Extended Occupational and Positional Disorder in Pavonite Homologous Copper Bismuth Chalcogenide Halogenides

Andreas Heerwig, Cyril Louis Jaques Thybaut, Michael Ruck

► To cite this version:

Andreas Heerwig, Cyril Louis Jaques Thybaut, Michael Ruck. Extended Occupational and Positional Disorder in Pavonite Homologous Copper Bismuth Chalcogenide Halogenides. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2010, 636 (13-14), pp.2433. 10.1002/zaac.201000177 . hal-00592050

HAL Id: hal-00592050

<https://hal.science/hal-00592050>

Submitted on 11 May 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Zeitschrift für Anorganische und
Allgemeine Chemie

Extended Occupational and Positional Disorder in Pavonite Homologous Copper Bismuth Chalcogenide Halogenides

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000177.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	06-May-2010
Complete List of Authors:	Heerwig, Andreas; Technische Universität Dresden, Fachrichtung Chemie und Lebensmittelchemie Thybaut, Cyril Louis Jaques; Technische Universität Dresden, Fachrichtung Chemie und Lebensmittelchemie Ruck, Michael; Technische Universität Dresden, Fachrichtung Chemie und Lebensmittelchemie
Keywords:	Bismuth, Copper, One-dimensional ionic conductors, Pavonite, Thermoelectrics

Extended Occupational and Positional Disorder in Pavonite Homologous
Copper Bismuth Chalcogenide Halogenides

Andreas Heerwig^[a], Cyril Louis Jaques Thybaut^[a], and Michael Ruck^{*[a]}

Keywords: Bismuth; Copper; One-dimensional ionic conductors; Pavonite; Thermoelectrics

Running title: Copper Bismuth Chalcogenide Halogenides

[a] Prof. Dr. M. Ruck, Dr. C. L. J. Thybaut, Dipl.-Chem. A. Heerwig

Fachrichtung Chemie und Lebensmittelchemie,

Technische Universität Dresden,

D-01062 Dresden, Germany

Fax: +49-351-463-37287

E-mail: michael.ruck@chemie.tu-dresden.de

Abstract. Melting reactions of CuBr, BiBr₃ and Bi₂Q₃ (Q = S or Se) resulted in black needles of quaternary chalcogenide bromides. Cu_{1.5}Bi_{2.64}S_{3.42}Br_{2.58} has a melting point of 708(5) K and crystallizes in the monoclinic space group *C2/m* with *a* = 1315.1(3) pm, *b* = 410.28(5) pm, *c* = 937.2(2) pm, β = 90.33(2) ° at *T* = 293(2) K. The isostructural selenide Cu_{1.57}Bi_{2.37}Se_{2.68}Br_{3.32}, which melts at 724(5) K, has the lattice parameters *a* = 1353.9(3) pm, *b* = 417.54(5) pm, *c* = 960.4(2) pm, β = 91.13(2) °. Black needles of the selenide iodides Cu_{1.57}Bi_{4.69}Se_{7.64}I_{0.36} and Cu_{2.31}Bi₅Se_{8.31}I_{0.69} were obtained by chemical vapor transport of CuI and Bi₂Se₃. They also crystallize in space group type *C2/m* with *a* = 1373.9(4) pm, *b* = 417.4(1) pm, *c* = 1464.6(4) pm, β = 115.57(2) °, and *a* = 1369.1(3) pm, *b* = 416.6(1) pm, *c* = 1526.4(3) pm, β = 99.81(3) °, respectively. All four compounds belong to pavonite homologous series. Their structures are built up of two alternating types of layered modules parallel (001), denoted *A* and *B*. Composition and shape of module *A* are almost the same in all structures. They consist of paired rods $^1_{\infty}[\text{Bi}Q_{3/3}X_{2/2}Z_{2/2}]$ (*Z* = *Q/X*; *X* = Br, I) running along [010] and copper(I) cations that are distributed over various voids between the rods. Modules of type *B* are composed of [*MZ*₆] octahedra (*M* = Bi/Cu), which are arranged in NaCl-type fragments of thickness *N* = 1, 3 or 4. The Joint Probability Density Function (JPDF) reveals a continuous pathway for copper ion transport along [010] in the case of the sulfide bromide. The pseudo-potential for hopping of copper ions was calculated as 47 meV only. The electrical and thermal conductivities as well as the Seebeck coefficient were determined to evaluate the thermoelectric properties.

Introduction

Potentially good thermoelectric materials should have a sufficiently high electrical conductivity σ , a poor thermal conductivity κ , and a large Seebeck coefficient S . These parameters are combined in the dimensionless figure of merit $ZT = S^2 \cdot \sigma \cdot T / \kappa$ [1]. Within the phonon-glass electron-crystal model [2], small band gap semiconductors with only partial structural order are favored. Metallic characteristics are not desired, because high electronic conductivity is usually accompanied by high thermal conductivity [1]. Chalcogenides of heavy atoms like mercury, lead, or bismuth are well-known basic thermoelectrics, which can be improved further by chemical modification or nanostructuring [1]. An example for the first approach is $\text{K}_2\text{Bi}_8\text{Se}_{13}$, where the degree of mixed occupancies for Bi/K-positions strongly influences the thermoelectric parameters [3]. Parallel occupational disorder of cations as well as anions was found in silver bismuth chalcogenide halogenides, a wide class of compounds with tunable compositions, structures, and band gaps [4–11]. In the corresponding quaternary systems that are based on copper instead of silver an additional feature appears: positional disorder or even mobility of cations [12]. This unique combination of structural characteristics raises expectations for potentially good performance in thermoelectric energy conversion. Here we report on the syntheses, crystal structures and properties of four copper bismuth chalcogenide halogenides with a common structural principle: $\text{Cu}_{1.5}\text{Bi}_{2.64}\text{S}_{3.42}\text{Br}_{2.58}$ (**I**), $\text{Cu}_{1.57}\text{Bi}_{2.37}\text{Se}_{2.68}\text{Br}_{3.32}$ (**II**), $\text{Cu}_{1.57}\text{Bi}_{4.69}\text{Se}_{7.64}\text{I}_{0.36}$ (**III**), and $\text{Cu}_{2.31}\text{Bi}_5\text{Se}_{8.31}\text{I}_{0.69}$ (**IV**).

