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Preparation and Crystal Structure of $MnBiS_2Br$[#]

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Summary. Black single crystals of $MnBiS_2Br$ were obtained by the reaction of stoichiometric amounts of α-MnS, Bi, S, and $BiBr_3$ (3:2:3:1) at 600°C for 4 weeks. The compound crystallises in the monoclinic system, space group $C2/m$, with $a = 12.767(2)$, $b = 3.9468(4)$, $c = 9.574(1)$ Å, $\beta = 90.87(2)°$, and $Z = 4$. The crystal structure refinement based on 720 reflections converged at $R = 0.0244$ and $wR2 = 0.0579$, respectively. $MnBiS_2Br$ forms a layer structure consisting of MnS_6 octahedra, MnS_2Br_4 octahedra, and BiS_{3+2} pyramids.

Keywords. Manganese; Bismuth; Sulphur; Bromine; Sulfosalts; Crystal structure.

Introduction

One goal of modern solid state and materials chemistry is the synthesis of layered materials with interesting magnetic properties on the basis of transition elements. Usually these materials contain iron, chromium, or manganese. A mineral related group of compounds containing these ions are called sulfosalts, *e.g.*, $FeSb_2S_4$ (*berthierite*) [1]. We recently started to elucidate the existence of sulfosalts comparable to $Mn_{0.695}Bi_{2.2}S_{3.95}$ [2] (this compound will be denoted as $MnBi_2S_4$ in this text) which contain Mn^{2+} in a d^5 high spin configuration in octahedral environment. It was shown that $MnSb_2S_4$ can be obtained either by hydrothermal methods as an orthorhombic compound which is isotypic to $FeSb_2S_4$ [3], *i.e.*, *oP*28, or by solid state techniques as a monoclinic phase *mC*28 which is closely related to $MnBi_2S_4$ [4]. $MnSb_2Se_4$ *mC*28 could also be obtained by solid state preparation [5]. $MnSb_2S_4$ is a semiconductor and spin polarized DFT calculations confirmed the semiconducting behaviour of both phases of $MnSb_2S_4$ [5, 6]. Neutron powder diffraction experiments on $MnSb_2S_4$ *mC*28 and the heavier homologous compounds revealed that they show antiferromagnetic ordering below 25 K with a complicated helical ordering pattern [5, 7].

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# Dedicated to Prof. *Henri Brunner* on the occasion of his 70th birthday

Manganese ions are octahedrally coordinated by chalcogenide ions in these materials. The MnQ_6 octahedra ($Q = S$, Se) share common edges to give strands of octahedra along one crystallographic direction. These strands of octahedra are interlinked by chalcogenometalate ions to form layers. These are stacked above each other with only weak interactions between the layers [4]. There is some actual experimental evidence that the magnetic spins of the Mn^{2+} ions in the antiferromagnetic phases are coupled only along the strands of octahedra but not within the layers or even between the layers.

It is interesting to prepare new layered magnetic materials by changing the connectivity of these strands of octahedra by chemical modification of the compounds. Thus, new magnetic ordering patterns can be expected, especially when different types of octahedra are combined in a closer way than in $MnBi_2S_4$ and related compounds. One way how to change the connectivity is the partial substitution of chalcogenide ions by halide ions. Three examples for such compounds were recently described: monoclinic $MnSbSe_2I$ *mC*20 [8], the isotypic compound $MnBiSe_2I$ [9], and orthorhombic $MnSbS_2Cl$ *oP*20 [10]. The different radii and different ionicities of the constituting ions have obviously a certain influence on the structural arrangement of the resulting compounds. Thus, we find two different types of octahedra $MnSe_6$ and $MnSe_2I_4$ in $MnPnSe_2I$ ($Pn = Sb$, Bi) but only one type of octahedra MnS_4Cl_2 in $MnSbS_2Cl$. The different octahedra in $MnPnSe_2I$ share common edges formed either by two Se atoms or by two I atoms, respectively. In contrast, only common edges formed by one S and one Cl atom are found in $MnSbS_2Cl$. These strands of octahedra share common Q vertices in $MnPnSe_2I$ and also in $MnSbS_2Cl$. Herein, we report on the synthesis and structural characterization of $MnBiS_2Br$ which is isotypic with $MnPnSe_2I$.

