Homologous Silver Bismuth Chalcogenide Halides ^(N, x)P. I. Syntheses and Crystal Structures of the ^(0, 1)P Compound AgBi₂S₂Cl₃ and of Three Members of the ^(1, x)P Solid Solution Series Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}

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AgBi₂S₂Cl₃ and members Abstract. three of the $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ solid solution (x = 0.50 (I), x = 0.64 (II), and x = 0.73 (III)) were synthesized from Bi₂S₃, AgX and BiSX (X = Cl, Br) at 720 K. X-ray diffraction on single crystals revealed that the compounds crystallize in the monoclinic space groups C2/m(No. 12) with a = 1257.3(3), b = 400.0(1), c = 804.1(2) pm, $\beta =$ $111.0(1)^{\circ}$ for AgBi₂S₂Cl₃, a = 1331.3(5), b = 408.0(2), c =972.0(3) pm, $\beta = 90.8(1)^{\circ}$ for (I), a = 1328.9(4), b = 408.5(1), c =973.4(4) pm, $\beta = 90.9(1)^{\circ}$ for (II), and a = 1332.4(3), b = 409.3(1),c = 974.3(2) pm, $\beta = 90.4(1)^{\circ}$ for (III). AgBi₂S₂Cl₃ adopts a variant of the $InBi_2S_4Cl$ structure type, the isostructural compounds (I), (II) and (III) are related to the orthorhombic FeUS₃ type. All four compounds belong to homologous series with general formula $[BiSX]_2 \cdot [Ag_x Bi_{1-x}S_{2-2x}X_{2x-1}]_{N+1}$ (X = Cl, Br), which resemble minerals of the pavonite series. They are characterized by the parameters N and x and are denoted ^(N, x)P. In the crystal structures, two kinds of layered modules, A and B, alternate. Modules of type B are composed of chains of edge-sharing $[MBr_4Z_2]$ octahedra (M = Ag/Bi; X = Cl, Br; Z = S/X) and vary in thickness N. Modules of type A uniformly consist of rows of paired monocapped trigonal prisms around Bi atoms with $[MS_4Z_2]$ octahedra around mixed-occupied metal positions (M = Ag/Bi) between them. Ag-Bi₂S₂Cl₃ comprises modules of type A only (N = 0) and is the silver-rich end-member (x = 1) in the series ^(0, x)P. (I) to (III) belong to the ^(1, x)P series with B modules of thickness N = 1. Calculations of the electronic band structures indicate that the compounds should act as indirect semiconductors with band gaps between 1.5 and 0.6 eV.

Keywords: Bismuth; Silver; Solid solutions; Chalcogenides; Halides

Pavonit-Reihe gleichen. Sie werden durch die Parameter N und x

charakterisiert und mit ${}^{(N, x)}P$ bezeichnet. In den Kristallstrukturen wechseln sich zwei Typen schichtartiger Bauverbände A und B ab.

Ketten kantenverknüpfter Oktaeder $[MX_4Z_2]$ (M = Ag/Bi; X = Cl,

Br; Z = S/X bilden die *B*-Module, welche von unterschiedlicher

Mächtigkeit N sein können. Module des Typs A bestehen einheit-

Homologe Silber-Bismut-Chalkogenid-Halogenide $^{(N, x)}P$. I. Synthesen und Kristallstrukturen der $^{(0, 1)}P$ -Verbindung AgBi₂S₂Cl₃ und von drei Vertretern der $^{(1, x)}P$ -Mischkristallreihe Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}

Inhaltsübersicht. AgBi₂S₂Cl₃ und drei Verbindungen der Mischkristallreihe Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}(x = 0,50 (**I**), x = 0,64 (**II**) und x = 0,73 (**III**)) wurden bei etwa 720 K aus Bi₂S₃, AgX und BiSX (X = Cl, Br) synthetisiert. Aus Röntgenbeugungsuntersuchungen an Einkristallen geht hervor, dass die Verbindungen in den monoklinen Raumgruppen C2/m (Nr. 12) kristallisieren mit a = 1257,3(3), b = 400,0(1), c = 804,1(2) pm, $\beta = 111,0(1)^{\circ}$ für AgBi₂S₂Cl₃, a = 1331,3(5), b = 408,0(2), c = 972,0(3) pm, $\beta = 90,8(1)^{\circ}$ für (**II**) und a = 1332,4(3), b = 409,3(1), c = 974,3(2) pm, $\beta = 90,4(1)^{\circ}$ für (**III**). AgBi₂S₂Cl₃ kristallisiert in einer Variante des InBi₂S₄Cl-Typs, die isotypen Verbindungen (**I**), (**II**) und (**III**) haben dem orthorhombischen FeUS₃-Typ verwandte Strukturen. Alle vier Verbindungen gehören zu homologen Reihen der allgemeinen Formel [BiSX₁₂·[Ag_xBi_{1-x}S_{2-2x}X_{2x-1}]_{N+1} (X = Cl, Br), die Mineralen der

$a_3, a =$ lich aus Doppelsträngen einfach überdachter trigonaler Prismen $\mathbf{I}, a =$ um Bi-Atome sowie die Stränge verknüpfenden Oktaedern $[MS_4Z_2]$ \mathbf{II}) undum mischbesetzte Metallatompositionen (M = Ag/Bi). AgBi₂S₂Cl₃ $1)^\circ$ fürsetzt sich ausschließlich aus A-Modulen zusammen (N = 0) und21-Typs,stellt den silberreichsten Vertreter (x = 1) der Reihe $^{(0, x)}$ P dar. (I)0 ortho-bis (III) gehören zur $^{(1, x)}$ P-Reihe, in der die B-Module die DickeN = 1 haben. Rechnungen zur elektronischen Bandstruktur legen1,5 und 0,6 eV sein sollten.