Experimental Part

Syntheses

The starting materials for the syntheses of the chalcogenide bromides (**I**) and (**II**) were BiBr_3 (Alfa Aesar, 99.9 %; sublimated twice), CuBr (Fluka, > 98.0 %; purified according to [13]), Bi_2S_3 (Alfa Aesar, 99.9 %) or Bi_2Se_3 , which had been synthesized from Bi (Riedel de Haën, chemically pure; treated with H_2 at 520 K) and Se (Fluka, 99.99 %). In an argon filled glove box (M. Braun, $c(\text{O}_2) \leq 1$ ppm, $c(\text{H}_2\text{O}) \leq 1$ ppm), silica ampoules (150 mm in length, 15 mm inner diameter) were

loaded with about 1 g of approximately stoichiometric mixtures. In a tubular furnace, the evacuated ($p \approx 0.1$ Pa) and sealed ampoules were heated to 770 K, cooled to 620 K with $\Delta T / t = 1$ K/h, and tempered at 620 K for one week before quenching in water. The products consisted of needle-shaped black platelets with shiny surfaces. The compounds are inert to water and alcoholic solvents, but decompose in inorganic acids.

The selenide iodides were obtained in a similar procedure, starting from CuI (Riedel de Haen, > 99 %) and Bi_2Se_3 in the molar ratio 1 : 1 in case of (III) and 3 : 2 in case of (IV). The mixtures were heated to 670 K for five days, before they were placed in a temperature gradient from 670 K to 620 K. After one week, black and shiny needles had grown at the cooler end.

Thermal Analyses

Powdered samples of (I) and (II) ($m \approx 30$ mg) sealed in evacuated ($p \approx 0.1$ Pa) silica micro-ampoules were analyzed using a DTA-DSC device (Labsys DSC 12, Setaram). With a rate of $\Delta T / t = 5$ K/min the samples were heated to 770 K and subsequently cooled to ambient temperature. The residua of the thermal analysis were characterized by X-ray powder diffraction.

Thermoelectric measurements

Powdered and pressed samples of (I) and (II) with the dimensions $l = 35$ mm, $w = 15$ mm and $h = 10$ mm were analyzed for electrical and thermal conductivity as well as Seebeck coefficient in the temperature range between 2.9 K and 305 K with a step width of about 6 K using a Quantum Design PPMS with thermal transport option.

Crystallographic Structure Determinations

Powder diffractograms were measured with a Stadi-P diffractometer (Stoe) equipped with a position sensitive detector using $\text{Cu-K}\alpha_1$ radiation. Single-crystals of all four compounds were examined using Buerger precession method (Zr-filtered Mo radiation, imaging plate technique). The

collection of reflection intensities was carried out with a single-crystal diffractometer using monochromatized Mo- $K\alpha$ -radiation (IPDS I or II, Stoe; CAD 4, Enraf-Nonius) at 293(2) K (Table 1). The optically determined crystal descriptions were optimized using symmetry equivalent reflections [14] in case of IPDS data and ψ -scans in case of CAD 4 data. After the numerical absorption corrections [15], the structure solutions and refinements succeeded using direct methods and subsequent difference Fourier syntheses [16]. Due to the very similar X-ray scattering factors, the assignment of Se and Br atoms to the anion positions in **(II)** is based on bond-length bond-strength considerations [17]. For all Cu1x atoms on partially occupied sites only one (isotropic) displacement parameter was refined. The same holds for spatially separated mixed occupied positions Z = Se/I in **(III)** and **(IV)**. Anisotropic displacement parameters were determined for the other positions. In the case of mixed occupied sites $M = \text{Bi/Cu}$ or $Z = \text{Q/Br}$ the same atomic parameters were applied. In order to assure charge balance, the sum of occupancies of the Cu sites and the occupancy ratios of the mixed sites were constrained. Maxima of the residual electron density are close to heavy atom positions and seem to be artifacts of the structural disorder. Atomic parameters are listed in Tables 2 to 4. Selected interatomic distances can be found in Tables 5 and 6.

Further data, in the form of CIFs, have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (E-mail address: crysdata@fiz-karlsruhe.de), as supplementary material no. CSD-421681 **(I)**, CSD-421682 **(II)**, CSD-421683 **(III)**, and CSD-421684 **(IV)**. Graphical representations of the crystal structures were developed with Diamond [18].