Results

Structure Determination

Single crystals of the title compound suitable for a structure determination were obtained from the reaction of stoichiometric amounts of MnS, Bi, $BiBr_3$, and S; see the experimental section for details. X-Ray intensities were collected on a STOE IPDS-I using MoKα radiation, $\lambda = 0.71073$ Å. The compound crystallises in the monoclinic system with the lattice constants $a = 12.767(2)$, $b = 3.9468(4)$, $c = 9.574(1)$ Å, $\beta = 90.87(2)^\circ$, $V = 482.4(1)$ Å^3, and $Z = 4$. The space group $C2/m$ was derived from systematic extinctions and confirmed by the subsequent refinement. Direct methods were applied to solve the structure and provided the positions of one Bi, one Br, two S, and two Mn atoms. The refinement converged at $R = 0.0237$ for reflections with $I > 2\sigma_I$ and $R = 0.0244$ for all reflections. A total of 720 independent reflections were used for the refinement of 34 parameters. Anisotropic displacement parameters were used for all atoms. An extinction parameter was included in the last refinement cycles. Further crystallographic details are summarized in Table 1. Atomic coordinates and anisotropic displacement parameters are collected in Tables 2 and 3, respectively. Table 4 contains selected interatomic distances and angles calculated from these data.

Table 1. Crystallographic data for the structure analysis of $MnBiS_2Br$

Compound	$MnBiS_2Br$
Formula weight in $g\,mol^{-1}$	407.95
Crystal size in mm^3 and colour	$0.1\times0.05\times0.05$, black
Crystal system	monoclinic
Space group	$C2/m$ (No. 12)
Lattice constants in Å	$a = 12.767(2)$
From single crystal	$b = 3.9468(4)$
	$c = 9.574(1)$
	$\beta = 90.87(2)$
Cell volume in $Å^3$, Z	482.4(1), 4
ρ_{calc} in $g\,cm^{-3}$	5.618
Diffractometer	STOE IPDS, MoKα, $\lambda = 0.71073$ Å, oriented graphite monochromator
φ-range in °, $\Delta\varphi$ in °	$0.0 \le \varphi \le 255$, 1.0
μ(MoKα) in mm^{-1}	48.00
Absorption correction	numerical, crystal description with 6 faces, shape optimised with X-SHAPE [11]
No. of measured images	255
Irradiation time/image in min	8
Temperature in °C	20
2θ-range in °	$3.2 \le 2\theta \le 58.04$
hkl-range	$-17 \le h \le 17$
	$-5 \le k \le 5$
	$-13 \le l \le 13$
No. of reflections, R_{int}	3277, 0.0407
No. of independent reflections	720
No. of parameters	34
Program	SHELX 97 [12]
Final R, wR ($I > 2\sigma_I$)	0.0237, 0.0576
Final R, wR (all reflections)	0.0244, 0.0579
GooF	1.211
Largest difference peak $\Delta\rho_{max}$	2.855
and hole $\Delta\rho_{min}$ in $e\,Å^{-3}$	−1.133

Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), Fax: 0049 7247 808 666, E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-415307, the name of the authors, and the reference of the publication

Structure Description and Discussion

$MnBiS_2Br$ crystallises isotypic with $Mn\mathit{Pn}Se_2I$. The coordination spheres of the metal ions are shown in Fig. 1.

Bi is exclusively coordinated to S atoms in its first coordination sphere. As shown by the distances and angles the coordination of Bi towards S can be regarded as $3 + 2$, *i.e.*, we find the typical arrangement for sulfosalts. Three short bonds d(Bi–S) are in the range from 2.594–2.700 Å, and two medium range bonds d(Bi–S) = 3.061 Å are found. Three bromine atoms are located in a long distance d(Bi–Br) ≈ 3.6 Å. These distances d(Bi–Br) are significantly longer than those

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{eq} in Å^2 for $MnBiS_2Br$

Atom	x	y	z	U_{eq}[a]
Bi	0.2129(1)	0	0.8028(1)	0.017(1)
Mn1	0	1/2	0	0.018(1)
Mn2	0	1/2	1/2	0.018(1)
Br	0.1355(1)	0	0.4327(1)	0.018(1)
S1	0.1376(1)	0	0.0528(2)	0.014(1)
S2	0.0726(1)	1/2	0.7545(2)	0.015(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3. Anisotropic displacement parameters U_{ij} in Å^2 for $MnBiS_2Br$, $U_{12} = U_{23} = 0$ for all atoms

Atom	U_{11}	U_{22}	U_{33}	U_{13}
Bi	0.017(1)	0.017(1)	0.016(1)	0.003(1)
Mn1	0.016(1)	0.021(1)	0.017(1)	0.004(1)
Mn2	0.019(1)	0.018(1)	0.016(1)	−0.001(1)
Br	0.017(1)	0.018(1)	0.020(1)	0.003(1)
S1	0.014(1)	0.015(1)	0.014(1)	0.000(1)
S2	0.014(1)	0.016(1)	0.013(1)	−0.001(1)

Table 4. Selected interatomic distances (in Å), and angles (in degrees) for $MnBiS_2Br$ at room temperature

