The Channel Structure of $Mn_{0.86}In_{0.12}Ga_2S_4$

Hartmut Haeuseler, Michael Wagener, and Junyu Zhang

Inorganic Chemistry, University of Siegen, D-57068 Siegen, Germany

Reprint requests to Prof. Dr. H. Haeuseler.
Fax: +49 271 7402555.
E-mail: Haeuseler@chemie.uni-siegen.de

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By solid state reaction of the binary sulfides, a new compound, $Mn_{0.86}In_{0.12}Ga_2S_4$, has been synthesized and its crystal structure determined. The compound crystallizes in the space group $C2/m$ (no. 12) with a = 1232.6(2), b = 2636.9(5), c = 642.4(1) pm, β = 100.66(3)°, Z = 14. In the structure empty channels with a cross section of 320 × 1082 pm^2 running parallel to [001] are present.

Key words: Chalcogenide, X-Ray Structure Analysis, Transition Metal Compounds, Channel Structure

Introduction

Among the ternary chalcogenides of the general composition AB_2X_4 where A is a divalent and B a trivalent metal ion, the compounds $MnGa_2S_4$ and $MgGa_2S_4$ are unique with respect to their structures. While many of such compounds crystallize with the spinel structure, derivatives of the sphalerite type or layered structures of the $ZnIn_2S_4$ type, the gallium chalcogenides $MnGa_2S_4$ and $MgGa_2S_4$ exhibit a special structure [1], which was investigated by Romers *et al.* [2] (Mg) and by Rimet *et al*. [3] (Mn). The crystals are isotypic. According to these authors the structure can be described as a cubic close-packed array of the sulfide ions in which the trivalent gallium atoms occupy tetrahedral sites, and the divalent metal atoms Mg and Mn are octahedrally coordinated.

Some years ago we have published the phase width and the crystal structure of the layered phase $MnGaInS_4$ in the system MnS-Ga_2S_3-In_2S_3 [4] but excluded the gallium-rich part due to the fact that according to Pardo *et al.* [5, 6] there are many different compounds in the system MnS-Ga_2S_3 which makes it nearly impossible to solve the phase diagram from X-ray powder diffraction data only. In continuation of these studies we have now investigated the section $MnGa_2S_4$-"$InGa_{5/3}S_4$", *i. e.* a section in which the ratio between metal ions with a high octahedral site preference (Mn and In) to the number of sulfur ions in the formula unit is always 1 : 4. In this way the ratio of tetrahedrally coordinated metal ions (Ga) to the octahedrally coordinated ions, which is typically 2 : 1 in compounds adopting the $ZnIn_2S_4$ structure type, is reduced to smaller values for electroneutrality reasons. In the course of this study we now obtained a new compound with an interesting structure on which we report in the present paper.

Results and Discussion

Optical inspection of a sample of the title compound showed that the substance is not a single phase as it consisted of yellow and red transparent crystals, both types of crystals exhibiting platelet-like morphology. X-Ray powder data of the two different types of crystals revealed very clearly that the yellow crystals adopted a structure of the $ZnIn_2S_4$ type while the red crystals obviously had an unknown structure. A single crystal structure analysis of a red crystal gave the following results: The compound crystallizes in the monoclinic space group $C2/m$ (no. 12) with the lattice parameters a = 1232.6(2), b = 2636.9(5), c = 642.4(1) pm, β = 100.66(3)°, and Z = 14. The structure was refined to R_1 = 3.3 % and wR_2 = 8.9 %. The calculated fractional atomic coordinates and the site occupancies are given in Table 1. Selected bond lengths are given in Table 2 [7]. According to the site occupation factors for the different metal sites, the composition of the crystal is $Mn_{0.86}In_{0.12}Ga_2S_4$, and thus deviates slightly from the composition of the starting mixture.