In the case of the bromides, the Cu1 disorder can be described with only one anharmonically refined copper position [19]: **(I)** Cu1 in $\frac{1}{2}$, 0.18(2), 0 and a fourth order tensor; **(II)** Cu1 in $\frac{1}{2}$, 0.10(2), 0 and a third order tensor. For **(III)** two positions are necessary: one in $\frac{1}{2}$, 0.09(1), 0 with a third order tensor, and the other in 0.5460(9) $\frac{1}{2}$, 0.072(1) with a second order tensor (harmonically refined). In the case of **(IV)**, the same refinement strategy resulted in the positions $\frac{1}{2}$, 0.09(1), 0 and 0.528(1), $\frac{1}{2}$, 0.0660(9). All four anharmonic refinements do not show large negative residual

1
2 electron densities and can be regarded as adequate descriptions of the disorder [19]. Since the Joint
3
4 Probability Density Function (JPDF) of (**I**) reveals a continuous pathway, one particle potentials
5
6 and their errors were determined [19, 20]. The program VESTA was used for visualizing the JPDF
7
8
9 [21].
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 1. Crystallographic data and details of the structure refinements.

Compound no. (I)	(II)		(III)	(IV)
Composition	Cu _{1.49(6)} Bi _{2.646(1)} S _{3.42(2)} Br _{2.58(2)}	Cu _{1.57(5)} Bi _{2.370(1)} Se _{2.68(2)} Br _{3.32(2)}	Cu _{1.57(2)} Bi _{4.690(1)} Se _{7.640(8)} I _{0.360(8)}	Cu _{2.31(3)} Bi _{5.00(1)} Se _{8.31(1)} I _{0.69(1)}
<i>T</i> / K	293(2)			
Crystal system	monoclinic			
Space group	<i>C2/m</i> (no. 12)			
Lattice parameters	<i>a</i> = 1315.1(3) pm <i>b</i> = 410.28(5) pm <i>c</i> = 937.2(2) pm <i>β</i> = 90.33(2) ° <i>V</i> = 505.7(2) × 10 ⁶ pm ³	<i>a</i> = 1353.9(3) pm <i>b</i> = 417.54(5) pm <i>c</i> = 960.4(2) pm <i>β</i> = 91.13(2) ° <i>V</i> = 542.8(2) × 10 ⁶ pm ³	<i>a</i> = 1373.9(4) pm <i>b</i> = 417.4(1) pm <i>c</i> = 1464.6(4) pm <i>β</i> = 115.57(2) ° <i>V</i> = 758.2(4) × 10 ⁶ pm ³	<i>a</i> = 1369.1(3) pm <i>b</i> = 416.6(1) pm <i>c</i> = 1526.4(3) pm <i>β</i> = 99.81(3) ° <i>V</i> = 857.9(3) × 10 ⁶ pm ³
<i>Z</i>	2			
<i>ρ</i> _{calc} × cm ³ /g	6.33	6.56	7.57	7.49
Crystal size / mm ³	0.01 × 0.17 × 0.01	0.01 × 0.11 × 0.01	0.32 × 0.07 × 0.03	0.25 × 0.12 × 0.07
Measuring device	imaging plate diffractometer IPDS-II (Stoe)	imaging plate diffractometer IPDS-I (Stoe)	four-circle diffractometer CAD 4 (Enraf-Nonius)	
Radiation	Mo- <i>Kα</i> , <i>λ</i> = 71.073 pm			
Measuring range	2 <i>θ</i> ≤ 60.0 ° −18 ≤ <i>h</i> ≤ 18 −5 ≤ <i>k</i> ≤ 5 −13 ≤ <i>l</i> ≤ 13	2 <i>θ</i> ≤ 51.6 ° −16 ≤ <i>h</i> ≤ 16 −4 ≤ <i>k</i> ≤ 4 −11 ≤ <i>l</i> ≤ 11	2 <i>θ</i> ≤ 69.9 ° −22 ≤ <i>h</i> ≤ 22 −6 ≤ <i>k</i> ≤ 6 −23 ≤ <i>l</i> ≤ 23	2 <i>θ</i> ≤ 80.6 ° −24 ≤ <i>h</i> ≤ 24 −7 ≤ <i>k</i> ≤ 7 −27 ≤ <i>l</i> ≤ 27
Absorption correction	numerical; crystal description optimized using sets of symmetry equivalent reflections		numerical; crystal description optimized using 8 and 17 <i>ψ</i> -scans	
<i>μ</i> (Mo- <i>Kα</i>) × mm	59.8	62.5	75.4	72.7
Transmission factors	0.06 to 0.70	0.57 to 0.69	0.01 to 0.11	0.01 to 0.07
Measured reflections	3532	2897	6658	10048
Unique reflections	845	580	1852	2930
<i>R</i> _{int}	0.046	0.077	0.046	0.074
<i>R</i> _σ	0.032	0.050	0.033	0.052
Refinement	least squares method; full matrix; based on <i>F</i> ²			
Extinction parameter	23(3) × 10 ^{−4}	11(1) × 10 ^{−4}	12.8(2) × 10 ^{−4}	—
Parameters; restrictions	49; 1	39; 1	59; 1	68; 1
<i>Δρ</i> × 10 ⁶ pm ³ /e	+1.9 to −1.6	+2.6 to −3.0	+3.9 to −3.8	+3.9 to −3.6
<i>R</i> ₁ (all <i>F</i> _o)	0.041	0.074	0.055	0.107
<i>R</i> ₁ (<i>F</i> _o > 4σ(<i>F</i> _o))	0.038	0.049	0.033	0.040
<i>wR</i> ₂ (all <i>F</i> _o ²)	0.102	0.060	0.039	0.041

Table 2. Wyckoff positions, coordinates, occupancy factors (k) und displacement parameters of the atoms in the sulfide bromide (**I**) (upper lines) and the selenide bromide (**II**) (lower lines). U_{eq} is defined as one third of the trace of the orthogonalized tensor U_{ij} . $M = kBi + (1-k)Cu$; $Z = kQ + (1-k)Br$ with $Q = S, Se$.

