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Letter

MnGa₂Te₄-II, a high pressure modification of digallium manganese tetratelluride

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1. Introduction

 $MnGa_2Te_4$ has a very complicated crystal structure, in spite of its relatively simple stoichiometric AB_2X_4 composition [1, 2]. A preliminary crystal structure determination shows that the anions form a distorted cubic close-packed arrangement with all cations located in tetrahedral holes, as in the homologous compound $MnIn_2Te_4$ [3]. In contrast to $MnIn_2Te_4$, however, the occupied Te_4 tetrahedra are not only corner shared, but edge shared as well. Because the stability of manganese in tetrahedral coordination by tellurium decreases with increasing pressure, we expected a pressure-induced phase transformation for $MnGa_2Te_4$. The present paper describes the results of high pressure experiments with $MnGa_2Te_4$ and the structure refinement of the high pressure phase $MnGa_2Te_4$ -II.

2. Experimental details

The normal pressure phase $MnGa_2Te_4$ -I was synthesized from a stoichiometric mixture of the elements (Mn: Ventron, powder, M3N +; Ga: Merck, p.A.; Te: Ventron, pieces, M5N8, T5N +) in an argon-flushed, evacuated, sealed quartz ampoule (slow heating to 800 °C, reaction time 6 days, quenching to room temperature). The Guinier pattern of the homogeneous product could be indexed using an I-centered tetragonal unit cell with a = 8.4818(4) and c = 48.362(5) Å [2]. The very complicated X-ray pattern remained unchanged even after very long annealing (15 weeks at 700-500 °C). High pressure experiments were carried out in a modified belt-type apparatus [4], using sintered BN as crucible material. Temperature was varied in the range 600–1500 °C, pressure in the range 10–60 kbar. At 15 kbar, 800 °C MnGa₂Te₄ transforms completely into a quenchable high pressure modification (MnGa₂Te₄-II). This phase is remarkably stable at higher pressures. At 60 kbar, 1200 °C it becomes unstable again and decomposes.

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From a sample obtained at 30 kbar, 900 °C with subsequent quenching to ambient conditions a silvery crystal fragment could be isolated. Gandolfi and Guinier patterns showed the identity of crystal and bulk material [5]. For the data collection an Enraf-Nonius CAD-4 diffractometer was used (Mo K α , $\lambda = 0.71073$ Å, graphite monochromator in incident beam). Lattice parameters have been refined from 2 Θ values of 25 reflections in the range $9.5 \le \Theta \le 13.1^\circ$. Intensities were measured for $2 \le \Theta \le 25^\circ$; $\omega - 2\Theta$ scan technique, scan width (1.5 ± 0.4 tan Θ)°. Three standard reflections indicated no loss of intensity throughout data collection. Merging of the 1551 collected intensities ($\sin \Theta_{max}/\lambda = 0.59$ Å⁻¹; $0 \le h \le 32$, $-4 \le k \le 4$, $0 \le l \le 8$) gave 472 unique reflections with $I > \sigma(I)$, which were used for all calculations (program system SDP 3.1; Enraf-Nonius 1988).

3. Structural analysis

Weissenberg and Precession photographs showed the crystal to be orthorhombic, Laue class mmm. The observed reflection conditions $(k + l = 2n \text{ for } 0kl; 0 \le h \le 32, -4 \le k \le 4, 0 \le l \le 8)$ gave 472 unique reflections with $I > \sigma(I)$, which were used for all calculations (program system SDP 3.1; Enraf-Nonius 1988).

