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## Synthesis and crystal structure of $\beta$ -CuSe<sub>2</sub>O<sub>5</sub>, a new polymorph of copper diselenite

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In contrast to the layered structure of the previously known polymorph of copper diselenite, the crystal structure of a new polymorph,  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub>, is based on a 3D framework and has a higher structural complexity than the  $\alpha$ -phase.

(b)

β-CuSe<sub>2</sub>O

Recently, a large number of theoretical and experimental studies were devoted to industrially important inorganic copper compounds.<sup>1</sup> At the same time, selenium-containing oxo compounds are versatile materials in terms of a broad structural diversification.<sup>2,3</sup> The electronic properties of Se<sup>4+</sup> lead to materials with specific physical properties <sup>4,5</sup> owing to the presence of lone-pair electrons along with the Jahn–Teller effect typical of Cu<sup>2+</sup> ions with the  $d^9$  electron configuration.

Previously, we studied novel crystalline phases prepared by chemical vapour transport (CVT) reactions in the Cu–Se oxychloride system, which demonstrated a fascinated variety of structural architectures.<sup>6–9</sup> Many of the synthesized copper oxide phases prepared by this technique contain so-called 'additional' oxygen atoms, which are coordinated solely by copper cations.<sup>10</sup> In addition to a series of new compounds with complex crystal structures, our crystallization experiments using CVT reactions also lead to the formation of two polymorphs of simple selenite phases. Both of them, *i.e.*, recently reported new modification of selenious acid H<sub>2</sub>SeO<sub>3</sub><sup>11</sup> and the new form of CuSe<sub>2</sub>O<sub>5</sub> presented in this work, are very hygroscopic and metastable at room temperature and atmospheric pressure.

The only known polymorph of CuSe<sub>2</sub>O<sub>5</sub> (denoted herein as  $\alpha$ -CuSe<sub>2</sub>O<sub>5</sub>) was first described in 1976,<sup>12</sup> and then re-investigated in 2006.<sup>13</sup> The  $\alpha$ -modification is of interest for its specific magnetic behaviour, which was the subject matter of extensive studies.<sup>14–16</sup> Analysis of the new modification of CuSe<sub>2</sub>O<sub>5</sub> (denoted as  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub>), as detailed below, reveals its close structural relations to CuTe<sub>2</sub>O<sub>5</sub>.<sup>17</sup> The latter also has been intensively studied owing to its unusual magnetic and vibrational properties.<sup>18–20</sup>

Herein, we report the synthesis and structural characterization of a new modification of copper diselenite,  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub>, and discuss structural relations between the two polymorphs.

Single crystals [Figure 1(*a*)] of  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub> **1** have been prepared by CVT reactions<sup>†</sup> at 550 °C in a sealed silica ampoule from a mixture of CuO, CuCl<sub>2</sub>, SeO<sub>2</sub>, NaCl, and PbO taken in a



**Figure 1** Optical microscopy images of (*a*)  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub> and (*b*)  $\alpha$ -CuSe<sub>2</sub>O<sub>5</sub> crystals; (*c*) coordination of Se<sub>2</sub>O<sub>5</sub> and Cu<sub>2</sub>O<sub>10</sub> groups in  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub>. Interatomic distances are given in angstrom units. Displacement ellipsoids are drawn at a 50% probability level.

<sup>†</sup> A mixture of CuO (2 mmol, Alfa Aesar, 99%), CuCl<sub>2</sub> (1.5 mmol, Aldrich, 99%), SeO<sub>2</sub> (1 mmol, Alfa Aesar, 99%), NaCl (1 mmol, Alfa Aesar, 99%), and PbO (0.5 mmol, Aldrich, 99%) was used for the preparation of single crystals of β-CuSe<sub>2</sub>O<sub>5</sub>. Precursors were predried at 100 °C for 2 h and further rapidly mixed and ground in an agate mortar in air for 5 min. Then, the mixture was also dried at 100 °C for 1 h. Afterwards, it was loaded into a silica ampoule ( $\sim 15 \times 0.9$  cm), which was evacuated for 20 min to a pressure of 10<sup>-2</sup> mbar and then sealed. The ampoule was placed horizontally in a tubular furnace so that the precursor-filled zone was situated in the central part of the furnace, while the opposite precursor-free zone was turned out toward the furnace edge. This edge remained uncapped in the course of the experiment to create temperature gradient  $\Delta T \approx 50$  °C between the two zones of the ampoule. The furnace was heated to 550 °C for three days. Then, the temperature was lowered to 400 °C during 6 h. Afterwards, the furnace was switched off. Block-shaped blue single crystals of  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub> were found in a small amount in the deposition zone of the ampoule in association with transparent needles of recently reported new polymorph of H<sub>2</sub>SeO<sub>3</sub>.<sup>11</sup> The resulted crystals of these two phases were metastable and hygroscopic at room temperature and ambient pressure, and they were gradually dissolved in the next three days.