Bi–S1		2.594(2)	S1–Bi–S1		80.30(4)
Bi–S2	2×	2.700(1)	S1–Bi–S1	2×	79.65(4)
Bi–S1	2×	3.061(1)	S1–Bi–S2	2×	84.46(4)
			S2–Bi–S1	2×	90.77(3)
Mn1–S2	2×	2.539(2)	S2–Bi–S2		93.90(5)
Mn1–S1	4×	2.685(1)	S2–Bi–S1	2×	162.92(4)
			S1–Mn1–S1	2×	180
Mn2–Br	4×	2.7085(5)	S2–Mn1–S2		180
Mn2–S2	2×	2.594(2)	S1–Mn1–S1	2×	85.39(5)
			S1–Mn1–S2	4×	85.83(4)
			S1–Mn1–S2	4×	94.17(4)
			S1–Mn1–S1	2×	94.61(5)
			Br–Mn2–Br	2×	180
			S2–Mn2–S2		180
			S2–Mn2–Br	4×	89.82(3)
			Br–Mn2–Br	2×	86.46(2)
			Br–Mn2–Br	2×	93.54(2)
			S2–Mn2–Br	4×	90.18(3)
			Mn2–Br–Mn2		93.54(2)
			Mn1–S2–Mn2		137.66(7)

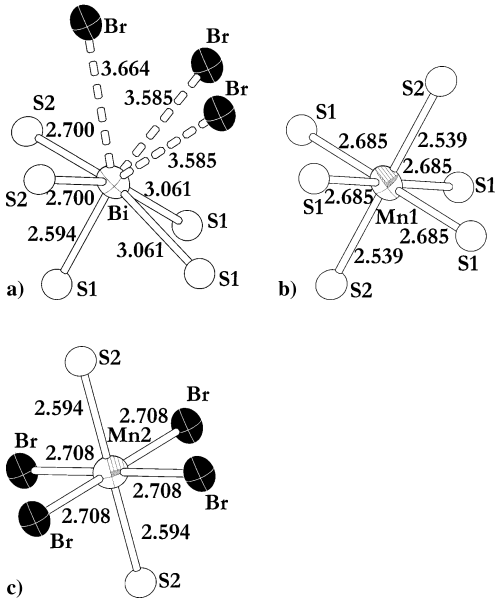

Fig. 1. Coordination spheres of the metal ions in $MnBiS_2Br$, distances are given in Å; displacement parameters are drawn at the 95% probability level

found in $BiBr_3$ [13]. Contrary to $MnBiSe_2I$ [9] where Bi shows $2 + 1$ long distances to I there are three almost equal distances to bromine in $MnBiS_2Br$, see Fig. 1a. Manganese ions are six-coordinate, either only by sulphide ions or by four bromine ions and two sulphide ions, see Figs. 1b and c. Both types of octahedra show two short axial bonds, *i.e.*, $d(\text{Mn1–S2}) = 2.539$ Å for $[MnS_6]$ and $d(\text{Mn2–S2}) = 2.594$ Å for $[MnS_2Br_4]$. The distances in the basal plane are longer, namely $d(\text{Mn1–S1}) = 2.685$ Å for $[MnS_6]$ and $d(\text{Mn2–Br}) = 2.7085$ Å for $[MnS_2Br_4]$.

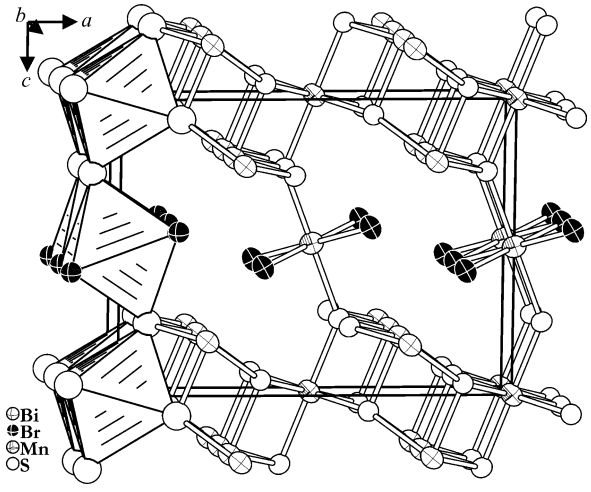

Fig. 2. Section of the crystal structure of $MnBiS_2Br$; Mn atoms are octahedrally coordinated and the octahedra form chains along *b*; BiS_{3+2} units connect the chains to form layers parallel (001); long contacts between Bi and Br are not shown here

Having the connectivity of the octahedra in mind, one finds a compression along the direction of the common vertices S2, *i.e.*, [001]. The longer bonds are found in the direction of the chains of octahedra, *i.e.*, [010], see Fig. 2.