TABLE 1

Space group	Pnma (Nr. 62)	
$a(\mathbf{A})$	27.448(42)	
$b(\mathbf{\dot{A}})$	4.192(1)	
c(Å)	6.993(1)	
V (Å ³)	804.63	
Z	4	
Unique reflections	472	
R, wR, S	0.080, 0.080, 2.64	

Crystallographic data for MnGa2Te4-IIa

	x	у	z	$B_{\rm eq}^{\ \rm b}$
Mn	0.3094(4)	1/4	0.3487(14)	1.7(3)
Ga(1)	0.1499(3)	1/4	0.4628(9)	1.4(2)
Ga(2)	0.0474(3)	1/4	0.0764(11)	1.4(2)
Te(1)	0.2333(2)	1/4	0.6305(5)	1.03(8)
Te(2)	0.8963(2)	1/4	0.3920(5)	1.02(8)
Te(3)	0.1419(2)	1/4	0.0848(5)	1.00(9)
Te(4)	0.9957(2)	1/4	0.7521(6)	1.03(9)

Atomic coordinates and thermal parameters $(Å^2)$

^aHere, and in the following tables, the e.s.d.s of the least significant figures are given in parentheses. ^b $B_{eq} = 8\pi^2/3 (U_{11} + U_{22} + U_{33}).$ structure refinement. The structure was solved by routine direct methods and subsequent difference Fourier syntheses. In the least-squares refinement |F|magnitudes were used to refine an overall scale factor, positional parameters, occupation factors and anisotropic temperature factors for all atoms. Convergence was obtained after a few cycles with SOFs corresponding to a stoichiometry MnGa₂Te₄ within two standard deviations. Consequently, the SOFs were fixed again at 100% before performing a numerical correction for absorption (program DIFABS [6]) and the final anisotropic refinement. Final R = 0.080, wR = 0.080, w = k/ $\sigma(F)^2 + g \cdot |F|^2$, $(\Delta/\sigma)_{max} < 0.001$ in final refinement cycle, 43 variables, S = 2.64, maximum features in the final $\Delta\rho$ map ± 3.8 eÅ⁻³ [7].

Crystallographic data for $MnGa_2Te_4$ -II, including atomic coordinates and equivalent isotropic thermal parameters, are given in Table 1.



Fig. 1. The MnGa₂Te₄-II structure projected along [010]. Thick and thin lines signify atoms and their connections at y = 1/4 and y = 3/4 respectively. The unit cell is indicated by broken lines.



Fig. 2. The connection of MnTe₆ octahedra and GaTe₄ tetrahedra in MnGa₂Te₄-II.

4. Discussion

 $MnGa_2Te_4$ -II is a true high pressure phase and only metastable at ambient conditions. This follows from the behaviour during annealing experiments at atmospheric pressure. The high pressure phase remains unchanged up to 400 °C. At this temperature it becomes unstable and decomposes into a mixture of B4-related $Mn_{0.7}Ga_{2.2}Te_4$ and $MnTe_2$.

The structure of $MnGa_2Te_4$ -II is very similar to that of the high pressure phase $MnIn_2Te_4$ -II [8], in spite of the different structure of both compounds in their

TABLE 2

Selected interatomic distances (Å) and angles (deg)

