



Synthesis and crystal structure analysis of the magnetic ternary compound Mn_2GeTe_4

Gerzon E. Delgado^{*1}, Luis Betancourt², Asiloé J. Mora¹, Jines E. Contreras¹, Pedro Grima-Gallardo³ and Miguel Quintero³

¹Laboratorio de Cristalografía, Departamento de Química,

²Laboratorio de Magnetismo en Sólidos, Departamento de Física,

³Centro de Estudios de Semiconductores, Departamento de Física,

Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela

(*) gerzon@ula.ve

Recibido: 08/12/2008

Revisado: 03/02/2009

Aceptado: 06/02/2009

*****F QKj wr u-lf qkoti B2075988 ICXCP S WKO 422; 0603023

Resumen:

Se prepararon muestras del ternario Mn_2GeTe_4 utilizando el método de fusión y recocido. Los resultados del estudio por difracción de rayos-X en muestras policristalinas, indican que este material cristaliza con simetría ortorrómbica, grupo espacial $Pnma$, y parámetros de celda unidad: $a = 13.950(2)$ Å, $b = 8.115(1)$ Å, $c = 6.592(1)$ Å, $V = 746.2(2)$ Å³. El refinamiento Rietveld convergió a los valores de las figuras de mérito $R_p = 6.9\%$, $R_{wp} = 8.6\%$, $R_{exp} = 5.6\%$ y $\chi^2 = 2.4$. Mn_2GeTe_4 es el primer derivado con telurio de la familia de compuestos del tipo $II_2-IV-VI_4$ que cristaliza con una estructura tipo olivina.

Palabras clave: Calcogenuros; semiconductores; síntesis química; difracción de rayos-X en polvo; estructura cristalina.

Abstract

Samples of the ternary phase Mn_2GeTe_4 were synthesized by direct fusion using the anneal method. X-ray powder diffraction results indicated that this material crystallizes with orthorhombic symmetry, space group $Pnma$, and unit cell parameters: $a = 13.950(2)$ Å, $b = 8.115(1)$ Å, $c = 6.592(1)$ Å, $V = 746.2(2)$ Å³. The Rietveld refinement converged to the figures of merit $R_p = 6.9\%$, $R_{wp} = 8.6\%$, $R_{exp} = 5.6\%$ and $\chi^2 = 2.4$. Mn_2GeTe_4 is the first telluride of the $II_2-IV-VI_4$ family that crystallizes with olivine-type structure.

Keywords: Chalcogenides; Semiconductors; Chemical synthesis; X-ray powder diffraction; Crystal structure.

Introduction

Magnetic semiconducting materials have interesting semiconducting properties and have received attention because of their potential application in optoelectronic and magnetic devices¹. The materials more frequently studied are known as semimagnetic semiconductors, obtained from the tetrahedrally coordinated derivatives of the II-VI binaries². One of these families is $II_2-IV-VI_4$, which belongs to one of the four possible families of the fourfold defect derivatives of the II VI binary semiconductors³. Concerning the crystal structure is important to mention that these materials generally crystallize in the olivine structure type with the VI anions forming a hexagonal close packing, and the cations in tetrahedral (IV) and octahedral (II) coordination⁴. However, a distorted spinel structure

with space group $I4_1/a$ have been reported for Fe_2SnS_4 ⁵, and an orthorhombic structure with space group $Cmmm$ for Mn_2SnS_4 ⁶. It should be noted that the transition metal containing olivine structures are known as multipurpose magnetic materials⁷.

In particular, for the system with composition Mn_2GeVI_4 (VI = S, Se, Te), the sulphide Mn_2GeS_4 ⁸ and selenide Mn_2GeSe_4 ^{9,10} compounds have been studied by means of single-crystal diffractometry and a detailed structural analysis have been described in each case. For Mn_2GeTe_4 , only preliminaries unit cell parameters obtained from powder diffraction results have been reported so far, from a systematic work about the magnetic properties of some $II_2-IV-VI_4$ materials with II = Fe, Mn, IV = Si, Ge, Sn and VI = Se, Te¹¹⁻¹³.

In this work, a complete structural study for the ternary semiconductor Mn_2GeTe_4 is performed by using X-ray powder diffraction data.

