Preparation and Crystal Structure of $MnBiSe_2I$

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Dedicated to Professor Gerd Becker on the Occasion of 65th Birthday

Abstract. Black single crystals of $MnBiSe_2I$ were obtained by the reaction of stoichiometric amounts of Mn, Bi, BiI_3, and Se at 600 °C for 7 days. The compound crystallizes in the monoclinic system, space group $C2/m$, with $a = 13.428(2)$, $b = 4.112(1)$, $c = 10.130(2)$ Å, $\beta = 90.97(2)°$, and $Z = 4$. The crystal structure refinement based on 849 reflections converged at $R = 0.0380$ and $wR2 = 0.0916$, respectively. $MnBiSe_2I$ forms a layer structure consisting of $MnSe_6$ octahedra, $MnSe_2I_4$ octahedra, and $BiSe_{3+2}$ pyramids.

Keywords: Manganese; Bismuth; Selenium; Iodine; Sulfosalts; Crystal structure

Introduction

The synthesis of layered materials with interesting magnetic properties on the basis of transition elements usually is focussed on iron, chromium, and manganese containing compounds. A mineral related group of compounds containing these ions are the so-called sulfo salts, e.g. $FeSb_2S_4$ (berthierite) [1]. Inspired by a publication dealing with a layered material of this composition, namely $MnBi_2S_4$ [2], we recently started to elucidate the existence of further sulfo salts of Mn^{2+}, which usually occurs as a d^5 high spin ion in octahedral environment in these compounds. 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. $oP28$, or by solid state reactions as a monoclinic phase $mC28$ which is closely related to $MnBi_2S_4$ [4]. The homologous $MnSb_2Se_4$ $mC28$ could also be obtained by solid state preparation [5]. Spin polarized DFT calculations confirmed the semiconducting behaviour of both phases of $MnSb_2S_4$ [5, 6]. Neutron powder diffraction experiments on $MnSb_2S_4$ $mC28$ and the heavier homologous compounds revealed that these compounds become antiferromagnetic below about 25 K. The magnetic spins show a complicated helical ordering pattern [5, 7]. 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, which are stacked above each other with weak interlayer interactions [4]. 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 ordering patterns of the spins can be expected. One way how to change the connectivity is the partial substitution of chalcogenide ions by halide ions. Two examples for such compounds were recently described: monoclinic $MnSbSe_2I$ $mC20$ [8] and orthorhombic $MnSbS_2Cl$ $oP20$ [9]. The different radii 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 $MnSbSe_2I$ but only one type of octahedra MnS_4Cl_2 in $MnSbS_2Cl$. The different octahedra in $MnSbSe_2I$ 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 $MnSbSe_2I$ and also in $MnSbS_2Cl$. The introduction showed up the close relations of $MnSb_2Q_4$ and $MnBi_2Q_4$. Thus, we prepared the heavier homologous compound $MnBiSe_2I$ and determined the crystal structure in order to further check the influence of the different ionic radii on the observed crystal structures.

Results

Structure determination

Single crystals of the title compound suitable for a structure determination could be obtained from different synthetic routes, see the experimental section for details. X-ray intensities were collected on a STOE IPDS-I using Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å. The compound crystallizes in the monoclinic system with the lattice constants $a = 13.428(2)$, $b = 4.112(1)$, $c = 10.130(2)$ Å, $\beta = 90.97(2)°$, $V = 559.3(1)$ 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 I, two Se and two Mn atoms. The refinement converged at

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$R = 0.0359$ for reflections with $I > 2\sigma_I$ and $R = 0.0380$ for all reflections. A total of 849 independent reflections was 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 Table 2 and Table 3, respectively. Table 4 contains selected interatomic distances and angles calculated from these data.

Table 1 Crystallographic data for the structure analysis of $MnBiSe_2I$

Compound	$MnBiSe_2I$
Formula weight in g mol^{-1}	548.74
Crystal size in mm^3 and colour	0.1 x 0.1 x 0.07, black
Crystal system	monoclinic
Space group	*C*2/*m* (No. 12)
Lattice constants in Å	$a = 13.428(2)$
from single crystal	$b = 4.112(1)$
	$c = 10.130(2)$
	$\beta = 90.97(2)°$
Cell volume, Z	559.3(1) Å^3, 4
ρ_{calc} in g cm^{-3}	6.517
Diffractometer	STOE IPDS-I, MoKα, λ = 0.71073 Å, oriented graphite monochromator
φ-range in °, $\Delta\varphi$ in °	$0.0 \le \varphi \le 191.8$, 1.4
μ(MoKα) in mm^{-1}	52.05
Absorption correction	numerical, crystal description with 7 faces, shape optimizes with X-SHAPE [10]
No. of measured images	137
Irradiation time/image in min	8
Temperature in °C	20
2θ-range in °	$4.2 \le 2\theta \le 58.6$
hkl-range	$-16 \le h \le 18$
	$-5 \le k \le 5$
	$-13 \le l \le 13$
No. of reflections, R_{int}	2875, 0.0463
No. of independent reflections	849
No. of parameters	34
Program	SHELX 97 [11]
Final *R*/*wR* ($I > 2\sigma_I$)	0.0359, 0.0906
Final *R*/*wR* (all reflections)	0.0380, 0.0916
GooF	1.054
Largest difference peak $\Delta\rho_{max}$	2.238
and hole $\Delta\rho_{min}$ in e Å^{-3}	−1.772

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-415138, the name of the authors, and the reference of the publication.

