Synthesis and characterization of ternary compound, Mn_2SnTe_4

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Abstract. Mn_2SnTe_4 **was synthesized by direct fusion using the anneal method. X-ray powder diffraction analysis indicated that this material crystallizes in the olivine-type structure, space group** *Pnma*, **Z = 4, with unit cell parameters:** $a = 14\cdot020(2)$ Å, $b = 8\cdot147(1)$ Å, $c = 6\cdot607(1)$ Å, $V = 754\cdot7(2)$ Å^3**. The Rietveld refinement converged to the figures of merit,** $R_p = 6\cdot9\%$, $R_{wp} = 8\cdot5\%$, $R_{exp} = 6\cdot0\%$, $\chi^2 = 2\cdot0$ **and** $S = 1\cdot4$**.**

Keywords. **Semiconductor; chemical synthesis; X-ray powder diffraction; Rietveld refinement; crystal structure.**

1. Introduction

Magnetic semiconducting materials have attractive properties and have received attention because of their potential application in optoelectronic and magnetic devices (Furdyna and Kossut 1988). The materials more frequently studied are known as semimagnetic semiconductors, obtained from the tetrahedrally coordinated derivatives of the II–VI binaries (Parthé 1995). One of these families is II_2–IV–VI_4, which belongs to one of the four possible families of the fourfold defect derivatives. These materials can be regarded as derived from the II–VI binaries, in which the cation has been substituted by two types of cations and an array of vacancies is introduced (Delgado 1998).

From the crystallographic point of view, three different structures have been reported for the II_2–IV–VI_4 family of compounds; a distorted spinel structure with tetragonal space group $I4_1/a$ (N° 88) for Fe_2SnS_4 (Jumas *et al* 1977), an orthorhombic structure with space group *Cmmm* (N° 65) for Mn_2SnS_4 (Witenberger and Jumas 1980), and an orthorhombic structure with space group *Pnma* (N° 62) known as olivine-type, which comes from the crystal structure of the mineral, Mg_2SiO_4 (Bragg and Brown 1926). It is important to mention that these materials generally crystallize in the olivine-type structure, and particularly those containing transition metals are known as versatile magnetic materials (Lamarche *et al* 1994). In this type of structures, the anions (VI) form a hexagonal close packing, with the cations in tetrahedral (IV) and octahedral (II) coordination (Vincent *et al* 1976).

To our knowledge, only one telluride in the olivine group family of the system II_2–IV–VI_4 have been studied by means of a single-crystal diffractometry and a detailed structural analysis has been done. This is the recently reported compound, Mn_2GeTe_4 (Delgado *et al* 2009). In this work, a complete structural study for the ternary Mn_2SnTe_4, a new telluride with olivine-type structure, is performed by means of the Rietveld method using X-ray powder diffraction data.

2. Experimental

2.1 *Synthesis*

Polycrystalline sample of the ternary phase, Mn_2SnTe_4, was synthesized by direct fusion of stoichiometric quantities of Mn, Sn and Te (3N–6N purity) in a sealed, evacuated quartz ampoule, which was previously subjected to pyrolysis in order to avoid reaction of the starting materials with quartz. The fusion process (14 days), was carried out into a furnace in 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.

2.2 *Chemical analysis*

Chemical composition of the resultant ingot was determined at several regions by energy dispersive X-ray (EDS) analysis using a Kevex Model Delta-3 system connected to a Hitachi Model S-2500 scanning electron microscope (SEM). Three different regions of the ingot were scanned, and the average atomic percentages are: Mn (14·4%), Sn (28·5%) and Te (57·1%), very close to the ideal composition 2 : 1 : 4. The error in standardless analysis was around 5%.