Table 1 Crystallographic data for  $\alpha$ -CuSe<sub>2</sub>O<sub>5</sub>,<sup>13</sup>  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub> 1, and CuTe<sub>2</sub>O<sub>5</sub>.<sup>17</sup>

Crystal	$M/\mathrm{g}~\mathrm{mol}^{-1}$	Space group	a/Å	b/Å	c/Å	$\beta$ /deg	$V/\text{\AA}^3$	Ζ	$d_{\rm calc}/{\rm g~cm^{-3}}$	$\mu/\mathrm{mm}^{-1}$
$\alpha$ -CuSe <sub>2</sub> O <sub>5</sub> <sup>13</sup>	301.46	C2/c	12.3869(19)	4.8699(7)	7.9917(13)	111.953(15)	447.13	4	4.478	21.08
β-CuSe <sub>2</sub> O <sub>5</sub>	301.46	$P2_{1}/c$	6.918(3)	8.8172(4)	7.5714(4)	108.570(2)	440.56(4)	4	4.545	21.39
CuTe <sub>2</sub> O <sub>5</sub> <sup>17</sup>	398.75	$P2_{1}/c$	6.871(2)	9.322(2)	7.602(2)	109.08(1)	460.17(2)	4	5.755	17.73

molar ratio of 2:1.5:1:1:0.5. Note that the CVT experiments performed in a temperature range of 250-550 °C (50 °C per step) with a mixture of CuO and SeO<sub>2</sub> taken in a ratio of 1:2 did not result in the crystallization of **1**, but they led to the formation of  $\alpha$ -CuSe<sub>2</sub>O<sub>5</sub> [Figure 1(*b*)],<sup>13</sup> Cu(HSeO<sub>3</sub>)<sub>2</sub>,<sup>21</sup> and  $\beta$ -H<sub>2</sub>SeO<sub>3</sub>.<sup>11</sup> The absence of the  $\beta$ -polymorph in this case can be explained by the absence of Cl<sup>-</sup> ions involved in the CVT reactions. Earlier, it was demonstrated<sup>2,6,8</sup> that the selenite systems containing Cl<sup>-</sup> anions exhibit a noticeably greater structural variety than Cl-free systems and that chlorine acts as both a transport agent and a structureforming component in such systems. Note that, despite the preliminary drying of precursors, final products have been found to contain hydroselenites, which suggest that absorbed water together with hydrogen halides can also play an important role in the system.

The structure of **1** was studied using single-crystal X-ray diffraction analysis.<sup>‡</sup> The new phase  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub> is isotypic with the previously reported CuTe<sub>2</sub>O<sub>5</sub>,<sup>17</sup> which so far was reported to exist in one form only. Selected structural data for  $\alpha$ -CuSe<sub>2</sub>O<sub>5</sub>,  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub>, and CuTe<sub>2</sub>O<sub>5</sub> are given in Table 1.

The crystal structure of **1** contains one crystallographically independent Cu site, which has a Jahn–Teller-distorted octahedral coordination with the four short Cu–O bonds (1.948–1.975 Å) that define a CuO<sub>4</sub> square complemented by two longer Cu–O bonds (2.268 and 2.680 Å).

In the structure of 1, there are two Se sites in a triangular pyramidal coordination with Se atoms located at the apices, in agreement with the stereochemical activity of lone electron pairs. Two SeO<sub>3</sub> pyramids share a common O(1) atom to form a Se<sub>2</sub>O<sub>5</sub> diselenite group [Figure 1(c)]. The bridging Se–O(1)<sub>br</sub> distances (1.823 Å) are essentially longer than the terminal Se–O<sub>t</sub> bonds (1.675 Å). This type of a dimeric unit is quite common for metal selenites, and it was observed, e.g., in the series of compounds with the general formula  $MSe_2O_5$  ( $M^{2+} = Mn$ , Co, Cu, Pd, Zn, Cd, Pb, Mg, Ca, Sr, and Ba). The structural analysis of phases in this group revealed the steric flexibility of the diselenite group due to the rotation of selenite pyramids around the O<sub>br</sub> bridging corner. It is also noteworthy that, in most cases, the diselenite group has a twofold symmetry axis with one crystallographically independent Se site, whereas compound 1 and several phases with large cations, such as BaSe<sub>2</sub>O<sub>5</sub>,<sup>22</sup> SrSe<sub>2</sub>O<sub>5</sub>,<sup>23</sup> CaSe<sub>2</sub>O<sub>5</sub>,<sup>24</sup> and PbSe<sub>2</sub>O<sub>5</sub>,<sup>25</sup> contain two inequivalent Se sites.

