SYNTHESIS AND CRYSTALLOGRAPHIC STUDY OF THE TERNARY SEMICONDUCTOR COMPOUND Fe₂GeTe₄

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The ternary compound Fe₂GeTe₄ 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 \(a = 13.655(2) \text{ Å}, b = 7.898(1) \text{ Å}, c = 6.482(1) \text{ Å}, V = 699.3(2) \text{ Å}^3\). It structure consists of a three-dimensional arrangement of distorted FeTe₆ octahedra and GeTe₄ tetrahedra connected by common faces.

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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 II₂-IV-VI₄, 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 Fe₂SnS₄ [5], and an orthorhombic structure with space group Cmmm for Mn₂SnS₄ [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 Fe₂GeVI₄ (VI = S, Se, Te), the sulphide Fe₂GeS₄ [4] and selenide Fe₂GeSe₄ [8] compounds have been studied by means of single-crystal diffractometry and a detailed structural analysis have been described in each case. For Fe₂GeTe₄, 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 Fe₂GeTe₄ was synthesized using the melt and annealing technique. Stoichiometric quantities of highly pure Fe, Ge and Te elements were charged in an...
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$_2$GeTe$_4$.

![SEM image of Fe$_2$GeTe$_4$ synthesized by the melt and annealing technique.](image)

The X-ray powder diffraction data was collected, at 273 K, in a Phillips PW-1250 goniometer with CuK$_\alpha$ radiation ($\lambda = 1.5418$ 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 10-100° (2θ) with steps of 0.02° (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$_2$GeTe$_4$ 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 $Pnma$ (Nr 62), similar to the other members of the Fe$_2$GeVI$_4$ (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$_2$GeSe$_4$ [8] were used as starting parameters for the refinement of Fe$_2$GeTe$_4$. 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$_2$GeTe$_4$. 

![SEM image of Fe$_2$GeTe$_4$ synthesized by the melt and annealing technique.](image)
### Table 1. Unit cell parameters, atomic coordinates, isotropic temperature factors and interatomic distances for Fe₂GeTe₄.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Ox.</th>
<th>Site</th>
<th>X</th>
<th>y</th>
<th>Z</th>
<th>foc</th>
<th>Biso (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₁</td>
<td>+2</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.6(5)</td>
</tr>
<tr>
<td>Fe₂</td>
<td>+2</td>
<td>4c</td>
<td>0.243(1)</td>
<td>¼</td>
<td>0.506(1)</td>
<td>1</td>
<td>0.6(5)</td>
</tr>
<tr>
<td>Ge</td>
<td>+4</td>
<td>4c</td>
<td>0.409(1)</td>
<td>¼</td>
<td>0.073(1)</td>
<td>1</td>
<td>0.6(5)</td>
</tr>
<tr>
<td>Te₁</td>
<td>-2</td>
<td>8d</td>
<td>0.332(1)</td>
<td>0.006(1)</td>
<td>0.258(1)</td>
<td>1</td>
<td>0.6(5)</td>
</tr>
<tr>
<td>Te₂</td>
<td>-2</td>
<td>4c</td>
<td>0.415(2)</td>
<td>¼</td>
<td>0.690(2)</td>
<td>1</td>
<td>0.6(5)</td>
</tr>
<tr>
<td>Te₃</td>
<td>-2</td>
<td>4c</td>
<td>0.582(2)</td>
<td>¼</td>
<td>0.251(1)</td>
<td>1</td>
<td>0.6(5)</td>
</tr>
</tbody>
</table>

| Fe₁-Te₁(i) | 2.78(1) x2 | Fe₁-Te₂(ii) | 2.60(1) x2 | Fe₁-Te₃(iii) | 2.79(1) x2 |
| Fe₂-Te₁(iv) | 2.79(1) x2 | Fe₂-Te₁ | 2.79(1) x2 | Fe₂-Te₂ | 2.63(3) |
| Fe₂-Te₃(vi) | 2.76(3) | Ge-Te₁ | 2.50(1) x2 | Ge-Te₂ | 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.

\[ R_p = 100 \frac{\sum |y_{obs} - y_{calc}|}{\sum |y_{obs}|}, \quad R_{wp} = 100 \left( \frac{\sum w |y_{obs} - y_{calc}|^2}{\sum w^2 |y_{obs}|^2} \right)^{1/2}, \quad R_{exp} = 100 \left[ \frac{(N-P+C)}{\sum w (y_{obs}^2)} \right]^{1/2}, \quad S = R_{wp}/R_{exp} (= \text{goodness of fit}), \quad \chi^2 = \left( \frac{R_{wp}^2}{R_{exp}^2} \right)^{1/2}, \]  
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 Fe₂GeTe₄. The Bragg reflections are indicated by vertical bars.

Fe₂GeTe₄, as well as Fe₂GeS₄ [4] and Fe₂GeSe₄ [8], crystallize in an olivine-type structure which consists of a three-dimensional arrangement of distorted FeTe₆ octahedra and GeTe₄ tetrahedra connected by common faces. The olivine structure can be described as a hexagonal close packing of Te⁻² anions with the Fe²⁺ cations occupying half of the octahedral sites and the Ge⁴⁺ 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 Fe₂CrTe₄ [15], Cu₃GeTe₃ [16], Cu₂ZnGeTe₄ [17] and Mn₂GeTe₄ [18].

![Unit cell diagram for the ternary compound Fe₂GeTe₄](image)

Fig. 3. Unit cell diagram for the ternary compound Fe₂GeTe₄, showing the arrangement of FeTe₆ octahedra and GeTe₄ tetrahedra along the ac plane.

Table 2 shows a relationship among the molecular weight and crystallographic parameters for the system Fe₂GeVI₄ (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 S²⁻, 1.98 Å for Se²⁻ and 2.21 Å for Te²⁻ [16]. Fe₂GeTe₄ corresponds to a new telluride member of the II₂-IV-VI₄ family with olivine structure; the others are the recently reported Mn₂GeTe₄ [18] and Mn₂SnTe₄ [20].

<table>
<thead>
<tr>
<th>Phase</th>
<th>MW (g/mol)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>Fe-VI (Å)</th>
<th>Ge-VI (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂GeS₄</td>
<td>312.52</td>
<td>12.467(2)</td>
<td>7.213(1)</td>
<td>5.902(1)</td>
<td>530.7(1)</td>
<td>2.517(3)</td>
<td>2.219(3)</td>
<td>[4]</td>
</tr>
<tr>
<td>Fe₂GeSe₄</td>
<td>500.12</td>
<td>13.069(1)</td>
<td>7.559(1)</td>
<td>6.204(1)</td>
<td>612.8(1)</td>
<td>2.625(4)</td>
<td>2.370(6)</td>
<td>[8]</td>
</tr>
<tr>
<td>Fe₂GeTe₄</td>
<td>694.70</td>
<td>13.655(2)</td>
<td>7.898(1)</td>
<td>6.482(1)</td>
<td>699.3(2)</td>
<td>2.72(2)</td>
<td>2.53(2)</td>
<td>[*]</td>
</tr>
</tbody>
</table>
4. Conclusion

The crystal structure refinement of the ternary compound Fe$_2$GeTe$_4$ 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

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References