MnTe _e octahedra			
Mn - Te(1)	$2.846(7)2 \times$	Te(1)—Mn— $Te(1)$	93.9(3) 2 ×
-Te(1)	2.870(10)	$-\mathrm{Te}(1)$	94.8(3)
-Te(2)	2.921(11)	$-\mathrm{Te}(2)$	$91.5(2)2 \times$
$-\mathrm{Te}(3)$	$2.983(7)2 \times$	$-\mathrm{Te}(2)$	171.9(4)
		$-\mathrm{Te}(3)$	$87.0(2) 2 \times$
(Mn-Te)	2.908	$-\mathrm{Te}(3)$	$87.9(1)2 \times$
		$-\mathrm{Te}(3)$	$177.0(3) 2 \times$
		Te(2)-Mn- $Te(3)$	87.3(3) 2 ×
		Te(3)— Mn — $Te(3)$	89.3(3)
GaTe₄ tetrahedra	,	0,11, <u>11, 11, 11, 11, 11, 11, 11, 11, 11</u>	
Ga(1)-Te(1)	2.572(9)	Te(1)- $Ga(1)$ - $Te(2)$	$104.5(2) 2 \times$
-Te(2)	$2.656(5)2 \times$	$-\mathrm{Te}(3)$	121.9(3)
-Te(3)	2.652(7)	Te(2)— $Ga(1)$ — $Te(2)$	104.5(3)
$\langle Ga(1)-Te \rangle$	2.634	$-\mathrm{Te}(3)$	$110.0(2) 2 \times$
Ga(2)-Te(3)	2,595(9)	Te(3)-Ga(2)-Te(4)	123.4(3)
-Te(4)	2.673(9)	$-\mathrm{Te}(4)$	115.4(2) 2 ×
-Te(4)	$2.690(6)2 \times$	Te(4)— $Ga(2)$ — $Te(4)$	98.3(2) 2 ×
(Ga(2)—Te)	2.662	$-\mathrm{Te}(4)$	102.4(3)
Te-Ga(Mn) polyhedra	1		
Te(1)— $Ga(1)$	2.572(9)	Ga(1)— $Te(1)$ — Mn	83.0(3) 2 ×
Mn	$2.846(7)2 \times$	—Mn	109.6(3)
Mn	2.870(1)	Mn - Te(1) - Mn	94.9(2)
		—Mn	131.9(2) 2 ×
Te(2)-Ga(1)	$2.652(5)2 \times$	Ga(1)— $Te(2)$ — $Ga(1)$	104.5(2)
Mn	2.921(11)	—Mn	80.2(2) 2 ×
$T_{0}(2) - C_{0}(2)$	2 505(10)	$G_{2}(1)$ -Te(3)-G ₂ (2)	96 1 (3)
-Ga(1)	2.595(10) 2.652(7)	Ga(1) = IC(3) = Ga(2) -Mn	$120.9(2) 2 \times 10^{-1}$
	2.032(7) 2.083(7) 2 x	G_{2} $-Mn$	$120.9(2) 2 \times 115.8(2) 2 \times 115.8(2)$
14733	2.705(1/20	Mn-Te(3)-Mn	89.3(2)
	0 (70(0))		
Te(4)-Ga(2)	2.673(9)	Ga(2) - 1e(4) - Ga(2)	81.7(2)2×
-Ga(2)	2.690(6) 2 ×	-Ga(2)	102.4(2)

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TABLE 3

Edge lengths (Å) of the MnTe₆ and GaTe₄ polyhedra

MnTe.:			
Te(1)— $Te(1)$	$4.178(5)2 \times$		
$-\mathrm{Te}(1)$	4.192		
$-\mathrm{Te}(2)$	$4.132(7)2 \times$		
$-\mathrm{Te}(3)$	4.048(6) 2 ×		
$-\mathrm{Te}(3)$	4.029(7) 2 ×		
Te(2)-Te(3)	4.076(5)2×		
Te(3)-Te(3)	4.192		
(Te-Te)	4.109		
Ga(1)Te ₁ :		Ga(2) Te ₄ :	
Te(1)-Te(2)	$4.132(7)2 \times$	Te(3) - Te(4)	4.639(7)
$-\mathrm{Te}(3)$	4.567(6)	-Te(4)	$4.467(7)2 \times$
Te(2) - Te(2)	4.192	Te(4)— $Te(4)$	$4.058(5)2 \times$
$-\mathrm{Te}(3)$	4.345(5)2×	$-\mathrm{Te}(4)$	4.192
(Te-Te)	4.285	(Te-Te)	4.314

low pressure modifications. It can be derived from a b.c.c. arrangement of the tellurium atoms by appropriate distortion and occupation of some of the (pseudo-). tetrahedral and (pseudo-)octahedral voids by metal atoms (Fig. 1). The distortions of the square nets, necessary for the accommodation of differently sized metal atoms, have already been discussed elsewhere [8]. The manganese atoms are coordinated octahedrally by tellurium atoms, the gallium atoms tetrahedrally. Figure 2 shows the connection of the GaTe₄ tetrahedra and MnTe₆ octahedra. Both, octahedra and tetrahedra, are considerably distorted (see Tables 2 and 3).

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- 5 The evaluated Guinier pattern of $MnGa_2Te_4$ -II will be deposited with JCPDS and can be obtained from the authors (K.-J.R.) as well.
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- 7 Tables containing $F_{\rm o}/F_{\rm c}$ values, anisotropic thermal parameters and a complete list of interatomic distances and angles have been prepared and may be obtained from the authors (K.-J.R.).
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