Table 2 Atomic coordinates and equivalent isotropic displacement parameters U_{eq} in Å^2 for $MnBiSe_2I$

Atom	*x*	*y*	*z*	U_{eq}[a]
Bi	0.2092(1)	0	0.8102(1)	0.024(1)
Mn1	0	1/2	0	0.024(1)
Mn2	0	1/2	1/2	0.025(1)
I	0.1371(1)	0	0.4266(1)	0.024(1)
Se1	0.1364(1)	0	0.0570(1)	0.020(1)
Se2	0.0714(1)	1/2	0.7559(1)	0.020(1)

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

Structure description and discussion

$MnBiSe_2I$ crystallizes isotypic with $MnSbS_2I$. The coordination spheres of the metal ions are shown in Figure 1.

Table 3 Anisotropic displacement parameters U_{ij} in Å^2 for $MnBiSe_2I$. $U_{12} = U_{23} = 0$

Atom	U_{11}	U_{22}	U_{33}	U_{13}
Bi	0.024(1)	0.023(1)	0.024(1)	0.004(1)
Mn1	0.024(1)	0.024(1)	0.023(1)	0.004(1)
Mn2	0.026(1)	0.023(1)	0.026(1)	0.001(1)
I	0.022(1)	0.022(1)	0.028(1)	0.004(1)
Se1	0.020(1)	0.021(1)	0.020(1)	0.000(1)
Se2	0.022(1)	0.019(1)	0.020(1)	−0.001(1)

Table 4 Selected interatomic distances (in Å), and angles (in degrees) for $MnBiSe_2I$ at room temperature

Bi-Se1		2.700(1)	Se1-Bi-Se1		79.94(3)
Bi-Se2	2 x	2.8140(8)	Se1-Bi-Se1	2 x	81.55(3)
Bi-Se1	2 x	3.201(1)	Se1-Bi-Se2	2 x	86.22(3)
			Se2-Bi-Se1	2 x	91.83(2)
Mn1-Se2	2 x	2.667(1)	Se2-Bi-Se2		93.89(4)
Mn1-Se1	4 x	2.8069(8)	Se2-Bi-Se1	2 x	166.12(3)
			Se1-Mn1-Se1	2 x	180
Mn2-I	4 x	2.8666(6)	Se2-Mn1-Se2		180
Mn2-Se2	2 x	2.748(1)	Se1-Mn1-Se1	2 x	85.80(3)
			Se1-Mn1-Se2	4 x	86.98(3)
			Se1-Mn1-Se2	4 x	93.02(3)
			Se1-Mn1-Se1	2 x	94.20(3)
			I-Mn2-I	2 x	180
			Se2-Mn2-Se2		180
			Se2-Mn2-I	4 x	88.32(3)
			I-Mn2-I	2 x	88.34(2)
			I-Mn2-I	2 x	91.66(2)
			Se2-Mn2-I	4 x	91.68(3)
			Mn2-I-Mn2		91.66(2)
			Mn1-Se2-Mn2		138.52(5)

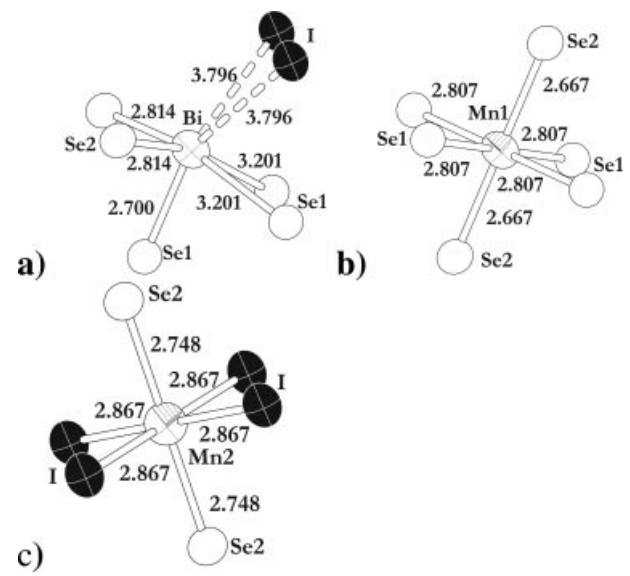

Figure 1 Coordination spheres of the metal ions in $MnBiSe_2I$, distances are given in Å. Displacement parameters are drawn at the 95 % probability level.