The crystal structure of $Mn_{0.86}In_{0.12}Ga_2S_4$ shown in Fig. 1 in a projection parallel to [001] can be described as a packing of ribbons running parallel to [001]. These ribbons are composed of layers of (Mn,In)S_6 octahedra which are connected on both sides to GaS_4 tetrahedra by common corners similar to the structural units in the $ZnIn_2S_4$ type though in this reference case there are no ribbons but two-dimensional infinite layers [1]. The ribbons found in $Mn_{0.86}In_{0.12}Ga_2S_4$ are stacked in a way that large channels are generated with a cross-section of 320 × 1020 pm^2. However, since only about 9 % of the octahedra at the left- and

Table 1. Fractional atomic coordinates and site occupancy factors (sof) for the compound $Mn_{0.86}In_{0.12}Ga_2S_4$.

Atom	*x*	*y*	*z*	sof
In1	0.0000	0.42507(2)	0.0000	0.264(2)
Mn1	0.0000	0.42507(2)	0.0000	0.74
In2	0.0000	0.5000	0.5000	0.285(2)
Mn2	0.0000	0.5000	0.5000	0.71
Mn3	0.0000	0.35104(2)	0.5000	1
Mn4	0.0000	0.27681(3)	0.0000	0.845(3)
Mn5	0.0000	0.7948(3)	−0.5000	0.089(3)
Ga1	0.29298(3)	0.57023(1)	0.42145(5)	1
Ga2	−0.20366(3)	0.85814(1)	−1.07662(5)	1
Ga3	−0.20758(4)	0.0000	−0.07870(6)	1
Ga4	−0.18597(3)	0.79204(1)	−0.58032(5)	0.892 (2)
Ga5	−0.1830(2)	0.7220(1)	−0.0798(4)	0.111(2)
S1	−0.11902(6)	0.79357(3)	−0.8787(1)	1
S2	0.11009(6)	0.57472(2)	0.3769(1)	1
S3	0.37522(6)	0.36274(2)	0.6222(1)	1
S4	−0.10940(8)	0.5000	0.1239(1)	1
S5	0.36908(6)	0.43037(2)	0.1152(1)	1
S6	−0.12583(5)	0.72149(3)	−0.3813(1)	1
S7	0.36954(8)	0.5000	0.6151(1)	1
S8	−0.11197(6)	0.35073(3)	0.1233(1)	1

Table 2. Selected interatomic distances (pm) in the crystal structure of $Mn_{0.86}In_{0.12}Ga_2S_4$.

In1	S2	254.73(10)	Mn5	S3	257.7(5)	Ga3	S4	222.06(11)
In1	S4	259.86(8)	Mn5	S1	259.83(11)	Ga3	S5	231.95(8)
In1	S8	260.35(9)	Mn5	S6	267.6(5)	Ga3	S7	233.79(11)
In2	S4	253.99(12)	Ga1	S2	222.24(9)	Ga4	S1	222.31(9)
In2	S2	259.72(8)	Ga1	S3	230.92(8)	Ga4	S6	230.08(8)
Mn3	S8	255.47(10)	Ga1	S7	233.08(8)	Ga4	S6	231.47(8)
Mn3	S2	258.76(9)	Ga1	S5	233.08(10)	Ga4	S3	231.82(8)
Mn3	S6	266.12(9)	Ga2	S8	224.52(9)	Ga5	S1	233.9(3)
Mn4	S1	257.42(9)	Ga2	S1	226.13(8)	Ga5	S8	239.3(3)
Mn4	S8	259.53(9)	Ga2	S3	232.33(9)	Ga5	S1	244.0(3)
Mn4	S6	264.63(10)	Ga2	S5	235.40(8)			

right-hand borders of these channels are occupied, the width of the channels in the [010] direction is in large parts even wider than 1020 pm. The S–S distance over this cavity in the [100] direction varies between 382 and 357 pm. In the part of the structure where the ribbons overlap, which is indicated by the arrows in Fig. 1, the tetrahedra are connected *via* common edges with a Ga4–Ga5 distance of 249.2 pm. These tetrahedra are linked to the neighboring octahedra by common planes, such that the distances between the centers of these tetrahedra and the octahedra (Mn4–Ga5: 221.9 pm; Mn5–Ga4: 225.6 pm) are relatively short, and therefore the site occupancy of Mn4 and Mn5 is reduced to 0.845 and 0.089, respectively, and that of Ga4 and Ga5 to 0.892 and 0.111, respectively (see Table 1).