Introduction

During the past three decades, investigations of ternary bismuth chalcogenides have resulted in the discovery of a great

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number of new compounds, for example $ABiQ_2$ (A = alkali metal; Q = chalcogen) [1–5], ABi_3S_5 (A = K, Cs, Rb) [6–8], Cs $Bi_{3.67}Se_6$ [9], Cs Bi_4Te_6 [10], $A_xBi_4Se_7$ (x = 1, 2; A = Rb, Cs) [11], α and β -K $Bi_{6.33}S_{10}$ [12, 13], K $_2Bi_8S_{13}$ [12, 13], α and β -K $_2Bi_8Se_{13}$ [5, 14], $A_2Bi_8Se_{13}$ (A = Rb, Cs) [9], K $_{2.5}Bi_{8.5}Se_{14}$ [14], Cs $_3Bi_7Se_{12}$ [15], BaBiSe $_3$ [16], BaBiTe $_3$ [17], α and β -BaBi $_2S_4$ [18], BaBi $_2Se_4$ [9], and Sr $_4Bi_6Se_{13}$ [19].

Within the last five years, quaternary bismuth chalcogenides have also been reported in the systems A/Bi/M/Q (A = K, Cs, Rb; M = Cu, Ag, Sn, Pb; Q = S, Se). These include



Fig. 1 Representation of the structure principle of pavonite homologues showing the two types of building units A and B. The thickness of the NaCl-like module, B, increases with the number N of edge-sharing octahedra. Black atoms: Bi; medium grey atoms: M =(Ag, Cu, Pb, Bi, Fe,...); light grey atoms: S.

 $K_3Bi_5Cu_2S_{10}$ [20], $CsBi_2CuS_4$ [20], $RbBi_{2.66}CuSe_5$ [20], $CsBiAg_2S_3$ [20], $A_3Bi_5Cu_2S_{10}$ (A = Rb, Cs) [21] and KBi_2CuS_4 [22]. In addition to these synthetic phases, many naturally occurring bismuth chalcogenides have been discovered and structurally characterized. Most are in the *M*/Bi/ S (M = Cu, Ag, Pb, Fe,...) systems. A large number of these so-called sulphosalts are members of homologous series.

One of them is the pavonite homologous series, which includes structures that are composed of two alternating kinds of modules parallel to (001) (Fig. 1). In the slab denoted A, $[MS_6]$ octahedra alternate with paired $[BiS_7]$ monocapped trigonal prisms. The NaCl-like slabs, denoted B, are composed of parallel, N-membered chains of edge-sharing octahedra. Different members of the series are denoted by the symbol ^NP [23]. The general chemical formula is $M^{\text{oct}}_{N+1}\text{Bi}_2Q_{N+5}$ [23], where M^{oct} represents the octahedrally coordinated metal positions in the structure. In the ternary system Ag/Bi/S the series includes "AgBi₆S₉" (N = 4) [24], $Ag_2Bi_6S_{10}$ (N = 5) [20] and $Ag_3Bi_7S_{12}$ (N = 7) [25]. In their structures, Ag/Bi disorder is generally observed in the octahedrally coordinated metal sites. In addition to these phases, the existence of AgBiS₂ [26] has been reported and Ag/Bi mixed occupancy was also found in the metal positions (statistical NaCl structure type). All compounds belong to the pseudo-binary section $Ag_2S-Bi_2S_3$.

In order to study the nature of the cation disorder observed in the structures of pavonite homologues in the system Ag/Bi/S and to explore the possibility of a solid solution leading to more ordered phases, we have started the investigation of the quaternary systems Ag/Bi/Q/X where Q = S, Se and X = Cl, Br. The strategy consists of partial substitution of bivalent sulphur atoms by univalent halogen atoms in the structures of various known and hypothetical pavonite homologues in the ternary system Ag/Bi/S. This operation introduces a variation of charge in the crystal lattice and might open a way to structural ordering of both cations and anions.

At the beginning of the investigation, only a limited number of quaternary phases consisting of a transition metal and several types of p-block elements were known. In the systems T - Pn - Q - X (T = transition metal; Pn = P, As, Sb, Bi; Q = S, Se, Te; X = F, Cl, Br, I), the most prevalent examples are copper-containing compounds. These include Cu₆PS₅Br (an ion-conducting argyrodite) [27], $(CuBr)_{3}P_{4}Se_{4}$ [28], $(CuI)P_{4}Se_{4}$ [29], $(CuI)_{3}P_{4}Se_{4}$ [30], $(CuI)_{2}P_{8}Se_{3}$ [31], $(CuI)_{2}Cu_{3}SbS_{3}$ [32], $Bi_{2}Cu_{3}S_{4}X$ (X = Cl, Br) [33, 34], Cu_{3.1}Bi_{9.4}Se_{15.3}I_{0.7} [35], Cu_{4.5}Bi₁₀Se_{16.5}I_{1.5} [35] CuHgSeCl [36], CuHgSeBr [37], CuHgSX (X = Cl, Br, I) [38]. Examples with other d-block elements are $CdSb_6S_8I_4$ [39], $Hg_3AsQ_4X (Q = S, Se; X = Cl, Br, I)$ [40], $MnSbSe_2I$ [41], AgHgSX (X = Br, I) [37] and Ag_2HgSI_2 [42]. The isostructural bismuth indides $InBi_2S_4X (X = Cl, Br)$ [43] are also known.