Experimental

Samples of the ternary phase Mn_2GeTe_4 were synthesized by direct fusion of stoichiometric quantities of Mn, Ge and Te (3N-6N purity) in a sealed, evacuated quartz ampoule. The fusion process (14 days in each case) was carried out into a furnace (vertical position) heated up to 1050 °C. Then, the temperature was gradually lowered to 500 °C. Finally, the furnace was turned off and the ingots were cooled to room temperature. Chemical composition of the resultant ingots was determined at several points by energy dispersive X-ray (EDX) on a Kevex Model Delta-3 system connected to a Hitachi Model S-2500 scanning electron microscope (SEM). This analysis indicated a Mn:Ge:Te ratio of 2:1:4.

A small quantity of the sample was ground mechanically in an agate mortar and pestle. The resulting fine powder was mounted on a flat holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction data were collected, at room temperature, on a Phillips PW-1250 goniometer, using Bragg-Brentano geometry, in θ/θ reflection mode, and $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The specimen was scanned over an angular range of 10-100° (2θ) with steps of 0.02° (2θ) and counting time of 15 s step^{-1} . Silicon was used as an external standard

Results and Discussion

Figure 1 shows the resulting X-ray powder diffractogram for the Mn_2GeTe_4 compound. The 20 first measured reflections were completely indexed using the program DICVOL04¹⁴, which gave a unique solution in an orthorhombic cell with parameters $a = 13.937(1) \text{ \AA}$, $b =$

$8.1357(7) \text{ \AA}$ and $c = 6.5636(5) \text{ \AA}$. The lack of systematic absence condition $h+k+l$ in the general reflections of the type hkl , indicate a P-type cell. A revision of the diffraction lines taking into account the sample composition, cell parameters and P lattice-type suggested that this material is isostructural with the olivine-type compound, which crystallize in the orthorhombic space group $Prma$ (N° 62), similar to the other members of the Mn_2GeVI_4 (VI = S, Se, Te) system⁸⁻¹⁰.

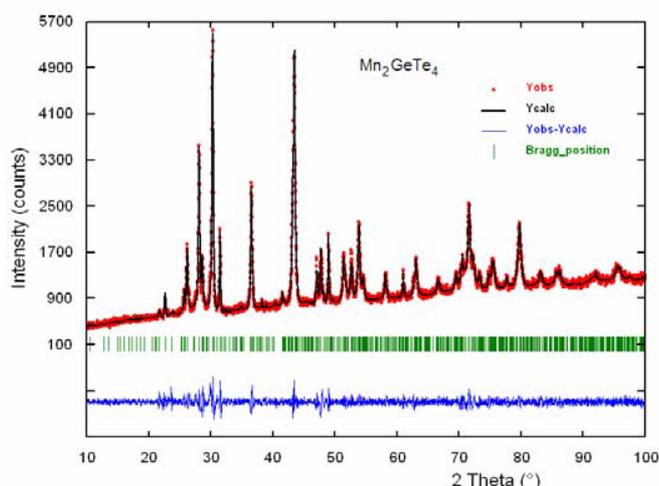


Figure 1: Rietveld refinement plot for Mn_2GeTe_4 showing the observed, calculated and difference pattern. The Bragg reflections are indicated by vertical bars.

The Rietveld refinement¹⁵ of the whole diffraction pattern was carried out using the FULLPROF program^{16,17}. The atomic coordinates of the isomorphous compound Fe_2GeSe_4 ¹⁸ were used as initial model for the refinement of Mn_2GeTe_4 . The angular dependence of the peak full width

Table 1: Atomic coordinates, isotropic temperature factor and interatomic distances for Mn_2GeTe_4 .

Atom	Ox.	Site	x	y	z	foc	$B_{\text{iso}} (\text{\AA}^2)$
Mn1	+2	4a	0	0	0	1	0.6(3)
Mn2	+2	4c	0.242(1)	¼	0.503(1)	1	0.6(3)
Ge	+4	4c	0.408(1)	¼	0.073(1)	1	0.6(3)
Te1	-2	8d	0.328(1)	0.008(1)	0.251(1)	1	0.6(3)
Te2	-2	4c	0.416(2)	¼	0.689(2)	1	0.6(3)
Te3	-2	4c	0.583(2)	¼	0.230(1)	1	0.6(3)
Ge-Te1		2.55(1) x2	Ge-Te2 ⁱ	2.53(2)	Ge-Te3		2.65(3)
Mn1-Te1 ⁱⁱ		2.91(1) x2	Mn1-Te2 ⁱⁱⁱ	2.65(1) x2	Mn1-Te3 ^{iv}		2.94(1) x2
Mn2-Te1 ^v		2.83(1) x2	Mn2-Te1	2.84(1) x2	Mn2-Te2		2.72(3)
Mn2-Te3 ⁱⁱⁱ		2.70(3)					

Symmetry codes: (i) $x, y, -1+z$; (ii) $-0.5+x, y, 0.5-z$; (iii) $-0.5+x, 0.5-y, 0.5-z$; (iv) $0.5-x, -y, -0.5+z$; (v) $0.5-x, -y, 0.5+z$; (vi) $x, 0.5-y, z$.