Atom	Position	x	y	z	k	U_{eq}, U_{iso}
Bi1	$4i$	0.77578(4)	0	0.18698(5)	1	432(2)
	$4i$	0.77223(8)	0	0.18842(9)	1	468(5)
$M2$	$2d$	$\frac{1}{2}$	0	$\frac{1}{2}$	0.646(1)	511(3)
	$2d$	$\frac{1}{2}$	0	$\frac{1}{2}$	0.370(1)	393(7)
Cu1a	$4i$	0.552(2)	0	0.056(2)	0.077(5)	288(17)
	$4i$	0.547(1)	0	0.043(2)	0.179(7)	310(30)
Cu1b	$8j$	0.517(1)	0.079(5)	0.020(2)	0.067(4)	$U_{iso}(Cu1a)$
	$2b$	$\frac{1}{2}$	0	0	0.16(2)	$U_{iso}(Cu1a)$
Cu1c	$4g$	$\frac{1}{2}$	0.210(6)	0	0.180(6)	$U_{iso}(Cu1a)$
	$4g$	$\frac{1}{2}$	0.179(5)	0	0.212(8)	$U_{iso}(Cu1a)$
Cu1d	$8j$	0.498(1)	0.334(6)	0.036(2)	0.063(4)	$U_{iso}(Cu1a)$
	—	—	—	—	—	—
Cu1e	$4i$	0.493(2)	0.5	0.082(3)	0.050(4)	$U_{iso}(Cu1a)$
	—	—	—	—	—	—
Br1	$4i$	0.14515(9)	0	0.4379(1)	1	377(3)
	$4i$	0.1426(2)	0	0.4393(2)	1	332(7)
$Q1$	$4i$	0.1503(2)	0	0.0681(3)	1	228(5)
	$4i$	0.1447(2)	0	0.0701(2)	1	213(6)
$Z2$	$4i$	0.4300(1)	0	0.2178(2)	0.711(8)	297(6)
	$4i$	0.4294(2)	0	0.2232(2)	0.339(9)	287(9)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 3. Wyckoff positions, coordinates, occupancy factors (k) und equivalent isotropic displacement parameters of atoms in the selenide iodide (III). U_{eq} is defined as one third of the trace of the orthogonalized tensor U_{ij} . $M = kBi + (1-k)Cu$.

Atom	Position	x	y	z	k	U_{eq}, U_{iso}
Bi1	$4i$	0.28391(3)	0	0.13995(3)	1	385(1)
$M2$	$4i$	0.65457(2)	0	0.35888(3)	1	256.1(8)
$M3$	$2c$	0	0	$\frac{1}{2}$	0.6901(9)	195(1)
Cu1a	$2b$	$\frac{1}{2}$	0	0	0.105(5)	351(8)
Cu1b	$4i$	0.4679(4)	0	0.0336(5)	0.192(3)	$U_{iso}(Cu1a)$
Cu1c	$4g$	$\frac{1}{2}$	0.174(1)	0	0.253(3)	$U_{iso}(Cu1a)$
Cu1d	$4i$	0.5454(6)	$\frac{1}{2}$	0.0711(7)	0.133(2)	$U_{iso}(Cu1a)$
Se1	$4i$	0.87591(5)	0	0.05070(6)	1	179(1)
Se2	$4i$	0.99761(7)	0	0.30225(9)	0.885(2)	222(2)
Se3	$4i$	0.6450(1)	0	0.15965(9)	0.935(2)	178(2)
Se4	$4i$	0.33267(5)	0	0.42410(6)	1	176(1)
I2	$4i$	0.9900(4)	0	0.3388(4)	0.115(2)	$U_{eq}(Se2)$
I3	$4i$	0.645(1)	0	0.179(1)	0.065(2)	$U_{eq}(Se3)$

Table 4. Wyckoff positions, coordinates, occupancy factors (k) und equivalent isotropic displacement parameters of atoms in the selenide iodide (IV). U_{eq} is defined as one third of the trace of the orthogonalized tensor U_{ij} . $M = kBi + (1-k)Cu$.

Atom	Position	x	y	z	k	U_{eq}, U_{iso}
Bi1	$4i$	0.24321(3)	0	0.12284(2)	1	450(1)
$M2$	$4i$	0.54909(3)	0	0.31293(2)	0.748(2)	277(1)
$M3$	$4i$	0.84829(3)	0	0.43633(3)	0.751(2)	285(1)
Cu1a	$2b$	$\frac{1}{2}$	0	0	0.137(6)	400(9)
Cu1b	$4i$	0.4533(5)	0	0.0318(4)	0.193(3)	$U_{iso}(Cu1a)$
Cu1c	$4g$	$\frac{1}{2}$	0.176(1)	0	0.256(3)	$U_{iso}(Cu1a)$
Cu1d	$4i$	0.5290(6)	$\frac{1}{2}$	0.0662(5)	0.138(3)	$U_{iso}(Cu1a)$
Se1	$4i$	0.86189(5)	0	0.04452(4)	1	195(1)
Se2	$4i$	0.90490(9)	0	0.26944(9)	0.852(3)	211(2)
Se3	$4i$	0.59690(6)	0	0.14157(8)	0.928(2)	218(2)
Se4	$4i$	0.20550(7)	0	0.37167(7)	0.8722(8)	242(2)
Se5	$2d$	$\frac{1}{2}$	0	$\frac{1}{2}$	1	205(2)
I2	$4i$	0.8889(3)	0	0.2958(3)	0.148(3)	$U_{eq}(Se2)$
I3	$4i$	0.5990(6)	0	0.1757(6)	0.072(2)	$U_{eq}(Se3)$
I4	$4i$	0.1937(3)	0	0.4136(3)	0.1278(1)	$U_{eq}(Se4)$