In the quaternary systems M/Bi/Q/X (M = Cu, Ag, Q =S, Se; X = Cl, Br) we have recently reported the syntheses and crystal structures of $Ag_2Bi_2S_3Cl_2$ [44], $AgBi_2Q_3Cl$ (Q = S, Se) [45] and MBiSCl₂ (M = Cu, Ag) [46]. All of them exhibit the desired ordering of atoms. Our current investigation is expected to elucidate the order or disorder of Ag and Bi atoms, the type of cation sites influenced by the Ag and Bi substitution, the type of anion sites affected by the Q and X substitution, as well as the distortions of the ideal framework (pavonite homologues) connected with these phenomena. In addition, the variation in the bonding pattern of Bi as a consequence of the substitution processes will be examined. Here we report the syntheses, and the crystal and electronic structures of AgBi₂S₂Cl₃ and three members of the Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x} solid solution series. These compounds belong to a new bivariant class of quaternary solids denoted (N, x)P with general formula $[\text{Bi}_{Q}X]_{2} \cdot [\text{Ag}_{x}\text{Bi}_{1-x}Q_{2-2x}X_{2x-1}]_{N+1}$ (Q = S, Se; X = Cl, Br). This first contribution on the chemistry of ^(N, x)P compounds will be continued soon with reports on ${}^{(2, x)}P$, ${}^{(3, x)}P$, $^{(4, x)}P$, $^{(5, x)}P$ and $^{(7, x)}P$ compound and a detailed discussion of general principles.

Experimental Section

Syntheses

The following chemicals were used as starting materials: Bi_2S_3 , AgCl, AgBr, BiSBr, and BiBr₃. Bi_2S_3 (Alfa Aesar, 99.9 %), AgCl (Merck, > 99.4 %) and AgBr (Merck, 99.7 %) were used as obtained without any further treatment for purification.

BiBr₃: BiBr₃ was synthesized from a mixture of 4.70 g of Bi powder and 1.75 ml of Br₂ (3.2 g/ml) handled under nitrogen atmosphere. It was necessary to cool the bottom of the ampoule in liquid nitrogen during the introduction of Br₂. The mixture was then allowed to pre-react by slowly heating the external wall of the ampoule until the contents melted. The reaction was completed by sublimation of the $BiBr_3$ from 620 K to room temperature using a tubular oven. The air-sensitive yellow product obtained was ground into powder and used for the synthesis of BiSBr.

BiSBr: An equimolar mixture of Bi_2S_3 and $BiBr_3$ was thoroughly ground under a dry argon atmosphere in a glove box and transferred into a silica tube, which was flame-sealed under a pressure of 10^{-3} Torr. The tube was heated to 430 K in 5 h, kept at 430 K for 60 h and further heated to 500 K in 5 h. After 2 days at 500 K, the ampoule was allowed to cool to room temperature in 10 h. The dark-red product was ground into powder and used for further reactions.

AgBi₂S₂Cl₃: A mixture of AgCl and BiSCl in the molar ratio 1:2 was thoroughly ground and loaded into a silica tube, which was flame-sealed under a pressure of 10^{-3} Torr. The tube was placed in a tubular oven, heated at 720 K for 5 days and then quenched to room temperature. Well-formed black plate-like crystals of AgBi₂S₂Cl₃ with dimensions up to $0.5 \times 0.25 \times 0.05$ mm³ were found in the polycrystalline product mixture. Crystals of AgBi₂S₂Cl₃ were found to be stable in air for at least one year. Microcrystalline powder of AgBi₂S₂Cl₃ with approximately 95 % purity can be obtained by annealing a stoichiometric mixture of starting materials at 630 K for 5 days. AgBi₂S₂Cl₃ melts incongruently near 650 K (LABSYS DSC 12, Netzsch).

 $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$, (I) (x = 0.50): Single crystals of (I) were obtained from a reaction involving Bi_2S_3 , AgBr and BiSBr in the molar ratio 1 : 1 : 1. A well-ground mixture of the starting materials was loaded into a silica tube, which was flame-sealed under a pressure of 10^{-3} Torr. The tube was heated to 670 K in 2 days, kept at that temperature for 2 days and then further heated at 740 K for 15 days. The ampoule was then cooled to room temperature at a rate of 5 K/h.

 $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$, (II) (x = 0.64): Single crystals of (II) were first obtained from a reaction involving an equimolar mixture of AgBr and Bi_2S_3 at 720 K. The compound was later synthesized with better yield starting from Bi_2S_3 , AgBr and BiSBr in the molar ratio 13 : 13 : 7. The procedure for the synthesis was similar to the one described for (I).

 $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$, (III) (x = 0.73): The synthesis procedure was similar to that for (I). A mixture of Bi_2S_3 , AgBr and BiSBr in the molar ratio 3 : 3 : 1 was used. For (I), (II) and (III), the products consisted of agglomerates of black plate-like crystals. All of the $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ compounds were found to be stable in air.

EDX analysis

The chemical composition of a single crystal of **(II)** was determined by EDX analysis. The crystal used for the investigation was first checked with the Buerger precession camera for identification. The rough lattice parameters obtained correspond to those of the crystal used for the structure determination. The crystal was then cut and the analysis was carried out on different points of the new face. The experiment was performed on a LEO 982 digital scanning electron microscope. Data were acquired using an accelerating voltage of 20 kV and a 1 min accumulation time. The semi-quantitative analysis of the spectrum was performed with the program Analyse Voyager [47]. The presence of all four elements in the crystal corresponding to the average composition $Ag_{1.3}Bi_{2.7}S_{3.5}Br_{2.5}$ was confirmed; the crystal structure determination gives $Ag_{1.27(1)}B_{3.46(2)}Br_{2.54(2)}$.

Single-crystal X-ray crystallography

In order to investigate their symmetry and diffraction quality, the 0kl, 1kl, hk0, hk1 photographs of single crystals of all four compounds were recorded on a Buerger precession camera. The symmetry of the diffraction patterns corresponds to Laue class 2/m. In all cases the reflection condition observed on the photographs was h + k = 2n for hkl, suggesting C2/m, Cm or C2 as possible space groups. For information about the collection of intensity data refer to Table 1.