The distances of manganese to sulphur in the present structure are comparable to several related compounds, and the distances to bromine are at the upper end of related materials. The compression of the octahedral environments is similar to the isotypic Mn*Pn*Se_2I [8, 9]. Obviously the monoclinic structure type is preferred for the present combination of elements. It seems to be essential for this structure type that the bonds Mn–*Q* are shorter than the bonds Mn–*X* (*X* = Cl, Br, I). In case of $MnSbS_2Cl$ [10] the bonds Mn–Cl are significantly shorter than the bonds Mn–S. This results in a modified coordination behaviour of the manganese atoms and a completely different three dimensional crystal structure is formed.

In the introduction we mentioned our approach to modify the crystal structure of MnPn_2Q_4 by the partial substitution of chalcogenide ions by halide ions and to conserve at least a basic building block of the crystal structure. Figure 3 shows a section of the crystal structures of $MnBiS_2Br$ and of $MnBi_2S_4$. For the latter one the layer showing no disorder of Mn and Bi is drawn. It becomes obvious that the building blocks are identical with respect to the connectivity modes of the atoms, *i.e.*, Mn has a compressed octahedral coordination by six S atoms and Bi has a $3 + 2$ coordination by S atoms. Even the distances differ only slightly.

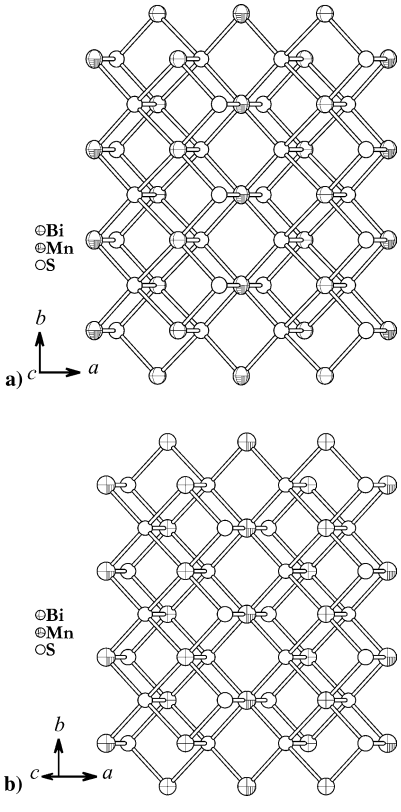

Fig. 3. Section of the crystal structures of a) $MnBiS_2Br$ and b) $MnBi_2S_4$; data for b) are taken from Ref. [2]; $MnBi_2S_4$ shows some Mn deficiency and some surplus Bi

A comparison of the corresponding lattice constants shows the close relationship. Thus, $a = 12.767$ and $b = 3.9468$ Å are found for $MnBiS_2Br$ and $a = 12.869$ and $b = 3.9546$ Å for $MnBi_2S_4$ (data taken from Ref. [2]). The difference between the two compounds is the nature of the second layer which connects the layers under discussion. In $MnBiS_2Br$ the layer shown in Fig. 3a has the composition $[MnBi_2S_4]$ and the second layer is $[MnBr_{4/2}]$ when the sulphur vertices are neglected. $MnBiS_2Br$ results as the chemical formula. In case of $MnBi_2S_4$ both layers have the same composition, *i.e.*, $[MnBi_2S_4]$ neglecting the partial disorder of the second layer. The same close relationship of the a and b lattice constants is found for the couple $MnSb_2Se_4$ [5, 14] and $MnSbSe_2I$ [8]. To date no other combinations of Mn, *Pn*, *Q*, and *X* are known. However, it might be just a question of appropriate synthesis to obtain the other compounds.

Experimental

$MnBiS_2Br$ was obtained by reaction of stoichiometric amounts of α-MnS, Bi, $BiBr_3$, and S (3:2:1:3). MnS was obtained from Mn (99.9%, Ventron) and S (99.999%, ChemPur) by high temperature reaction (heating to 800°C and subsequent annealing at 500°C for three days). $BiBr_3$ was prepared from a solution of Bi_2O_3 (purum, Fluka) in aqueous HBr (47%, reinst, Merck). Elemental Bi was used as available (99.9999%, ChemPur). The reaction mixtures were sealed in evacuated quartz ampoules and were then annealed at 600°C for 4 weeks. The title compound was isolated as black shiny needle shaped crystals from an inhomogeneous reaction product. This finding is reproducible but despite several experimental efforts we are yet not able to prepare phase pure samples. This is similar for all four known $MnPnQ_2X$ phases [8–10] and remains to be explained.

Single crystals were fixed on thin walled glass capillaries and then mounted on a Stoe IPDS-I single crystal diffractometer providing monochromatic MoKα radiation. Crystallographic data are collected in Table 1. Absorption was corrected after the optimization of the description of the crystal shape with the X-SHAPE routine [11].

Acknowledgement

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