Table 5. Selected interatomic distances (/ pm) for the chalcogenide bromides (**I**) and (**II**). $M = \text{Bi/Cu}$; $Q = \text{S, Se}$; $Z = Q/\text{Br}$. Symmetry operators: (i): x, y, z ; (ii): $1-x, -y, -z$; (iii): $x+1/2, y-1/2, z$; (iv): $x+1/2, y+1/2, z$; (v): $1-x, -y, 1-z$; (vi): $1/2-x, -y-1/2, 1-z$; (vii): $1/2-x, 1/2-y, 1-z$; (viii): $1/2-x, 1/2-y, -z$; (ix): $x, y+1, z$.

		(I)	(II)
Bi1–	$Q1^{\text{ii}}$	259.6(4)	274.6(2)
	$Q1^{\text{iii, iv}}$	285.9(3)	292.0(2)
	$Z2^{\text{iii, iv}}$	290.2(4)	299.1(2)
	$\text{Br}1^{\text{iii, iv}}$	357.8(4)	366.1(2)
$M2$ –	$Z2^{\text{i, v}}$	280.2(4)	280.3(2)
	$\text{Br}1^{\text{iii, iv, vi, vii}}$	287.0(3)	290.8(2)
Cu1a–	$Z2$	222(2)	237(1)
	$Q1^{\text{iii, iv}}$	243(1)	248(1)
	$Z2^{\text{ii}}$	259(2)	258(1)
Cu1b–	$Z2$	220(2)	236.5(2)
	$Z2^{\text{ii}}$	237(2)	236.5(2)
	$Q1^{\text{iv}}$	250(1)	292.8(2)
	$Q1^{\text{viii}}$	292(3)	292.8(2)
	$Q1^{\text{iii}}$	299(3)	292.8(2)
	$Q1^{\text{v}}$		292.8(2)
Cu1c–	$Q1^{\text{iv, viii}}$	239(1)	245(1)
	$Z2^{\text{i, ii}}$	241.2(9)	248.0(7)
Cu1d–	$Q1^{\text{iv}}$	214(2)	—
	$Q1^{\text{viii}}$	229(2)	—
	$Z2$	237(1)	—
	$Z2^{\text{ii}}$	292(3)	—
Cu1e–	$Q1^{\text{iv}}$	208(3)	—
	$Q1^{\text{viii}}$	235(3)	—
	$Z2^{\text{i, ix}}$	256(2)	—

Table 6. Selected interatomic distances (/ pm) for the selenide iodides (III) and (IV). *M* = Bi/Cu; *Z* = Se/I. Symmetry operators: (i): *x*, *y*, *z*; (ii): 1−*x*, −*y*, −*z*; (iii): *x*−1/2, *y*−1/2, *z*; (iv): *x*−1/2, *y*+1/2, *z*; (v): *x*+3/2, −*y*−1/2, −*z*; (vi): 3/2−*x*, 1/2−*y*, −*z*; (vii): *x*, *y*+1, *z*; (viii): *x*+1/2, *y*−1/2, *z*; (ix): *x*+1/2, *y*+1/2, *z*; (x): 1−*x*, −*y*, 1−*z*; (xi): *x*−1, *y*, *z*; (xii): 1/2−*x*, −*y*−1/2, 1−*z*; (xiii): 1/2−*x*, 1/2−*y*, 1−*z*.

		(III)	(IV)
Bi1–	Se1 ⁱⁱ	270.8(1)	271.0(1)
	Se3 ^{iii, iv}	292.5(1)	293.75(8)
	Se1 ^{iii, iv}	301.52(8)	301.17(8)
	I3 ^{iii, iv}	305(1)	307.1(6)
	Se2 ^{iii, iv}	355.0(1)	354.4(1)
	I2 ^{iii, iv}	370.7(4)	367.3(3)
M2–	I3	258(1)	231.1(9)
	Se2 ^{iii, iv}	285.48(8)	286.89(9)
	Se3	286.6(1)	280.2(1)
	I2 ^{iii, iv}	299.6(3)	300.4(3)
	Se4 ^{viii, ix}	303.93(8)	301.23(9)
	Se4 ^x	310.9(1)	—
	Se5	—	304.29(7)
	I4 ^{viii, ix}	—	309.6(3)
M3–	I2 ^{x, xi}	230.8(6)	—
	Se2 ^{x, xi}	288.4(2)	—
	Se4 ^{iii, iv, xii, xiii}	294.46(8)	—
	I2	—	230.6(5)
	I4 ^x	—	245.5(5)
	Se2	—	278.6(2)
	Se4 ^{viii, ix}	—	291.16(9)
	I4 ^{viii, ix}	—	294.7(3)
	Se5 ^{viii, ix}	—	298.49(6)
	Se4 ^x	—	314.1(1)
Cu1a–	Se3 ^{i, ii}	232.8(2)	233.5(1)
	I3 ^{i, ii}	252(2)	279.1(9)
	Se1 ^{iii, iv, v, vi}	298.46(7)	296.88(7)
Cu1b–	Se3	233.5(6)	235.7(6)
	I3	244(2)	270(1)
	Se1 ^{iii, iv}	250.8(3)	245.5(3)
	Se3 ⁱⁱ	257.6(7)	261.8(6)
	I3 ⁱⁱ	282(2)	312(1)
Cu1c–	Se3 ^{i, ii}	243.9(2)	244.7(2)
	Se1 ^{iv, vi}	253.0(3)	251.0(3)
	I3 ^{i, ii}	262(2)	288.5(9)
Cu1d–	Se1 ^{iv}	221.6(8)	225.6(8)
	Se1 ^{vi}	245.5(8)	243.8(8)
	Se3 ^{i, vii}	252.6(5)	248.2(4)
	I3 ^{i, vii}	262(1)	273.9(8)