The structure of AgBi₂S₂Cl₃ was solved in the centrosymmetric space group C2/m using direct methods and refined by the full-matrix least-squares technique [48]. Two crystallographically independent metal positions, M(1) and M(2), and three anion positions, Z(1), Z(2) and Z(3), were located. The M(1) and M(2) sites were easily assigned to Bi and Ag. The sulphide and chloride anions present almost the same X-ray scattering factors and therefore could not be directly differentiated by Fourier synthesis. The assignment of S and Cl positions was done calculating of the bond valence sums [49]. The structure was refined to a residual value R_1 of about 10 % using this model. This value dropped to about 5 % after absorption correction and inclusion of anisotropic displacement parameters for all atoms in the structure. At this stage the difference electron density around Bi was very high (+7.3 and -5.0 e)10⁶ pm³), and the ellipsoid for the Bi atom was highly elongated. Therefore, the position was split into two close positions, Bi(a) and Bi(b), which were constrained to have the same displacement parameters and a sum of occupancies of one. Refinement of this model yielded a more acceptable shape for the Bi atom.

The fractional atomic coordinates and isotropic displacement parameters of all atoms with estimated standard deviations are listed in Table 2. The connectivity between the cations and anions in the structure and their coordination numbers are given in Table 3. Interatomic bond distances are given Table 4.

The structure of (II) was solved by direct methods in the space group C2/m and refined with a full-matrix leastsquares program [48]. Three cation positions, Bi(1), M(2)and M(3), as well as three anion positions, S(1), Br(1) and Z(2), were found in the asymmetric unit. A disorder model was applied for the M and Z positions and the sum of the occupation factors for each site was constrained to be 100 %. The atoms sharing the same site were forced to have the same coordinates and displacement parameters. The site occupation factors of the M and Z positions were restrained to maintain the electroneutrality of the compound. The following compositions were obtained: M(2) =[83.0(1)% Ag + 17.0(1)% Bi], M(3) = [45.0(1)% Ag +55.0(1) % Bi] and Z(2) = [73.0(4) % S + 27.0(4) % Br]. The formula of the compound based on this refinement was Ag_{1.27(1)}Bi_{2.73(1)}S_{3.46(2)}Br_{2.54(2)}. The final refinement after absorption correction and including the secondary extinction correction as well as anisotropic displacement parameters for all atoms yielded the *R* indices given in Table 1.

Formula sum		$AgBi_2S_2Cl_3$	AgBi ₃ S ₄ Br ₂ (I)	$Ag_{1.27}Bi_{2.73}S_{3.46}Br_{2.54}$ (II)	Ag _{1.46} Bi _{2.54} S _{3.09} Br _{2.91} (III)	
Crystal system; Space grou	p; Z	monoclinic; <i>C2/m</i> (No. 12); 2				
Density $(\rho_{cal})/(g/cm^3)$		6.12	6.43	6.42	6.38	
Crystal size [mm ³]; Colour		$0.35 \times 0.21 \times 0.03$; black	$0.08 \times 0.05 \times 0.03$; black	$0.16 \times 0.07 \times 0.02$; black	$0.08 \times 0.03 \times 0.02$; black	
Lattice parameters/pm; °	a =	1257.3(3)	1331.3(4)	1328.9(4)	1332.4(3)	
	<i>b</i> =	400.0(1)	408.0(1)	408.50(8)	409.3(1)	
	<i>c</i> =	804.1(2)	972.0(2)	973.4(4)	974.3(2)	
	$\beta =$	110.98(3)	90.80(3)	90.90(4)	90.40(3)	
Diffractometer	-	CCD (Mercury);	IPDS	-I (Stoe); graphite monochron	nator	
		graphite monochromator				
Radiation/pm		$\tilde{\lambda}(\hat{M}oK_{\alpha}) = 71.073$	$\lambda(MoK_{\alpha}) = 71.073$	$\lambda(\mathrm{Ag}K_{\alpha}) = 56.087$	$\lambda(MoK_{\alpha}) = 71.073$	
ϕ range; $\Delta \phi/^{\circ}$; T/K		200; 0.6; 295(1)	200; 1.5; 297(1)	200; 0.8; 293(1)	270; 1.0; 297(1)	
$2\theta_{\rm max}$; index range		$63^{\circ}; -17 \le h \le 14,$	$56^{\circ}; -17 \le h \le 16,$	$51.6^{\circ}; -20 \le h \le 20,$	$57.6^\circ; -17 \le h \le 18,$	
		$-5 \le k \le 3, -11 \le l \le 11$	$-4 \le k \le 5, -12 \le l \le 12$	$-5 \le k \le 6, -14 \le l \le 15$	$-5 \le k \le 5, -13 \le l \le 13$	
Measured reflections		2334	1418	3612	2465	
Unique reflections		598	600	1118	743	
$R_{\rm int} \hat{I} R_{\sigma}$		0.066 / 0.038	0.070 / 0.049	0.029 / 0.027	0.066 / 0.061	
Corrections		background, Lorentz factor, polarization factor				
Absorption correction		numerical, crystal description optimised using equivalent reflections				
μ/cm^{-1}		560	600	315	561	
Structure refinement			least-squares method; fu	Ill matrix; based on F^2 ;		
anisotropic displacement parameters [48]						
No. of parameters		31	36	37	35	
Extinction correction $x =$		$22(7) \cdot 10^{-4}$	$24(4) \cdot 10^{-4}$	$66(2) \cdot 10^{-4}$	$6(1) \cdot 10^{-4}$	
Difference electron density	$(e/10^6 pm^3)$	+2.5 to -2.9	+1.8 to -1.6	+3.3 to -2.4	+1.9 to -1.7	
$R_1(F_0 > 4\sigma(F_0))$		0.035	0.046	0.027	0.040	
$wR_2(all)$		0.093	0.109	0.042	0.073	