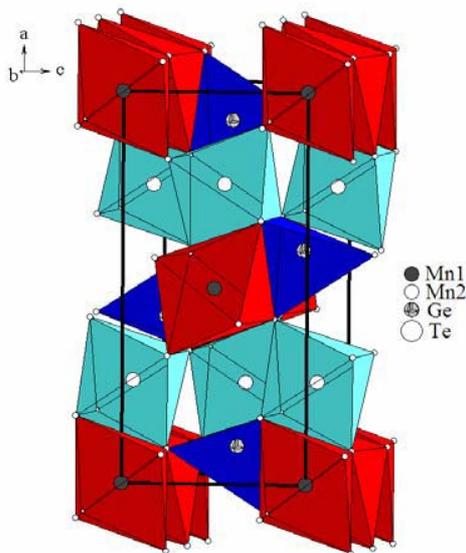


Figure 2: Unit cell projection for the Mn_2GeTe_4 compound, showing the arrangement of MnTe_6 octahedra and GeTe_4 tetrahedra along the [001] direction.

at half maximum (FWHM) was described by Caglioti's formula¹⁹. Peak shapes were described by the pseudo-Voigt profile function. The background variation was described by a polynomial with six coefficients. The thermal motion of the atoms was described by one overall isotropic temperature factor. The final figures of merit for 26 instrumental and structural variables were: $R_p = 6.9\%$, $R_{wp} = 8.6\%$, $R_{exp} = 5.6\%$ and $\chi^2 = 2.4$ for 4501 step intensities. Atomic coordinates, isotropic temperature factors and bond distances are shown in Table 1. The final Rietveld plot is shown in Figure 1. Figure 2 shows the unit cell diagram of Mn_2GeTe_4 .

Mn_2GeTe_4 crystallize in an olivine-type structure which consists of a three-dimensional arrangement of distorted MnTe_6 octahedra and GeTe_4 tetrahedra connected by common faces. This olivine structure can be described as a hexagonal close packing of Te^{2-} anions with the Mn^{+2} cations occupying half of the octahedral sites and the Ge^{+4} cations occupying an eighth of the tetrahedral sites. Fig. 2 shows how the octahedra and tetrahedra share faces. The

inter-atomic distances are shorter than the sum of the respective ionic radii for structures tetrahedrally bonded²⁰. The Mn-Te bond distances, mean value 2.81(2) Å, is in good agreement with those found in related compounds such as MnIn_2Te_4 (2.78 Å)²¹, and the Ge-Te bond distance, mean value 2.57(2) Å, compare well with the same distance in Cu_2GeTe_3 (2.62 Å)²² and $\text{Cu}_2\text{ZnGeTe}_4$ (2.574 Å)²³.

Table 2 shows a comparison between the molecular weight, unit cell parameters and bond distances for the three phases of the compounds Mn_2GeVI_4 (VI = S, Se, Te). The variations of the unit cell volume (V) and bond distances against the molecular weight (MW) for the Mn_2GeVI_4 olivine compounds are shown in Fig. 3. It is seen from this figure that the volume and bond distances increase with increasing in MW. These results are to be expected since the MW increases with the size of the VI anions (ionic radius: 1.84 Å S^{2-} , 1.98 Å Se^{2-} , 2.21 Å Te^{2-} ²⁰).

Table 2: Comparative unit cell parameters and bond distances for the Mn_2GeVI_4 system (VI = S, Se, Te). [*] This work.