The bismuth atom is exclusively coordinated by Se atoms in its first coordination sphere. As shown by the distances and angles the coordination of Bi towards Se can be regarded as 3 + 2, i.e. we find the typical arrangement for

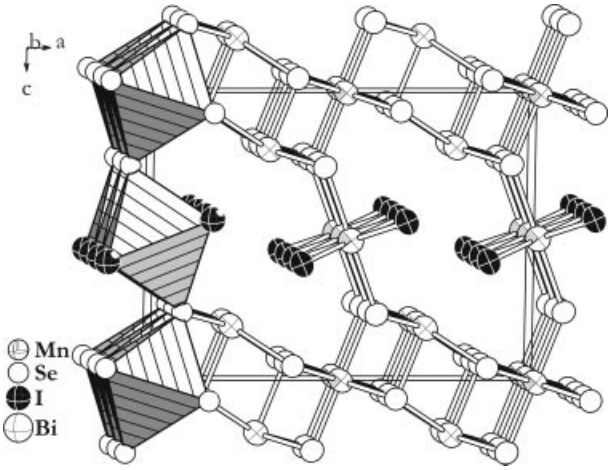

Figure 2 Section of the crystal structure of $MnBiSe_2I$. Mn atoms are octahedrally coordinated and the octahedra form chains along *b*. $BiSe_{3+2}$ units connect the chains to form layers parallel (001).

sulfo salts. Three short bonds *d*(Bi-Se) are in the range from 2.700−2.814 Å, and two medium range bonds *d*(Bi-Se) = 3.201 Å are found. Two iodine atoms are located in a long distance *d*(Bi-I) = 3.796 Å. These distances *d*(Bi-I) are much longer than those found in BiI_3, *d*(Bi-I) ≤ 3.124 Å [12]. Manganese ions are six-coordinate, either only by selenide ions or by four iodide ions and two selenium ions. Both types of octahedra show two short axial bonds, i.e. *d*(Mn-Se2) = 2.667 Å for $[MnSe_6]$ and *d*(Mn-Se2) = 2.748 Å for $[MnSe_2I_4]$. The distances in the basal plane are longer, namely *d*(Mn-Se1) = 2.807 Å for $[MnSe_6]$ and *d*(Mn-I) = 2.867 Å for $[MnSe_2I_4]$. Having the connectivity of the octahedra in mind, one finds a compression along the direction of the common vertices Se2, i.e. [001]. The longer bonds are found in the direction of the chains of octahedra, i.e. [010], see Figure 2.

The distances of the manganese atom to the surrounding atoms are similar to those found in the isotypic compound $MnSbSe_2I$ [8]. Obviously the monoclinic structure type is preferred for the present combination of elements. The volumes of the unit cells of $MnSbSe_2I$ (V = 543 Å^3) and of $MnBiSe_2I$ (V = 559 Å^3) differ only slightly, especially when the measuring temperature of 153 K for $MnSbSe_2I$ is taken into account. The same is found for the couple $MnSb_2S_4$ (V = 669 Å^3) and $MnBi_2S_4$ (V = 672 Å^3). Obviously the volume which is occupied by the tri-valent cations Sb^{3+} and Bi^{3+} is almost the same. This is probably due to the fact that the difference between short bonds Sb-Q and long bonds Sb-Q (the so-called non bonding distances) is much bigger than in case of Bi-Q, where these distances are evened out to a certain degree. In case of $MnSbS_2Cl$ [9] 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. At the moment $MnBiS_2Br$ is under investigation and this compound is also isotypic with $MnBiSe_2I$ and $MnSbSe_2I$, due to similarly long bonds Mn-Br as compared to Mn-S. In this case the monoclinic angle β = 90.87° is even closer to 90° than in $MnBiSe_2I$ [13].

Experimental Section

$MnBiSe_2I$ was obtained either by reaction of stoichiometric amounts of Mn, BiI_3, Bi, and Se (3 : 1 : 2 : 6) or by reaction of $Mn_3Bi_2Se_6$ with BiI_3 (1 : 1). Both reaction mixtures were sealed in evacuated quartz ampoules and then heated to 600 °C for **7** days. The title compound was isolated as black shiny needle shaped crystals. However, in both cases no phase pure product could be obtained. The by-products could not yet be identified in detail. However, MnSe is always one of the impurities.

X-ray powder diffraction patterns were recorded on a Stoe STADI P running with germanium monochromatized $CuK\alpha_1$ radiation. Single crystals were fixed on thin walled glass capillaries and then mounted on a Stoe IPDS 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 [10].

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