Table 1 Selected crystallographic data and details of the structure determinations

Table 2 Wyckoff positions (W.p.), site occupation factors (k), atomic coordinates, and equivalent isotropic displacement parameters (U_{eq} / pm^2) for all atoms in the asymmetric unit of AgBi₂S₂Cl₃. Estimated standard deviations corresponding to the last digit are indicated in brackets. All atoms are at y = 0

Atom	W.p.	k	X	Ζ	U_{eq}
Bi(a)	4 <i>i</i>	0.96(1)	0.3036(1)	0.3180(2)	191(3)
Bi(b)	4i	0.04(1)	0.2920(1)	0.2550(4)	191(3)
Ag	2b	1	0.5	0	294(4)
CI(1)	2c	1	0	1/2	219(7)
Cl(2)	4i	1	0.1347(2)	0.9484(3)	179(5)
S	4i	1	0.3358(2)	0.6758(3)	130(5)

Table 3 Connectivity of atoms in the structure of $AgBi_2S_2Cl_3$ and their coordination numbers

Atom	Cl(1)	Cl(2)	S	c.n.
Bi(a/b)	2/4	3/3	3/3	8
Ag	0/0	4/2	2/1	6
c.n.	4	5	4	

The structures of (I) and (III) were refined using the atomic positions of (II) as a starting point. Similar procedures were used for the refinements. In the case of (I), significant mixed occupancy was found only in metal positions M(2) = [64.0(1) % Ag + 36.0(1) % Bi], and M(3) = [36.0(1) % Ag + 64.0(1) % Bi], resulting in a composition very close to AgBi₃S₄Br₂.

In (III), only the M(3) = [45.0(4) % Ag + 55.0(4) % Bi]and Z(2) = [55.0(4) % S + 45.0(4) % Br] positions show **Table 4** Selected interatomic distances (pm) in AgBi₂S₂Cl₃. Standard deviations corresponding to the last digit are indicated in brackets. Operators for generating equivalent atoms: (i) x, y, z-1; (ii) 1/2-x, -1/2-y, 1-z; (iii) 1/2-x, 1/2-y, 1-z; (iv) 1/2+x, 1/2+y, z; (v) 1/2+x, y-1/2, z; (vi) 1-x, -y, 1-z; (vii) 1/2+x, 1/2+y, z-1; (viii) 1/2+x, y-1/2, z-1

$\begin{array}{llllllllllllllllllllllllllllllllllll$	Bi(b) - Cl(2i)Bi(b) - S(ii, iii)Bi(b) - Cl(2ii, 2iii)Bi(b) - S	254.9(6) 274.4(2) 293.4(3) 322.7(4)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$Bi(b) - Cl(1^{iv}, 1^{v})$	332.2(5)

substantial mixed occupancy corresponding to the formula $Ag_{1.46(1)}Bi_{2.54(1)}S_{3.09(2)}Br_{2.91(2)}$.

The fractional atomic coordinates and isotropic displacement parameters of all atoms with estimated standard deviations are listed in Table 5. In order to simplify comparison, the parameters for the three crystals are grouped according to the Wyckoff positions and with respect to increasing silver content. The connectivity between the cations and anions in the structure and their coordination numbers are given in Table 6. Interatomic bond distances in these three phases are compared in Table 7.

Further details of the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository numbers CSD-413938 (AgBi₂S₂Cl₃), CSD-413939 (AgBi₃S₄Br₂), CSD-413940 (Ag_{1.27}Bi_{2.73}S_{3.46}Br_{2.54}), and CSD-413941 (Ag_{1.46}-Bi_{2.54}S_{3.09}Br_{2.91}). Graphic representations of the crystal structures were made with the program Diamond [50], using the ellipsoid representation at the 95 % probability level.

Table 5 Wyckoff positions (W.p.), occupancies (q), atomic coordinates, and equivalent isotropic displacement parameters (U_{eq} / pm²) for all atoms in the asymmetric unit of AgBi₃S₄Br₂ (I), Ag_{1.27}Bi_{2.73}S_{3.46}Br_{2.54} (II) and Ag_{1.46}Bi_{2.54}S_{3.09}Br_{2.91} (III). Standard deviations corresponding to the last digit are indicated in brackets. All atoms are at y = 0. Occupancy of cation and anion positions: M = qBi + (1-q)Ag; Z = qS + (1-q)Br with $0 \le q \le 1$

Atom	W.p.	q	X	Ζ	U_{eq}
Bi(1)	4 <i>i</i>	1	0.7741(1)	0.1870(1)	378(1)
		1	0.7741(1)	0.1866(1)	334(1)
		1	0.7681(1)	0.1819(1)	386(3)
M(2)	2b	0.360(1)	1/2	0	546(7)
		0.172 (1)	1/2	0	415(3)
		0	1/2	0	680(8)
M(3)	2d	0.640(1)	1/2	1/2	438(5)
		0.554(1)	1/2	1/2	362(2)
		0.545(4)	1/2	1/2	475(4)
Br(1)	4i	0	0.1415(2)	0.4225(3)	324(2)
		0	0.1419(1)	0.4226(1)	286(2)
		0	0.1413(1)	0.4230(2)	325(4)
S(1)	4i	1	0.1479(3)	0.0558(5)	210(1)
		1	0.1481(1)	0.0557(2)	164(3)
		1	0.1479(3)	0.0571(4)	207(8)
Z(2)	4i	1	0.4167(1)	0.2425(2)	175(4)
		0.711(6)	0.4167(1)	0.2411(2)	296(4)
		0.545(4)	0.4179(2)	0.2391(3)	340(6)