Results and Discussion

Black, flat needles of the two copper bismuth chalcogenide bromides $\text{Cu}_{1.49(6)}\text{Bi}_{2.646(1)}\text{S}_{3.42(2)}\text{Br}_{2.58(2)}$ (**I**) and $\text{Cu}_{1.57(5)}\text{Bi}_{2.370(1)}\text{Se}_{2.68(2)}\text{Br}_{3.32(2)}$ (**II**) were crystallized from approximately stoichiometric melts of BiBr_3 , Bi_2Q_3 ($\text{Q} = \text{S}, \text{Se}$) and CuBr . According to X-ray powder diffraction, the yield of the syntheses exceeds 90 %. The melting points of the compounds are 708(5) K (**I**) and 724(5) K (**II**). (**I**) and (**II**) belong to the pseudo-ternary systems $\text{CuBr}/\text{BiBr}_3/\text{Bi}_2\text{Q}_3$, i.e. they are substantially richer in Bi and halogen compared to the iodides (**III**) and (**IV**), which belong to the system $\text{CuI}/\text{Cu}_2\text{Se}/\text{Bi}_2\text{Se}_3$.

In all probability, the formation of the copper bismuth selenide iodides $\text{Cu}_{1.57(2)}\text{Bi}_{4.690(1)}\text{Se}_{7.640(8)}\text{I}_{0.360(8)}$ (**III**) and $\text{Cu}_{2.31(3)}\text{Bi}_{5.00(1)}\text{Se}_{8.31(1)}\text{I}_{0.69(1)}$ (**IV**) proceeds during tempering CuI and Bi_2Se_3 at 670 K. In the temperature gradient from 670 K to 620 K that is applied subsequently, an auto-transport [22] via the gas phase takes place. The dominant gas phase species should be $\text{BiI}_{(\text{g})}$, $\text{Se}_{2(\text{g})}$, and $\text{Cu}_3\text{I}_{3(\text{g})}$ [23]. The fact that Bi_2Se_3 is more easily transported than CuI is reflected in the composition of the quaternary compounds: The deposited $\text{Cu}_{1.57}\text{Bi}_{4.69}\text{Se}_{7.64}\text{I}_{0.36}$ (**III**) = $0.153 \text{ CuI} \cdot 0.258 \text{ Cu}_2\text{Se} \cdot \text{Bi}_2\text{Se}_3$ has a Cu content of 67 % compared to the source, which is based on an equimolar mixture of CuI and Bi_2Se_3 . The CuI richer mixture ($\text{CuI} : \text{Bi}_2\text{Se}_3 = 3 : 2$) yields $\text{Cu}_{2.31}\text{Bi}_5\text{Se}_{8.31}\text{I}_{0.69}$ (**IV**) = $0.276 \text{ CuI} \cdot 0.324 \text{ Cu}_2\text{Se} \cdot \text{Bi}_2\text{Se}_3$, i.e. an iodine-rich compound with 62 % of the Cu content of the source.

Figure 1. Crystal structures of $N = 1$ pavonite homologue $\text{Cu}_{1.5}\text{Bi}_{2.64}\text{S}_{3.42}\text{Br}_{2.58}$ (**I**). Ellipsoids cover 95 % probability density, as in all following figures.

All four compounds crystallize in the monoclinic space group type $C2/m$ (for lattice parameters cf. Table 1). They can be categorized as members of pavonite homologous series, similar to those

found in the Ag/Bi/Q/X systems ($X = \text{Cl}, \text{Br}$) [4–6]. The bromides (I) and (II) are isostructural with members of the solid solution series $\text{Ag}_{2x}\text{Bi}_{4-2x}\text{S}_{6-4x}\text{Br}_{4x}$ [4]. The Bi^{III} atoms are coordinated by three Q, two Br, and two mixed occupied $Z = \text{Q/Br}$ atom positions (Figure 1). The mono-capped $[\text{BiQ}_3\text{Br}_2\text{Z}_2]$ prisms share faces and edges to form paired rods ${}^1_\infty[\text{BiQ}_{3/3}\text{Br}_{2/2}\text{Z}_{2/2}]$ along [010]. While in the corresponding Ag compounds the octahedral voids between the rods are mixed occupied with Bi/Ag, here Cu^{I} atoms are distributed over numerous octahedral, tetrahedral, and trigonal voids. Between these layers parallel to (001), which are denoted as A modules, mixed occupied octahedrally coordinated cation positions $M = \text{Bi/Cu}$ form the B modules. The $[\text{MBr}_4\text{Z}_2]$ octahedra share *trans* edges along [010].