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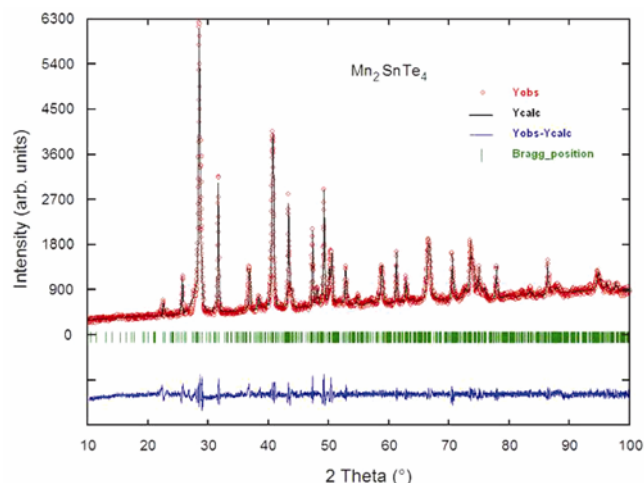
Table 1. Rietveld refinement results for Mn_2SnTe_4.

Molecular formula	Mn_2SnTe_4	Data range 2θ (°)	10–100°
Molecular weight (g/mol)	739·0	Step size 2θ (°)	0·02
Crystal system	Orthorhombic	Counting time (s)	15
Space group	*Pnma* (N° 62)	N° step intensities	4501
a (Å)	14·020(2)	Peak-shape profile	Pseudo-Voigt
b (Å)	8·147(1)	N° refined parameters	26
c (Å)	6·607(1)	R_p (%)	6·9
V (Å^3)	754·7(2)	R_{wp} (%)	8·5
Z	4	R_{exp} (%)	6·0
D_{calc} (g/cm^3)	6·58	χ^2	2·0
Temperature (K)	273(2)	S	1·4

$R_p = 100 \sum |y_{obs} - y_{calc}| / \sum |y_{obs}|$; $R_{wp} = 100 [\sum_w |y_{obs} - y_{calc}|^2 / \sum_w |y_{obs}|^2]^{1/2}$; $R_{exp} = 100 [(N - P + C)/\sum_w (y_{obs}^2)]^{1/2}$; $\chi^2 = [R_{wp}^2/R_{exp}^2]^{1/2}$; $S = R_{wp}/R_{exp}$ (goodness of fit); $N - P + C$ is the number of degrees of freedom.

Table 2. Atomic coordinates, isotropic temperature factors and interatomic distances for Mn_2SnTe_4.

Atom	Ox.	Site	x	y	z	f_{oc}	B_{iso} (Å^2)
Mn1	+2	4*a*	0	0	0	1	0·5(2)
Mn2	+2	4*c*	0·241(1)	1/4	0·503(1)	1	0·5(2)
Sn	+4	4*c*	0·404(1)	1/4	0·072(1)	1	0·5(2)
Te1	−2	8*d*	0·327(1)	0·007(1)	0·255(1)	1	0·5(2)
Te2	−2	4*c*	0·416(2)	1/4	0·689(2)	1	0·5(2)
Te3	−2	4*c*	0·583(2)	1/4	0·249(1)	1	0·5(2)

Mn1–Te1^{ii}	2·92(1) × 2	Mn1–Te2^{iii}	2·66(1) × 2	Mn1–Te3^{iv}	2·87(1) × 2
Mn2–Te1^{v}	2·84(1) × 2	Mn2–Te1	2·84(1) × 2	Mn2–Te2	2·74(3)
Mn2–Te3^{iii}	2·77(3)				
Sn–Te1	2·56(1) × 2	Sn–Te2^{i}	2·54(2)	Sn–Te3	2·77(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 1. Rietveld refinement plot for Mn_2SnTe_4 showing the observed, calculated and difference pattern. The Bragg reflections are indicated by vertical bars.

2.3 *X-ray powder diffraction*

X-ray powder diffraction pattern was collected at room temperature, in a Phillips PW-1250 goniometer using monochromatized CuKα radiation ($\lambda = 1.5418$ Å). A small quantity of the sample was ground mechanically in an agate mortar and pestle and mounted on a flat holder covered with a thin layer of grease. The specimen was scanned from 10–100°2θ, with a step size of 0·02° and counting time of 15 s. Silicon was used as an external standard.

3. Results and discussion

X-ray powder diffractogram of Mn_2SnTe_4 is shown in figure 1, which indicates a single phase. The 20 first measured reflections were completely indexed using the program DICVOL04 (Boultif and Löuer 2004), which gave a unique solution in an orthorhombic cell with parameters $a = 14.017(1)$ Å, $b = 8.138(1)$ Å and $c = 6.599(1)$ Å. Systematic absence of analysis indicates a P-type cell, which suggested along with the sample composition and cell parameter dimensions that this material is isostructural with the olivine-type compounds, crystallizing in the orthorhombic space group *Pnma* (N° 62) with 4 molecules in the asymmetric unit ($Z = 4$).