In the crystal structure of  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub>, two CuO<sub>6</sub> octahedra share a common O···O edge to form a dimeric Cu<sub>2</sub>O<sub>10</sub> unit with the Cu···Cu distance of 3.267 Å [Figure 1(*c*)]. The shortest interdimeric Cu···Cu distance is about 5.17 Å. The copper dimers



Figure 2 Projections of the crystal structure of  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub>. Cu, Se, and O atoms are shown by cyan, orange, and red balls, respectively.

linked *via* diselenite groups are oriented along [101], as shown in Figure 2(a).

In the two isotypic phases,  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub> and CuTe<sub>2</sub>O<sub>5</sub>,<sup>17</sup> the main difference between their lattice parameters is in the *b* parameter, which differs by  $\Delta b \approx 0.5$  Å. Structurally this can be easily explained by the fact that the distance along the *b*-axis between the copper dimers parallel to (010) is controlled by the size of the Se<sub>2</sub>O<sub>5</sub> and Te<sub>2</sub>O<sub>5</sub> groups.

In contrast to the 3D framework structure of  $\beta$ -CuSe<sub>2</sub>O<sub>5</sub> consisting of copper dimeric units (Figure 2), the crystal structure of  $\alpha$ -CuSe<sub>2</sub>O<sub>5</sub> is based upon the corrugated chains of cornersharing octahedra linked by Se<sub>2</sub>O<sub>5</sub> groups to form layers parallel to (100). Owing to such contrasting architectures of the two polymorphs, they differ in their unit-cell volumes (447.13 Å<sup>3</sup> for the  $\alpha$ -phase *vs.* 440.56 Å<sup>3</sup> for the  $\beta$ -phase) and density (4.478 *vs.* 4.545 g cm<sup>-3</sup>, respectively). Therefore, it is of interest to compare two polymorphs in terms of their structural complexity expressed by a Shannon information content per atom and per unit cell.<sup>26,27</sup>

The calculations using the ToposPro<sup>28</sup> software indicated that the  $\beta$ -polymorph ( $I_G = 3.00$  bits per atom,  $I_{G,total} = 96.00$  bits per cell) is more complex than the  $\alpha$ -polymorph ( $I_G = 2.25$  bits per atom,  $I_{G,total} = 36.00$  bits per cell). The higher complexity of the framework-based  $\beta$ -phase compared to the layered  $\alpha$ -phase agrees quite well with their higher density mentioned above. In general, we suggest that the  $\beta$ -phase reported here can be a lowtemperature (or high-pressure) polymorph of copper diselenite. Generally, a high-temperature polymorph is structurally simpler

<sup>&</sup>lt;sup>‡</sup> Intensities of 3386 reflections were measured with a Bruker X8 APEX II CCD diffractometer [ $\lambda$ (MoK $\alpha$ ) = 0.71073 Å, a  $\theta$  range of 3.1–31.5°] and 1459 independent reflections ( $R_{int} = 0.030$ ) were used in a further refinement. The unit-cell parameters are given in Table 1. The structure of **1** was solved by a direct method and refined by the full-matrix leastsquares technique against  $F^2$  in the anisotropic approximation. The refinement converged to  $wR_2 = 0.0362$  and GOF = 1.061 for all independent reflections [ $R_1 = 0.0167$  was calculated against  $F^2$  for 1305 observed reflections with  $F^2 > 2\sigma(F^2)$ ]. All calculations were performed using SHELXL-2013 program.<sup>32</sup>

CSD 431114 contains the supplementary crystallographic data for this paper. These data can be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, http://www.fiz-karlsruhe.de/.

than its low-temperature counterpart (due to an increase in both vibrational and configurational entropies<sup>29</sup>), which, together with the data on density and unit-cell volumes, strongly suggest that the  $\alpha$ - and  $\beta$ -modifications of CuSe<sub>2</sub>O<sub>5</sub> are high- and low-temperature polymorphs, respectively. This conclusion is consistent with the 2D and 3D characters of their structures, respectively, which is frequently observed in polymorphic inorganic compounds (that is, the structural dimensionality of a low-temperature polymorph is higher than that of its high-temperature counterpart<sup>30,31</sup>).

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