Compound	MW (g/mol)	A (Å)	B (Å)	C (Å)	V (Å ³)	Mn-VI (Å)	Ge-VI (Å)	Ref.
Mn_2GeS_4	310.71	12.776	7.441	6.033	573.5	2.608(1)	2.215(1)	⁸
Mn_2GeSe_4	498.31	13.350(3)	7.765(2)	6.307(1)	653.8(2)	2.715(1)	2.350(1)	⁹
Mn_2GeTe_4	692.89	13.950(2)	8.115(1)	6.592(1)	746.2(2)	2.81(2)	2.57(2)	(*)

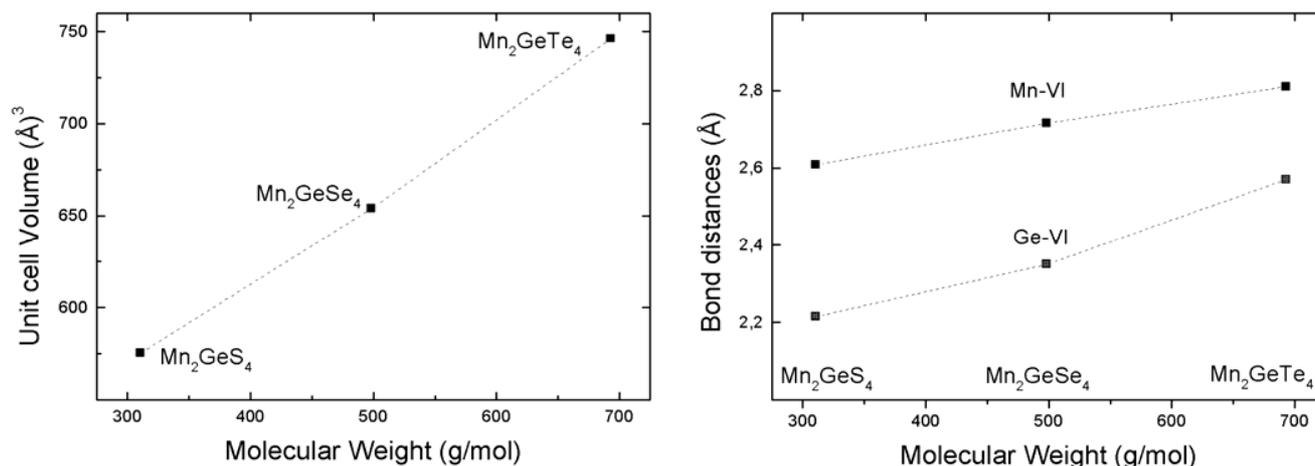


Figure 3: Unit cell volume and bond distances as function of the molecular weight for the three members of the system Mn_2GeVI_4 (VI = S, Se, Te).

Also, it is found that, within the limits of experimental errors, the volume V seems to increase almost linearly with the MW, but a small bowing of about 3.5 \AA^3 is observed in the V vs MW curve, indicating that V does not follow the Vegard's law. The reason for this behavior would be due to that the difference between the Mn-VI and Ge-VI bond distances decreases as the size of the VI anion is increased. Thus, the main contribution to the bowing of V is give by the Ge-VI bond distance, which increases nonlinearly and more rapidly with the anion VI size than the Mn-VI bond distance, the latter varies linearly with VI size.

Conclusion

The crystal structure of the ternary magnetic compound Mn_2GeTe_4 was refined by the Rietveld method using X-ray powder diffraction data. This compound crystallizes in an olivine-type structure, and consists of a three-dimensional arrangement of distorted $MnTe_6$ octahedra and $GeTe_4$ tetrahedra connected by common faces. Mn_2GeTe_4 is the first telluride compound that crystallizes with olivine structure.

Acknowledgements

The authors are grateful to CDCHT-ULA (C-1436-06-05-AA) and FONACIT (Grant LAB-97000821) for financial support.

