8(c) into 48(g) splitted sites ($x, 1/4, 1/4$) (Cu ion disordering in $\langle 100 \rangle$ directions) or with anisotropic temperature factors in some of the models. However, all these models give a very high correlation of the parameters and instability under refinement. Model #4 is therefore the preferred average structure model for this phase, not only because of the marginally better fitting, but also because it has a more realistic Cu thermal displacement factor and disordering is towards the faces of the octahedra, rather than the octahedra edges.

The results of the modelling can be summarized as follows. Copper ions are distributed predominantly over the tetrahedrally coordinated sites with a significant cation density in the octahedral interstices. In addition the occupancy of the 32(f_2) sites indicates that copper ions within the tetrahedral cavities undergo extensive anharmonic thermal vibrations in the $\langle 111 \rangle$ directions and will, on occasion, venture into a neighbouring octahedron. However, the cation does not undergo diffusion in this direction through the centre of the octahedron, which is the 4(b) ($1/2, 1/2, 1/2$) position. Considerable decrease of R -Bragg factor at the splitting of 4(b) site to the 32(f_2) positions and huge thermal displacement factor for copper ions in 4(b) position shows that the ideal octahedral site may actually be a minimum in the cation density and the octahedral sites should, therefore, be considered as avoided rather than occupied. Therefore, a cation diffusion mechanism with cation jumps between nearest neighbour sites via the periphery of the octahedral interstitials in the model proposed (Fig. 11). The diffusion pathway does not exactly correspond to $\langle 111 \rangle$ or $\langle 100 \rangle$; it can be named as a “skewed” $\langle 100 \rangle$ direction rather than $\langle 111 \rangle$ direction.

The temperature dependence of the structure parameters in the frame of the Model #4 can be described as follows. The isotropic thermal displacement parameters B_{Se} , B_{Cu_1} and B_{Cu_2} increase monotonically with temperature in all compounds; the copper positional parameter x_{Cu_2} is temperature independent in the limit of the experimental error. The copper population in the 32(f_2) lattice site increases with copper content. Population in 32(f_2) lattice site increases with temperature and simultaneous decrease in the 8(c) sites according to constraints in the refinement. The redistribution of copper ions between the 32(f_2) and 8(c) positions with temperature is more pronounced in $\text{Cu}_{1.75}\text{Se}$ than in $\text{Cu}_{1.85}\text{Se}$ and $\text{Cu}_{1.95}\text{Se}$ as displayed in Fig. 12. The temperature dependence of the copper population of 32(f_2) sites in $\text{Cu}_{1.75}\text{Se}$ is characterized by two regions with different rate of increase of the site occupancy; the change of slope takes place at 470 K that correlates with the temperature of disappearance

Fig. 11. Schematic diagram of the structure of $\beta\text{-Cu}_{1.75}\text{Se}$ at room temperature (a) and at 423 K (b). These pictures correspond to the structural Model #4, which is described in Tables 1 and 2.

of the (200) Bragg reflection. Occupancy of the 32(f_2) sites in $\text{Cu}_{1.85}\text{Se}$ increases with temperature without any variation in its temperature dependence.

Despite the simplicity of our model and the absence of analysis of anisotropic terms, the results give additional indications of diffusion for $\beta\text{-Cu}_{2-\delta}\text{Se}$ ($\delta = 0, 0.15, 0.25$). In the frame of SSM static disorder and anharmonicity of the thermal vibration of mobile ions are modelled by splitting of ideal tetrahedral and octahedral sites to a group of crystallographically equivalent sites. Though both these contributions are not distinguishable, our results show a diffusion pathway in $\beta\text{-Cu}_{2-\delta}\text{Se}$: through the

Fig. 12. Copper site occupancies of 32(f₂) at (x_{Cu_2} , x_{Cu_2} , x_{Cu_2}) with $1/3 < x_{\text{Cu}_2} < 1/2$ in $\beta\text{-Cu}_{1.75}\text{Se}$ (full squares), $\beta\text{-Cu}_{1.85}\text{Se}$ (empty circles), $\beta\text{-Cu}_{1.95}\text{Se}$ (inverse triangles) and $\beta\text{-Cu}_2\text{Se}$ (triangle).

periphery of the octahedral cavities. The occupancy of the 32(f₂) sites should be a limiting factor for copper ion diffusion. This is confirmed by the ionic conductivity measurements, which have shown that ionic conductivity in $\text{Cu}_{1.75}\text{Se}$ is several times lower than in Cu_2Se at the same temperature [1,2]. Regardless of the superionic β -phase, conductivity in $\text{Cu}_{1.75}\text{Se}$ should be lower than in Cu_2Se and $\text{Cu}_{1.85}\text{Se}$ due to a low occupation of the 32(f₂) sites. Changes of copper population in the 32(f₂) sites with temperature in $\text{Cu}_{1.75}\text{Se}$ and $\text{Cu}_{1.85}\text{Se}$ correlate with anomalous behaviour of thermal expansion coefficient and disappearance of the (2 0 0) diffraction line in the patterns of $\beta\text{-Cu}_{2-\delta}\text{Se}$ reported in [4,16].

4. Summary

Diffraction, thermogravimetry and differential scanning calorimetry measurements revealed the thermal behaviour of copper selenide $\text{Cu}_{2-\delta}\text{Se}$ at a wide range of temperature. Copper selenide is unstable under heating in air and decompose into Cu and Se, which in its turns oxidize. Therefore, the time average structure of copper selenide has been analyzed at their temperature range of existence.

The detailed powder diffraction studies described in this paper have shown that time average distribution of copper ions can be described in the frame of the same model for all compounds studied (space group $Fm\bar{3}m$). Cu undergoes thermal vibrations about ideal tetrahedral sites and along $\langle 111 \rangle$ directions, but diffuse to neighboring sites along “skewed” $\langle 100 \rangle$ directions. The ideal octahedral site 4(b) is not occupied. The copper density near the boundary of the octahedral and tetrahedral voids increases with temperature and total copper content in $\beta\text{-Cu}_{2-\delta}\text{Se}$. Occupancy of 32(f) sites with copper in (x ,

x , x), $1/3 < x < 1/2$ appear to be a limiting factor of the diffusion. Anomalous behaviour of the thermal expansion coefficient observed in $\beta\text{-Cu}_{1.75}\text{Se}$ and $\beta\text{-Cu}_{1.85}\text{Se}$ is associated with a redistribution of copper ions between 8(c) and 32(f) sites with temperature. Temperature and composition dependence of copper ions distribution between different interstitial sites is a possible explanation for a number of different structural models of $\beta\text{-Cu}_{2-\delta}\text{Se}$ which are given in literature.

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