Since the various pavonite homologous series mainly differ in the thickness of module B, the number N of octahedra stacked perpendicular to (001) is a characteristic [6]. At constant N , the coupled modification of the Bi/Cu and the Q/Br ratios yields to a continuous series of isostructural compounds. In the case of the bromides (I) and (II), N equals 1. The two selenide iodides are members of pavonite homologous series with $N = 3$ (III) and $N = 4$ (IV), i.e. the NaCl-type modules B consist of three or four layers of octahedrally coordinated M cations (Figure 2). The modules A differ only in details from those found in (I) and (II). Corresponding Ag compounds belong to the series $\text{Ag}_{4x}\text{Bi}_{6-4x}\text{Q}_{10-8x}\text{X}_{8x-2}$ [5] and $\text{Ag}_{5x}\text{Bi}_{7-5x}\text{Q}_{12-10x}\text{X}_{10x-3}$ [6].

Figure 2. Crystal structure of $N = 3$ pavonite homologue $\text{Cu}_{1.57}\text{Bi}_{4.69}\text{Se}_{7.64}\text{I}_{0.36}$ (III).

For the Ag compounds the general sum formula $[\text{BiQX}]_2[\text{Ag}_x\text{Bi}_{1-x}\text{Q}_{2-2x}\text{X}_{2x-1}]_{N+1}$ with $N \geq 0$ and $1/2 \leq x \leq 1$ had been found [6]. Individual compounds are characterized by their parameters N and x in the symbol $^{(N, x)}\text{P}$. When the particular chalcogen and halogen are listed in a subscript, for example $^{(2, 0.67)}\text{P}_{\text{S,Cl}}$, this code properly defines a composition.

In the underlying Cu compounds, however, the Cu content in module A is an additional parameter, since the occupancy of the atoms around the octahedral void between the rods can

exceed unity — in the case of **(I)** $\Sigma k(\text{Cu1}) = 1.13$, **(III)** $\Sigma k(\text{Cu1}) = 1.26$, and **(IV)** $\Sigma k(\text{Cu1}) = 1.31$ — or fall below unity — in the case of **(II)** $\Sigma k(\text{Cu1}) = 0.94$ — by the displacement of the Cu atoms into tetrahedral or trigonal voids. The charge is compensated by the atomic ratios on the mixed cation positions M as well as on the anion positions Z . Thus, a general formula would be very complex and should not be set up on the basis of a few representatives.

Figure 3. Cu1 distribution (split atoms) in the sulfide bromide **(I)** and the respective JPDF isosurface at an electron density of $\eta = 0.08 \text{ e}/(10^6 \text{ pm}^3)$.

The modeling of the disordered Cu1 atoms in the sulfide bromide **(I)** either by split positions or by the Joint Probability Density Function (JPDF) reveals a continuous path along [010] (Figure 3), which can be used for cation transport. Using the relation $V(x) = V_0 - kT \ln[\text{pdf}(x)]$, the potential barriers were derived from the anharmonic refinement [19, 20]. The calculated potentials are very small, about 47 meV only (Figure 4), yet the effective potential could be substantially higher [19]. In the case of the chemically related compound $\text{Ag}_{10}\text{Te}_4\text{Br}_3$, which was identified as an excellent cation conductor, potentials of 450 meV were calculated with the same method [24]. In **(II)**, **(III)**, and **(IV)** the Cu1 atoms are more localized than in the sulfide bromide **(I)**, and the JPDF do not show continuous pathways through the crystals.

Figure 4. Left: JPDF based on an anharmonically (fourth order tensor) refined Cu1 atom in $\frac{1}{2}, 0.18, 0$. Sections in $x = 0.4924$ (top) and $z = -0.0532$ (bottom) with contour lines in intervals of $0.08 \text{ e}/(10^6 \text{ pm}^3)$. Right: Potentials following the defined paths (solid lines) and their errors estimated by Monte Carlo method (dashed lines).

With the phonon-glass electron-crystal model [2] in mind, the evaluated very high mobility of the Cu1 atoms in (I) stimulated measurement of the physical parameters that qualify the thermoelectric properties. The thermal conductivity was about 0.77 W/(K·m) and the Seebeck coefficient about 280 μV/K, which are desirable values for those parameters. Pressed powder pellets of (I) and (II) revealed semiconducting characteristics with a resistivity of about 23 Ω/m at 300 K. Due to the poor electrical conductivity the resulting $ZT = S^2 \cdot \sigma \cdot T / \kappa = 1.3 \cdot 10^{-6}$ at room temperature makes the specific compound not interesting for potential thermoelectric application.

Concluding Remark

Although at least the two bromides presented here do not seem to be suitable thermoelectrics, the class of compounds is promising, since the tunable composition and structures of the pavonite homologous series offers numerous chemical variables for optimizing the thermoelectric properties. Their chemical and thermal stability should allow application in the low and medium temperature regime up to 600 K.

Acknowledgement

We thank Mrs. *Gudrun Kadner* and Mrs. *Jutta Krug* for their support in synthesis, and Dr. *Peer Schmidt* for valuable discussions on the chemical transport reactions. Dr. *Walter Schnelle* and Mr. *Ralf Koban* (Max Planck Institute for Chemical Physics of Solids, Dresden) are gratefully acknowledged for the measurement of the thermoelectric parameters.