References

1. Furdyna JK, Kossut J. In: R.K. Willardson, A.C. Beer (Eds.), Diluted Magnetic Semiconductors, Semiconductors and Semimetals, vol. 25, Academic Press, New York, Chapter 1; 1988.
2. Parthé E. In: J. H. Westbrook, R. L. Fleischer (Eds.), Intermetallic Compounds, Principles and Applications, Vol. 1, John Wiley & Sons, Chichester, UK; 1995.
3. Delgado JM. Crystal chemistry of diamond-like and other derivative semiconducting compounds. *Inst. Phys. Conf. Series*, **152**, 45-50 (1998).
4. Vincent H, Bertaut EF, Baur WH, Shannon RD. Polyhedral deformations in olivine-type compounds and crystal-structure of Fe_2SiS_4 and Fe_2GeS_4 . *Acta Cryst.*, **B32**, 1749-1755 (1976).
5. Jumas JC, Philippot E, Maurin M. Structural study on tin thiospinel Fe_2SnS_4 . *Acta Cryst.*, **B33**, 3850-3854 (1977).
6. Wintenberger M, Jumas JC. Study of Mn_2SnS_4 by neutron-diffraction - refinement of crystallographic structure and determination of magnetic-structure. *Acta Cryst.*, **B36**, 1993-1996 (1980).
7. Lamarche G, Lamarche F, Lamarche AM. A possible 83K magnetic detector for high-energy particles. *Physica B*, **194-196**, 219-220 (1994).
8. Julien-Pouzol M, Jaulmes S, Barnier B. Crystal-structure refinement of manganese thiogermanate Mn_2GeS_4 . *J. Sol. Stat. Chem.*, **65**, 280-282 (1986).
9. Deiseroth HJ, Aleksandrov K, Kremer RK. Structural and magnetic properties of Mn_2GeSe_4 . *Z. Anorg. Allg. Chem.*, **631**, 448-450 (2005).
10. Mikus H., Deiseroth HJ, Aleksandrov K, Ritter C, R.K. Kremer RK The Magnetic Structure of Mn_2GeSe_4 . *Eur. J. Inorg. Chem.*, 1515-1518 (2007).
11. Quintero M, Morocoima M, Quintero E, Ferrer D, Caldera D, Marchan N, Bocaranda P, Delgado GE. Crystallographic and magnetic properties of Mn_2GeTe_4 and Fe_2GeTe_4 compounds. *Rev. Mex. Fis.*, **S53**, 154-157 (2007).

12. Quintero M, Ferrer D, Caldera D, Moreno E, Quintero E, Morocoima M, Grima P, Bocaranda P, Delgado GE, Henao JA. Lattice parameter values and magnetic properties for the Mn_2GeTe_4 , Fe_2GeTe_4 and Fe_2SnSe_4 compounds. **J. Alloys Compd.**, **469**, 4-8 (2009).
13. Quintero M, Quintero E, Caldera D, Moreno E, Morocoima M, Grima P, Ferrer D, Marchan N, Bocaranda P, Delgado GE, Henao JA, Macías MA, Pinto JL, Ponce CA. Magnetic properties for the Mn_2GeTe_4 compound. **J. Mag. Mag. Mater.**, **321**, 295-299 (2009).
14. Boultif A and Louër D. Powder pattern indexing with the dichotomy method. **J. Appl. Cryst.**, **37**, 724-731 (2004).
15. Rietveld HM. A profile refinement method for nuclear and magnetic structures. **J. Appl. Cryst.**, **2**, 65-71 (1969).
16. Rodriguez-Carvajal J, Fullprof: (version 4.4, 2008), Laboratoire Léon Brillouin (CEA-CNRS), France.
17. Roisnel T and Rodriguez-Carvajal J. WinPLOTR: A Windows tool for powder diffraction pattern analysis. **Mater. Sci. Fórum**, **378-383**, 118-123 (2001).
18. Henao JA, Delgado JM, Quintero M. X-ray powder diffraction data and structural study of Fe_2GeSe_4 . **Powder Diffr.**, **13**, 196-201 (1998).
19. Cagliotti G, Paoletti A, Ricci FP. Choice of collimators for a crystal spectrometer for neutron diffraction. **Nucl. Instrum.**, **3**, 223-228 (1958).
20. Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. **Acta Cryst.**, **A32**, 751-767 (1976).
21. Delgado GE, Chacón C, Delgado JM, Sagredo V. An examination of the cation ordering scheme in the room temperature phase of $MnIn_2Te_4$. **Phys. Stat. Sol. (A)**, **134**, 61-66 (1992).
22. Delgado GE, Mora AJ, Pirela M, Villarreal M, Velásquez A, Fernández BJ. Structural refinement of the ternary chalcogenide compound Cu_2GeTe_3 by X-ray powder diffraction. **Phys. Stat. Sol. (A)**, **201**, 2900-2904 (2004).
23. Parasyuk OV, Olekseyuk ID, Piskach LV. X-ray powder diffraction refinement of $Cu_2ZnGeTe_4$ structure and phase diagram of the Cu_2GeTe_3 -ZnTe system. **J. Alloys Compd.**, **397**, 169-172 (2005).