Table 6 Connectivity of cations and anions in the structure of $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ and their coordination numbers

Atom	Br(1)	S(1)	<i>Z</i> (2)	c.n.
Bi(1)	2/2	3/3	2/2	7
M(2)	0/0	4/2	2/1	6
M(3)	4/2	0/0	2/1	6
c.n.	4	5	4	

Table 7 Selected interatomic distances (pm) for AgBi₃S₄Br₂ (I), Ag_{1.27}Bi_{2.73}S_{3.46}Br_{2.54} (II) and Ag_{1.46}Bi_{2.54}S_{3.09}Br_{2.91} (III). Standard deviations corresponding to the last digit are indicated in brackets. Operators for generating equivalent atoms: (i) 1-x, -y, -z; (ii) 1/2+x, 1/2+y, z; (iii) 1/2+x, y-1/2, z; (iv) 1/2-x, -1/2-y, -z; (v) 1/2-x, 1/2-y, -z; (vi) 1-x, -y, 1-z; (vii) 1/2-x, -1/2-y, 1-z; (viii) 1/2-x, 1/2-y, 1-z; (ix) x-1/2, y-1/2, z; (x) x-1/2, 1/2+y, z

	(I)	(II)	(III)
Bi(1)-S(1 ⁱ)	259.2(3)	259.1(4)	259.1(3)
$B_1(1) = Z(2^n, 2^m)$	283.4(6)	283.1(2)	291.1(2)
$B_1(1) = S(1^{ii}, 1^{iii})$	292.4(6)	292.1(3)	286.4(3)
$\operatorname{Bi}(1) - \operatorname{Br}(1^{\mathrm{ii}}, 1^{\mathrm{iii}})$	355.4(7)	355.8(5)	355.1(4)
$M(2) - Z(2, 2^{i})$	261.8(3)	261.0(4)	258.0(3)
$M(2) - S(1^{ii}, 1^{iii}, 1^{iv}, 1^{v})$	288.2(6)	288.2(2)	289.2(2)
$M(3)-Z(2, 2^{vi})$	272.4(4)	273.7(5)	276.0(3)
$M(3)-Br(1^{ii}, 1^{iii}, 1^{vii}, 1^{viii})$	288.4(6)	288.8(2)	288.4(2)

Band structure calculations

AgBi₂S₂Cl₃: Relativistic DFT (density functional theory) calculations were carried out with the program WIEN97 [51] using the LAPW (linearized augmented plane wave) method. As Muffin tin radii 2.4 au was used for Ag and Bi, and 2.2 au was selected for Cl



Fig. 2 A representation of the structure of $AgBi_2S_2Cl_3$ showing the close relationship with the pavonite structure family (right hand) and the lillianite family (left hand).

and S. RKMAX and GMAX were equal to 8 and 14 au⁻¹, respectively. As density functional, the gradient-corrected functional according to *Perdew*, *Bourke* and *Ernzerhof* [52] was used. The Brillouin zone for the SCF-cycles was constructed using the tetrahedron method of *Bloechl* et al. [53] with 32 independent *k*-points, which corresponds to a number of 200 *k*-points in the entire Brillouin zone. Calculation of the density of states (DOS) was performed using 288 independent *k*-points (2000 *k*-points in the Brillouin zone).

 $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ (x = 1/2 and x = 1): The electronic band structures and the density of states (DOS) were calculated for the two hypothetical end members of the series of isostructural compounds, $AgBi_3S_4Br_2$ (x = 1/2) and $AgBiSBr_2$ (x = 1), in order to investigate the influence of the substitution coefficient x on the electronic properties. For the calculations, the same lattice parameters were considered for both compositions. The ordered structure models used for the calculations had Ag at M(2), Bi at M(3) and S at Z(2) positions for $AgBi_3S_4Br_2$, and Ag at M(2) and M(3) with Br at Z(2) positions for $AgBi_3SBr_2$. For the calculations within the scalar relativistic all-electron local density approximation (LDA) the program LMTO-ASA [54] was used.

Results and Discussion

The crystal structure of $AgBi_2S_2Cl_3$

AgBi₂S₂Cl₃ crystallizes in the monoclinic space group C2/m and adopts a variant of the InBi₂S₄Cl [43] structure type (Fig. 2).

The Ag atom is situated in an flattened octahedral environment (Table 3) distorted towards [2+4] coordination (Table 4) with two S atoms in *trans* positions (268 pm) and four Cl atoms in the equatorial plane (275 pm). A similar type of coordination is generally found for Ag^I atoms in the structures of silver-containing sulphides. Some typical examples include AgBi₃S₅ [20], Ag₃Bi₇S₁₂ [25] and Ag₂Bi₂S₃Cl₂ [44].

The Bi atom is surrounded by three S atoms and five Cl atoms (Fig. 3). The coordination polyhedron can be described as a bicapped trigonal prism, where four Cl and



Fig. 3 Environments of cations and anions in $AgBi_2S_2Cl_3$. For bond distances see Table 5.



Fig. 4 Projection of the structure of $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ (x = 0.64) (**II**) along [010] highlighting the double-chains of monocapped trigonal prisms around Bi(1). The two alternating types of building units *A* and *B* that form the structure are indicated.

two S atoms form the trigonal prism with the two $[S_2Cl_2]$ rectangular faces capped by additional S and Cl atoms. The



Fig. 5 Environments of cations and anions in $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$. For bond distances see Table 7.

central Bi atom is shifted from the *centroïd* [55] of the coordination polyhedron towards the S-S edge of the trigonal prism. The marginal splitting of the Bi position is attributed to minor statistical disorder of S and Cl over the anion positions in the coordination sphere.

