Chalcogenide Letters Vol. 7, No. 2, February 2010, p. 133 - 138

SYNTHESIS AND CRYSTALLOGRAPHIC STUDY OF THE TERNARY SEMICONDUCTOR COMPOUND Fe_2GeTe_4

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The ternary compound Fe_2GeTe_4 was synthesized by the melt and annealing technique. Its structure has been refined by the Rietveld method using X-ray powder diffraction data. This compound crystallizes in the orthorhombic space group *Pnma* (Nº 62) with an olivine-type structure, and unit cell parameters a = 13.655(2) Å, b = 7.898(1) Å, c = 6.482(1) Å, V = 699.3(2) $Å^3$. It structure consists of a three-dimensional arrangement of distorted $FeTe_6$ octahedra and $GeTe_4$ tetrahedra connected by common faces.

(Received January 26, 2009; accepted February 23, 2010)

Keywords: Chalcogenide, Semiconductor, Chemical synthesis, X-ray powder diffraction, Rietveld refinement, Crystal structure

1. Introduction

Magnetic semiconducting materials have interesting semiconducting properties and have received attention because of their potential application in optoelectronic and magnetic devices [1]. The materials more frequently studied are the known as diluted magnetic semiconductor (DMS), obtained from the tetrahedrally coordinated derivatives of the II-VI binaries [2]. 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 semiconductors [3]. 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) coordination [4]. However, a distorted spinel structure with space group *I4₁/a* has 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 olivine structure containing transition metal are known as multipurpose magnetic materials [7].

In particular, for the system with composition Fe_2GeVI_4 (VI = S, Se, Te), the sulphide Fe_2GeS_4 [4] and selenide Fe_2GeSe_4 [8] compounds have been studied by means of single-crystal diffractometry and a detailed structural analysis have been described in each case. For Fe_2GeTe_4, only unit cell parameters and the X-ray powder diffraction data have been reported [9,10]. Therefore, in the present work, a complete structural study for this ternary semiconductor is performed, and the description of the structure is done.

2. Experimental

Polycrystalline sample of Fe_2GeTe_4 was synthesized using the melt and annealing technique. Stoichiometric quantities of highly pure Fe, Ge and Te elements were charged in an

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evacuated quartz ampoule, previously subject to pyrolysis in order to avoid reaction of the starting materials with quartz. The fusion process, 14 days, 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 analysis was carried out by energy dispersive X-ray (EDS) 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 were: Mn (28.5%), Ge (14.2%) and Te (57.3%), close to the ideal composition 2:1:4. The error in standardless analysis was around 5%. Figure 1 show a SEM image of the synthesized Fe_2GeTe_4.

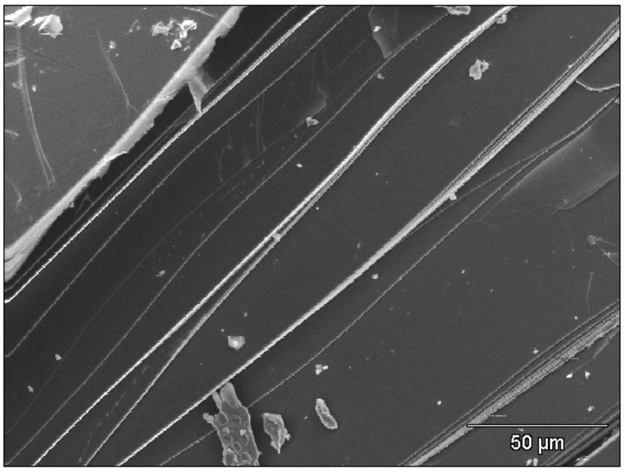

Fig. 1. SEM image of Fe_2GeTe_4 synthesized by the melt and annealing technique.

The X-ray powder diffraction data was collected, at 273 K, in a Phillips PW-1250 goniometer with CuKα radiation (λ= 1.5418 Å). 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 specimen was scanned over an angular range of 10-100º (2θ) with steps of 0.02º (2θ) and counting time of 15 s step^{-1}. Silicon was used as an external standard.

3. Results and discussion

The powder pattern of Fe_2GeTe_4 shows a single phase [10]. A close inspection of the diffraction pattern suggested that this material is isostructural with the olivine-type compound, which crystallize in the orthorhombic space group *Pnma* (Nº 62), similar to the other members of the Fe_2GeVI_4 (VI = S, Se, Te) system [4, 8].