The Rietveld refinement (Rietveld 1969) of the whole diffraction pattern was carried out using the FULLPROF program (Roisnel and Rodriguez-Carvajal 2001; Rodriguez-Carvajal 2008). The atomic coordinates of the isomorphic compound, Fe_2GeSe_4 (Henao *et al* 1998) were used as initial model for the refinement of Mn_2SnTe_4,
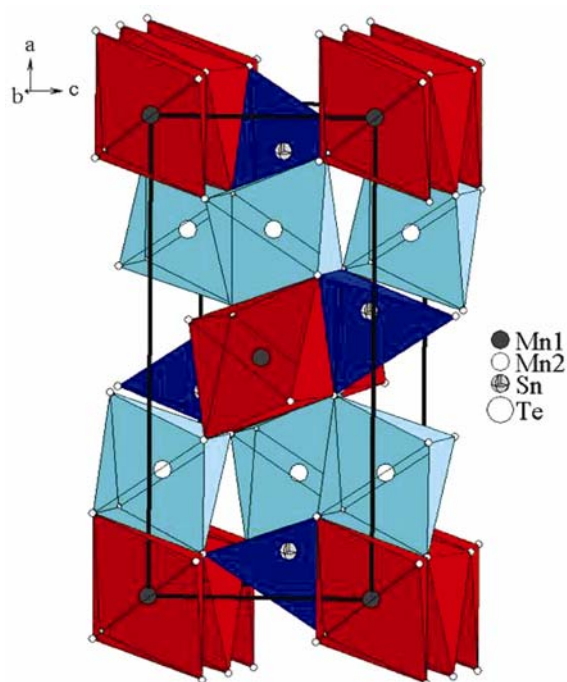
Figure 2. Unit cell protection for the Mn₂SnTe₄ compound showing the arrangement of MnTe₆ octahedra and SnTe₄ tetrahedra along the [100] direction.

with the unit cell parameters obtained in the indexing. The angular dependence of the peak full width at half maximum (FWHM) was described by Cagliotti's formula (Cagliotti *et al* 1958). 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 refinement converged to the final profile agreement factors summarized in table 1. Atomic coordinates, isotropic temperature factor and bond distances are shown in table 2. The final Rietveld plot is shown in figure 1. Figure 2 shows the unit cell diagram of Mn₂SnTe₄.

Mn₂SnTe₄ crystallizes in an olivine-type structure. This olivine structure can be described as a hexagonal close packing of Te^{-2} anions with the Mn^{+2} cations forming distorted MnTe₆ octahedra and SnTe₄ tetrahedra connected by common faces. Figure 2 shows how the octahedra and tetrahedra share faces and corners.

The interatomic distances are shorter than the sum of the respective ionic radii for structures tetrahedrally bonded (Shannon 1976). The Mn–Te bond distances, mean value 2·82(2) Å, is in good agreement with those found in related compounds such as MnIn₂Te₄ (2·78 Å) (Delgado *et al* 1992), Tl₂MnSnTe₄ (2·799 Å) and Tl₂MnGeTe₄ (2·777 Å) (McGuire *et al* 2005). The Sn–Te bond distance, mean value 2·61(2) Å, compares well with

the same distance in Cu₂SnTe₃ (2·61 Å) (Delgado *et al* 2008) but is shorter than those reported in Tl₂CdSnTe₄ (2·774 Å), Tl₂HgSnTe₄ (2·769 Å) and Tl₂MnSnTe₄ (2·770 Å) (McGuire *et al* 2005). All these phases were found in the ICSD database (ICSD 2008).

4. Conclusions

The crystal structure of the ternary compound, Mn₂SnTe₄, was refined by the Rietveld method using X-ray powder diffraction data. This compound crystallizes with an olivine-type structure, and consists of a three-dimensional arrangement of distorted MnTe₆ octahedra and SnTe₄ tetrahedra connected by common faces and corners.

Acknowledgements

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