The S atom is located in a distorted tetrahedral coordination environment of three Bi atoms and one Ag atom. Cl(1) displays distorted square coordination by four Bi atoms, while Cl(2) exhibits square pyramidal coordination by two Ag and three Bi atoms (Fig. 3).

In the crystal structure of AgBi₂S₂Cl₃, the bicapped trigonal prisms around Bi join common edges along [001] and share their triangular bases along [010] to form doublechains (Fig. 2), which alternate along [100] with the distorted octahedra around Ag atoms. This structural arrangement is similar to the *A* module found in the structures of different members of the homologous series [BiQX]₂ · [Ag_xBi_{1-x} $Q_{2-2x}X_{2x-1}$]_{N+1} (Q = S, Se; X = Cl, Br). AgBi₂S₂Cl₃ can thus be considered as the first member, ^(0, 1)P, of this series, consisting only of module *A*. Parallels with the structure of the fully (Ag,Bi)-substituted lillianite homologous series ^(N1, N2)L [56] with (N1, N2) = (1, 0) can also be seen (Fig. 2).

Fig. 6 Group-subgroup relationship between the structures of AgBiSCl₂ and Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}.

Comparison of the charge-balanced formulations $(Ag^+)(Bi^{3+})_2(S^{2-})_2(Cl(2)^-)_2(Cl(1)^-)$ and $(In^{3+})(Bi^{3+})_2$ - $(S(1)^{2-})_2(S(2)^{2-})_2(Cl^-)$ for $AgBi_2S_2Cl_3$ and $InBi_2S_4Cl$ [43] indicates that $AgBi_2S_2Cl_3$ corresponds to a halogen-rich analogue of the hypothetical family of isostructural compounds with general formula MBi_2Z_5 (M = metal; Z = anion, primarily chalcogen or halogen) in which the replacement of chalcogen atoms by halogen atoms is compensated by the introduction of a metal atom of lower charge.

The crystal structures of $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$

AgBi₃S₄Br₂ (I), Ag_{1.27}Bi_{2.73}S_{3.46}Br_{2.54} (II) and Ag_{1.46}. Bi_{2.54}S_{3.09}Br_{2.91} (III) are three members of the series of compounds with general composition Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x} (x = 0.50, x = 0.64 and x = 0.73). The structural motif associated with this series is shown in Figure 4.

The asymmetric unit of $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ contains three crystallographically different metal positions and three non-metal positions (Table 6). Examination of the Ag/ Bi mixed occupancy in the metal positions reveals that the sevenfold-coordinated Bi(1) is not substituted by Ag in any of the compounds. The coordination polyhedron around Bi(1) is a distorted monocapped trigonal prism (Fig. 5) of three S atoms, two Br atoms and two anions with varying character (Z = S/Br). In all compounds, the coordination polyhedra of the M(2) and M(3) positions exhibit a tetragonal distortion of the octahedron towards a [2+4] coordination with two short bonds *trans* to one another (Table 7). In any case, the octahedron around M(3) is less distorted than the one around M(2). This observation is in agreement with the analysis of the distribution of Ag (characteristic [2+4] coordination) and Bi atoms among the octahedral metal positions in the structures: the M(2) position is highly preferred by Ag atoms (64 % in (I), 83 % in (II) and 100 % in (III)) while in the M(3) position Bi atoms slightly dominate.

The S(1) and Br(1) positions show no mixed occupancy. The S(1) atom is located in a distorted square pyramid, while the Br(1) atom shows a distorted square coordination (Fig. 5). The nearest additional metal atom, M(2), that could complete a square pyramidal coordination of Br(1) is situated at a distance of 494 pm. The anion position Z(2)shows mixed S/Br occupancy and is located in a distorted tetrahedral environment of cations.

The structure of $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$, as indicated in Figure 4, is closely related to that of the pavonite family described in the introduction and to the structures of various members of the series $[BiQX]_2$. $[Ag_xBi_{1-x}Q_{2-2x}X_{2x-1}]_{N+1}$ (Q = S, Se; X = Cl, Br). It can be considered as the ^(1, x)P member of the quaternary series. In the structures of $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$, the S atoms located at the interface of modules A and B in the pavonite structures are completely replaced by Br atoms.

Relation to the structure of AgBiSCl₂

The monoclinic structure of the $^{(1, x)}P_{S,Br}$ compounds $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ can be derived from the orthorhombic structure of the $^{(1, 1)}P_{S,Cl}$ compound AgBiSCl₂ [46] by dis-

carding the mirror planes at z = 1/4 and 3/4. The groupsubgroup relationship between the two structures is depicted in Figure 6. The Cl position (8*f*) of AgBiSCl₂ is divided into two independent positions (4*i*) that are occupied by different anions, S(1) and Br(1), in the monoclinic structure. The higher affinity of Bi to S results in a shift of the Bi atom of 84 pm away from the corresponding position in AgBiSCl₂. Thereby, the coordination number of Bi is reduced from c.n. = 8 (bicapped trigonal prism) in AgBiSCl₂ to c.n. = 7 (monocapped trigonal prism) in Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}. The corrugated layer of bicapped trigonal prisms found in the orthorhombic structure is consequently broken into parallel double-chains of monocapped trigonal prisms. A similar structure type was recently reported for MnSbSe₂I [38].

Relations between composition and structure

One of the most important structural features of the $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ compounds is the "strategic" position of Z(2) in the structure. This anion position, which has the particularity of being connected to all metal atoms in the structure, shows mixed S/Br occupancy and seems to be the key to assuring the electroneutrality of the compounds. Due to the multiplicity of the point positions, the occupancies follow the simple relation q(M(2)) + q(M(3)) = q(Z(2)). Herein the occupancies of the *M* and *Z* positions are defined as 1 = q Bi + (1-q) Ag and 1 = q S + (1-q) Br with $0 \le q \le 1$. The amount of S found in the Z(2) position decreases with increasing Ag content according to the equation q(Z(2)) = 2(1-x).