The crystal structure refinement carried out by the Rietveld method [11] was performed using the Fullprof program [12], with the unit cell parameters obtained in the indexed. The atomic coordinates of the isomorphic compound Fe_2GeSe_4 [8] were used as starting parameters for the refinement of Fe_2GeTe_4. The instrumental and structural variables adjusted during the refinement were; zero shift, scale factor, symmetry parameter, six coefficients to define the polynomial variation of the background; three pseudo-Voigt parameters of the peak-shape function, three unit cell parameters, eleven positional parameters and one overall isotropic temperature factor. The refinement of 27 parameters, for 4501 step intensities, converged to the final profile agreement factors: $R_p = 6.1$ %, $R_{wp} = 7.9$ %, $R_{exp} = 5.9$ %, S = 1.3 and $\chi^2 = 1.8$ for 4501 step intensities and 33 independent reflections. Unit cell parameters, atomic coordinates, isotropic temperature factor and bond distances are shown in Table 1. Figure 2 show the observed, calculated and difference profile for the final cycle of refinements. Figure 3 show the unit cell diagram of Fe_2GeTe_4.

Table 1. Unit cell parameters, atomic coordinates, isotropic temperature factors and interatomic distances for Fe_2GeTe_4.

Space Group *Pnma* (N°62), Z = 4 ***a*** = 13.655(2) Å, ***b*** = 7.898(1) Å, ***c*** = 6.482(1) Å, V = 699.3(2) Å^3							
Atom	Ox.	Site	X	y	Z	foc	Biso (Å^2)
Fe1	+2	4a	0	0	0	1	0.6(5)
Fe2	+2	4c	0.243(1)	¼	0.506(1)	1	0.6(5)
Ge	+4	4c	0.409(1)	¼	0.073(1)	1	0.6(5)
Te1	-2	8d	0.332(1)	0.006(1)	0.258(1)	1	0.6(5)
Te2	-2	4c	0.415(2)	¼	0.690(2)	1	0.6(5)
Te3	-2	4c	0.582(2)	¼	0.251(1)	1	0.6(5)

Fe1-Te1$^{(ii)}$	2.78(1) x2	Fe1-Te2$^{(iii)}$	2.60(1) x2	Fe1-Te3$^{(iv)}$	2.79(1) x2
Fe2-Te1$^{(v)}$	2.79(1) x2	Fe2-Te1	2.79(1) x2	Fe2-Te2	2.63(3)
Fe2-Te3$^{(iii)}$	2.76(3)				
Ge-Te1	2.50(1) x2	Ge-Te2$^{(i)}$	2.49(2)	Ge-Te3	2.63(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.

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

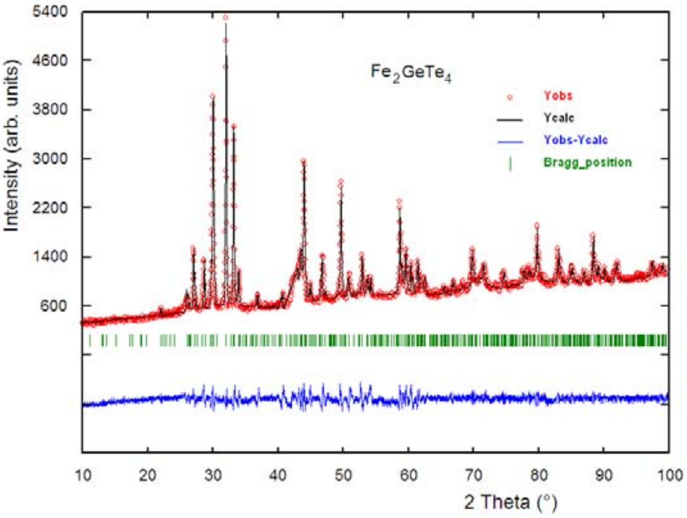

Fig. 2. Final Rietveld plot showing the observed (circles), calculated (solid line) and difference patterns of Fe_2GeTe_4. The Bragg reflections are indicated by vertical bars.

Fe_2GeTe_4, as well as Fe_2GeS_4 [4] and Fe_2GeSe_4 [8], crystallize in an olivine-type structure which consists of a three-dimensional arrangement of distorted $FeTe_6$ octahedra and $GeTe_4$ tetrahedra connected by common faces. The olivine structure can be described as a hexagonal close packing of Te^{-2} anions with the Fe^{+2} cations occupying half of the octahedral sites and the Ge^{+4} cations occupying an eighth of the tetrahedral sites. Figure 3 shows how the octahedra and tetrahedra share faces along the *ac* plane. The interatomic distances are shorter than the sum of the respective ionic radii for structures tetrahedrally bonded [13]. The Fe-Te [mean value 2.72(2) Å] and Ge-Te [mean value 2.53(2) Å] bond distances, compare well with the same distances found in related compounds [14] such as Fe_2CrTe_4 [15], Cu_2GeTe_3 [16], $Cu_2ZnGeTe_4$ [17] and Mn_2GeTe_4 [18].