The structure of $Mn_{0.86}In_{0.12}Ga_2S_4$ is very similar to the one of $MnGa_2S_4$ as in both cases the principal structural elements and their arrangement are the same. The main difference is found in the length of the *b* axis which is 2260.9 pm in the case of $MnGa_2S_4$ [3] and 2636.9 pm in the case of the

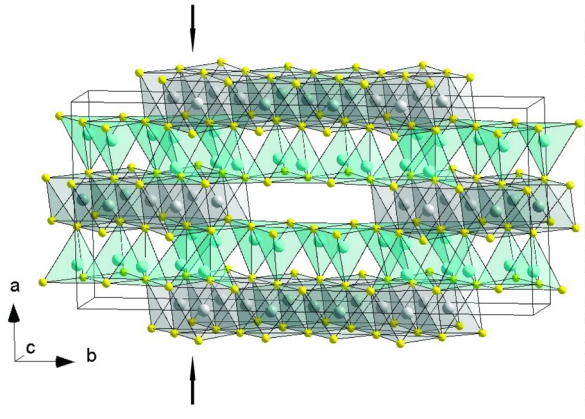

Fig. 1. Section of the crystal structure of $Mn_{0.86}In_{0.12}Ga_2S_4$ viewed approximately along [001]. The arrows mark the part of the structure which is shown in Fig. 2 in more detail.

title compound and thus in the widths of the ribbons and the channels. While the height of the channels, *i. e.* their spread in [100], is nearly the same in both cases (319.8 pm for $MnGa_2S_4$ and 323 pm for

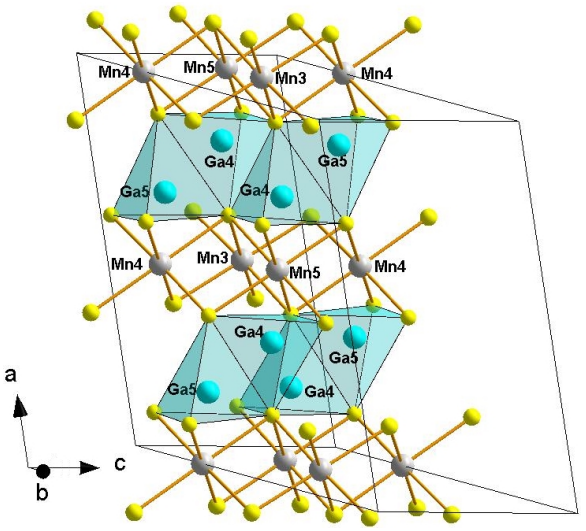

Fig. 2. Detail of the crystal structure of $Mn_{0.86}In_{0.12}Ga_2S_4$ in the region of the overlapping parts of the ribbons (see Fig. 1), showing the edge-sharing tetrahedra.

$Mn_{0.86}In_{0.12}Ga_2S_4$) the width in [010] is smaller by about 30 % in $Mn_{0.86}In_{0.12}Ga_2S_4$ (1316.4 pm compared to 1020 pm).