In line with the above crystallographic analysis, the solid solution is restricted to particular atomic positions in the structure. The structural adaptation – i.e. isomorphic substitution between Bi and Ag due to their similar effective ionic radii for c.n. = 6 (103 pm for Bi³⁺ and 115 pm for Ag⁺) [57] – observed in the Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x} series is facilitated by the flexibility introduced by the occupancy of the anion position Z(2) with either S or Br atoms. The coupled exchange process of cations and anions may yield a continuous spectrum of isostructural charge balanced compounds.

According to the structures of the present members, the series $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ is better represented by the structural formula $[BiSBr]_2 \cdot [Ag_{2x}Bi_{2(1-x)}S_{4(1-x)}Br_{2(2x-1)}]$ with $0.5 \le x \le 1$. The $[Ag_{2x}Bi_{2(1-x)}S_{4(1-x)}Br_{2(2x-1)}]$ part of the formula describes the coupled charge-balanced exchange process that takes place within the network of $[MS_4Z_2]$ and $[MBr_4Z_2]$ octahedra. Following this formula, the composition range of the series is confined between the two isostructural end members $AgBi_3S_4Br_2$ (x = 0.5) and $AgBiSBr_2$ (x = 1). As determined from the refinement of (I), the silver-poorest member $^{(1, 0.5)}P$ still shows Ag/Bi disorder at the metal sites M(2) and M(3), while the Z(2) position is fully occupied by S atoms. In the as yet hypothetical silver-richest end member $AgBiSBr_2$, full occupancy of

Fig. 7 Band structure and density of states (DOS) of $AgBi_2S_2Cl_3$ with "fat-band" representation of the Ag-5s state.

M(2) and M(3) by Ag atoms and of Z(2) by Br atoms is expected.

Another structural characteristic of this class of compounds is the selectivity of the substitution process for certain cation and anion positions. Substitution is only observed within the network of octahedra that share common vertices. i.e. it extends exclusively along the M(2)-Z(2)-M(3)-Z(2) zigzag pattern of *trans* short bonds. In the case of minimal silver content (x = 0.5), the composition of the zigzag pattern corresponds to the sequence (Ag/Bi)-S-(Ag/Bi)-S. With maximum silver content (x = 1), its composition should be Ag-Br-Ag-Br, although due to chemical reasons an atomic rearrangement is expected that will result in the sequence Ag-S-Ag-S, as found in the ordered structure of the homoeotypic sulphide chloride AgBiSCl₂ [46]. According to the structures of the three phases of the series that we have investigated, it seems that the structure type is moving towards orthorhombic symmetry as the Ag content increases (Table 1), which is consistent with the equivalence of the positions M(2) and M(3).

One of the most significant structural features of the $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ series is the strong dependence of the Bi-Z(2) and Bi-S bonds on the substitution coefficient x. The Bi-Z(2) distance rapidly increases with increasing x, whereas the Bi-S distance decreases (Table 7). This behaviour can be explained by the substitution of S^{2-} by larger and lower charged Br^- anions in the Z(2) position.

Fig. 8 Band structures and density of states (DOS) for cation-ordered $AgBi_3S_4Br_2$ (x = 0.5) (above) and $AgBiSBr_2$ (x = 1) (below).

Electronic band structure of AgBi₂S₂Cl₃

The electronic band structure of AgBi₂S₂Cl₃ (Fig. 7) obtained from the relativistic DFT calculations shows narrow valence bands suggesting large localization of the electrons, which is in agreement with the ionic description of the compound. The valence bands, which include the states over a range of approximately 5.2 eV directly below the Fermi level ($E_{\rm F}$), are above all Ag-4d, Bi-6p, Cl-3p and S-3p states. The Bi-6s orbital is strongly lowered in energy by relativistic effects and does not interfere in this range. The Ag-5s states lie essentially above the Fermi level. The small density of Ag-5s states in the valence bands reflects the phenomenon of $4d^{10-\delta}5s^{\delta}$ mixing, well-known for Ag^I cations. The calculated band gap of approximately 1.5 eV is consistent with the black colour of AgBi₂S₂Cl₃. The compound shows an indirect transition from A to L and a direct transition of similar energy at L.

Electronic band structures of $Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}$ with x = 0.5 and x = 1

As can be seen in Figure 8, the electronic band gap (E_g) is considerably diminished from the silver-poor compound AgBi₃S₄Br₂ (x = 0.5), for which $E_g = 0.9$ eV, to the silverrich phase AgBiSBr₂ (x = 1), for which $E_g = 0.6$ eV. Both values are consistent with the black colour of the crystals of Ag_{2x}Bi_{4-2x}S_{6-4x}Br_{4x}. As above, both compounds present small dispersion of the valence bands, suggesting large localization of the electrons. However, the valence band in AgBiSBr₂ (x = 1) is slightly broader, indicating that the compound, which contains more ions of low charge, may display more covalent character.

The electronic structure of $AgBi_3S_4Br_2$ exhibits indirect transitions from Z to M and, with slightly larger energy, from Z to A-M, as well as a direct gap at Z. In the case of AgBiSBr₂, two indirect transitions with similar energies, from Z to A and from M to A, are possible. The calculations clearly show that the simultaneous substitution of Bi by Ag in the metal positions and of S by Br in the anion positions strongly affects the electronic character of members of the solid solution series. The top of the valence band is influenced by substitutions in the Z(2) and M(2) positions while the bottom of the conduction band is influenced by substitution in the M(3) position. Conductivity measurements have yet to be carried out.

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