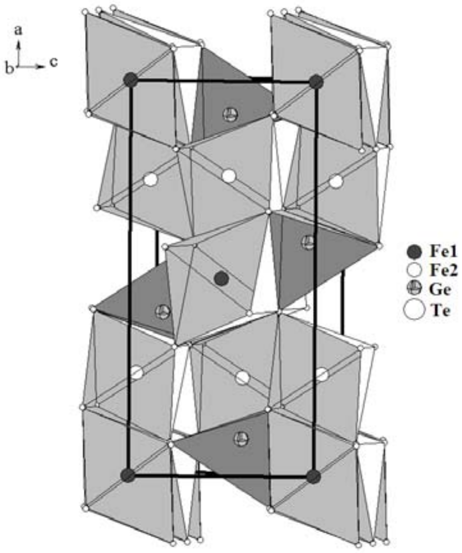

Fig. 3. Unit cell diagram for the ternary compound Fe_2GeTe_4, showing the arrangement of $FeTe_6$ octahedra and $GeTe_4$ tetrahedra along the ac plane.

Table 2 shows a relationship among the molecular weight and crystallographic parameters for the system Fe_2GeVI_4 (VI = S, Se, Te). Figure 4 shows these relations, and is possible observe as the unit cell volume and the bond distances increase linearly with the molecular weight and follows, within the limits of experimental error, Vegard's law [19]. The increase of these parameters can be expected in view of the difference of the ionic radius: 1.84 Å for S^{-2}, 1.98 Å for Se^{-2} and 2.21 Å for Te^{-2} [16]. Fe_2GeTe_4 corresponds to a new telluride member of the II_2-IV-VI_4 family with olivine structure; the others are the recently reported Mn_2GeTe_4 [18] and Mn_2SnTe_4 [20].

Table (2) Comparative unit cell parameters and bond distances for the Fe_2GeVI_4 system (VI = S, Se, Te); [*]- this work.

Phase	**MW (g/mol)**	***a* (Å)**	***b* (Å)**	***c* (Å)**	**V ($Å^3$)**	**Fe-VI (Å)**	**Ge-VI (Å)**	**Ref.**
Fe_2GeS_4	312.52	12.467(2)	7.213(1)	5.902(1)	530.7(1)	2.517(3)	2.219(3)	[4]
Fe_2GeSe_4	500.12	13.069(1)	7.559(1)	6.204(1)	612.8(1)	2.625(4)	2.370(6)	[8]
Fe_2GeTe_4	694.70	13.655(2)	7.898(1)	6.482(1)	699.3(2)	2.72(2)	2.53(2)	[*]

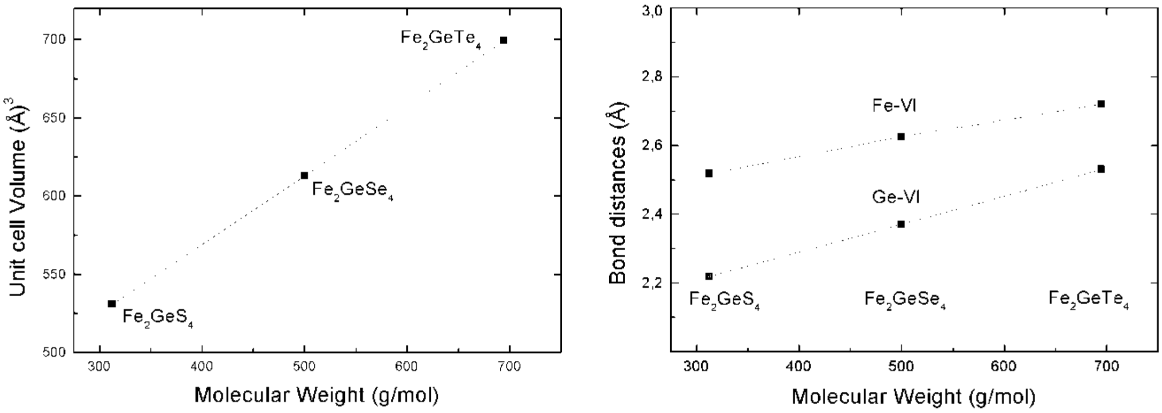

Fig. 4. Unit cell volume and bond distances as function of the molecular weight for the three members of the system Fe_2GeVI_4 (VI = S, Se, Te). The dot lines are a guide to the eyes.

4. Conclusion

The crystal structure refienement of the ternary compound Fe_2GeTe_4 was performed 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 $FeTe_6$ octahedra and $GeTe_4$ tetrahedra connected by common faces.

Acknowledgements

This work was supported by CDCHT-ULA and FONACIT (Grant LAB-97000821).

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