The reason for the unique structures of $MnGa_2S_4$ and $Mn_{0.86}In_{0.12}Ga_2S_4$ may be found in the cubic close-packing of the sulfur atoms. According to Hulliger [8] a hexagonal close-packing in the neighborhood of the van der Waals gap is more favorable. Such an arrangement of the sulfide anions gives rise to additional binding forces between the layers due to interactions of the tetrahedrally coordinated cations with sulfide anions of the neighboring layers (*i. e.* a 4+1 coordination). Such forces are not existent in a cubic close-packing, but instead of this the binding between the layers is enforced in the case of $Mn_{0.86}In_{0.12}Ga_2S_4$ by the edge-sharing $Ga4S_4$ tetrahedra (see Fig. 2) (Ga4–Ga4 distance: 301.25 pm) in the overlapping region of the above mentioned ribbons. As can be seen from Fig. 2, both of these $Ga4S_4$ tetrahedra are connected to the layers of octahedra by all 4 sulfur atoms, in that way forming a three-dimensional structure. Within the ribbons the tetrahedra are interconnected by common corners only, with Ga–Ga distances of about 370 – 373 pm.

Conclusion and Outlook

The results of the present investigation have shown that by replacing a part of the manganese by indium atoms the width in [010] of the channels present in $MnGa_2S_4$ can be varied from 1316.4 to 1020 pm in $Mn_{0.86}In_{0.12}Ga_2S_4$. It would be interesting to find out whether it is possible to replace in compounds of the composition $Mn_xIn_yGa_2S_4$ a part of the gallium by for instance zinc and lithium atoms, which could afford a one-dimensional ionic conductor with zinc on the tetrahedral Ga sites and mobile Li ions in the channels.

Table 3. Crystallographic data of the structure determination of $Mn_{0.86}In_{0.12}Ga_2S_4$.

Space group	$C2/m$ (no. 12)
Number of formula units, Z	14
a, pm	1232.6(2)
b, pm	2636.9(5)
c, pm	642.4 (1)
β, deg	100.66(3)
Unit cell volume, $\times 10^6$ pm^3	5878.9(2)
Formula weight, g mol^{-1}	331.0
Calculated density, g cm^{-3}	3.75
Temperature of measurement T, K	293
Range of 2θ, deg	2.86 – 30.37
Range of hkl	± 17, ± 37, $-8 \rightarrow +9$
No. of reflections measured	12373
R_{int}	0.058
No. of unique reflections	3151
No. of reflections with $I_o \geq 2\sigma(I)$	2471
Parameters refined	140
$R_1[I_o \geq 2\sigma(I)]$	0.033
$wR_2[I_o \geq 2\sigma(I)]$	0.089
$\Delta\rho_{\text{min/max}}$, $\times 10^{-6}$ e$^-$ pm^{-3}	$-1.6(3)$ / 1.7(3)

Experimental Section

$Mn_{0.86}In_{0.12}Ga_2S_4$

For the preparation of the title compound we started from 1 g of a mixture of the binary sulfides from the section x $MnGa_2S_4$-$(1-x)$ "$InGa_{5/3}S_4$" with x = 0.8, *i. e.* a composition 0.8 Mn : 0.2 In : 1.93 Ga : 4 S. The mixture was carefully ground in an agate mortar and transferred to a silica ampoule (8 mm diam.) which was sealed under a vacuum and fired at 800 °C for three days and then for another three days at 900 °C. After cooling, the ampoule was opened, the sample reground and once again fired in an evacuated silica ampoule at 800 °C for three days. After the second heat treatment the sample was allowed to cool slowly in the furnace.

The samples were characterized by X-ray powder diffraction using a Siemens powder diffractometer D5000 equipped with a primary monochromator (Ge) and a position-sensitive detector PSD-50M (Braun GmbH) with Cu$K_{\alpha 1}$ radiation (λ = 154.05 pm). The calculation of the lattice parameters was carried out with the program package VISUAL X^{POW} by Stoe.

X-Ray structure determination

For the single crystal structure determination, a small plate-like crystal was selected. Intensity data were collected

at r. t. on a Stoe IPDS (MoK_α radiation, λ = 71.07 pm, graphite monochromator) for $3 \leq 2\theta \leq 31°$. Absorption correction was applied empirically with the program X-SHAPE. Calculations were performed with the structure determination package SHELX94. A summary of the conditions of the crystal structure determination and some crystallographic data of $Mn_{0.87}In_{0.12}Ga_2S_4$ are given in Table 3 [7].

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