References

- [1] J. R. Sootsman, D. Y. Chung, M. G. Kanatzidis, *Angew. Chem.* **2009**, *121*, 8768 – 8792; *Angew. Chem. Int. Ed.* **2009**, *48*, 8616 – 8639.
- [2] a) G. A. Slack, V. Tsoukala. *J. Appl. Phys.* **1994**, *76*, 1665 – 1671; b) G. A. Slack, in: *CRC Handbook of Thermoelectrics* (Ed.: D. M. Rowe), CRC Press, Boca Raton **1995**, p. 407 – 440; c) G. S. Nolas, D. T. Morelli, T. M. Tritt, *Annu. Rev. Mater. Sci.* **1999**, *29*, 89 – 116.
- [3] T. Kyratsi, E. Hatzikraniotis, K. M. Paraskevopoulos, C. D. Malliakas, J. S. Dyck, C. Uher, M. G. Kanatzidis, *J. Appl. Phys.* **2006**, *100*, 123704.
- [4] P. F. P. Poudeu, T. Söhnel, M. Ruck, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1276 – 1285.
- [5] M. Ruck, P. F. P. Poudeu, *Z. Anorg. Allg. Chem.* **2008**, *634*, 475 – 481.
- [6] M. Ruck, P. F. P. Poudeu, *Z. Anorg. Allg. Chem.* **2008**, *634*, 482 – 490.
- [7] P. F. P. Poudeu, M. Ruck, *J. Solid State Chem.* **2006**, *179*, 3636 – 3644.
- [8] P. F. P. Poudeu, M. Ruck, *Acta Crystallogr.* **2005**, *C61*, i41 – i43.
- [9] M. Ruck, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1537 – 1540.
- [10] M. Ruck, *Z. Anorg. Allg. Chem.*, **2002**, *628*, 453 – 457.
- [11] M. Ruck, P. F. P. Poudeu, T. Söhnel, *Z. Anorg. Allg. Chem.* **2004**, *630*, 63 – 67.
- [12] a) A. Heerwig, M. Ruck, *Z. Anorg. Allg. Chem.* **2009**, *635*, 2162 – 2169; b) A. Heerwig, M. Ruck, *Z. Anorg. Allg. Chem.* **2010**, *636*, in print.
- [13] V. Kramb, W. Proske, V. Wiskamp, *Naturwissenschaft im Unterricht – Chemie* **1996**, *7*, 9.
- [14] *X-SHAPE, Crystal Optimisation for Numerical Absorption Correction Program*, Version 1.06, Stoe & Cie GmbH, Darmstadt, Germany **1999**.
- [15] *X-RED32, Data Reduction Program*, Version 1.01, Stoe & Cie GmbH, Darmstadt, Germany **2001**.
- [16] a) G. M. Sheldrick, *SHELX97, Programs for crystal structure determination*, Univ. Göttingen, Germany **1997**; b) G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.

- [17] N. E. Brese, M. O'Keeffe, *Acta Crystallogr.* **1991**, *B47*, 192 – 197.
- [18] K. Brandenburg, *Diamond 3.2d, Crystal and Molecular Structure Visualization*, Crystal Impact GbR, Bonn, Germany **2010**.
- [19] a) V. Petříček, M. Dušek, L. Palatinus, *Jana2000, the crystallographic computing system*. Institute of Physics, Praha, Czech Republic **2000**; b) V. Petříček, V., A. van der Lee, M. Evain, *Acta Crystallogr.* **1995**, *A51*, 529 – 535; c) L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786 – 790.
- [19] R. Bachmann, H. Schulz, *Acta Crystallogr.* **1984**, *A40*, 668 – 675.
- [20] R. Bachmann, K. D. Kreuer, A. Rabenau, H. Schulz, *Acta Crystallogr.* **1982**, *B38*, 2361 – 2364.
- [21] K. Momma, F. Izumi, *J. Appl. Crystallogr.* **2008**, *41*, 653 – 658.
- [22] H. Oppermann, M. Schmidt, P. Schmidt, *Z. Anorg. Allg. Chem.* **2005**, *631*, 197 – 238.
- [23] M. Schöneich, M. P. Schmidt, P. Schmidt, *Z. Anorg. Allg. Chem.* **2010**, *636*, in print.
- [24] S. Lange, T. Nilges, *Chem. Mater.* **2006**, *18*, 2538 – 2544.

Crystal structures of $N = 1$ pavonite homologue $\text{Cu}_{1.5}\text{Bi}_{2.64}\text{S}_{3.42}\text{Br}_{2.58}$ (**I**). Ellipsoids cover 95 % probability density, as in all following figures.
661x495mm (96 x 96 DPI)

Crystal structure of $N = 3$ pavonite homologue $\text{Cu}_{1.57}\text{Bi}_{4.69}\text{Se}_{7.64}\text{I}_{0.36}$ (III).
661x495mm (96 x 96 DPI)

Cu1 distribution (split atoms) in the sulfide bromide (**I**) and the respective JPDF isosurface at an electron density of $\eta = 0.08 \text{ e}/(10^6 \text{ pm}^3)$.

Left: JPDF based on an anharmonically (fourth order tensor) refined Cu1 atom in $\frac{1}{2}, 0.18, 0$. Sections in $x = 0.4924$ (top) and $z = -0.0532$ (bottom) with contour lines in intervals of $0.08 \text{ e}/(10^6 \text{ pm}^3)$. Right: Potentials following the defined paths (solid lines) and their errors estimated by Monte Carlo method (dashed lines).