

X-RAY POWDER DIFFRACTION DATA FOR THE TERNARY CHALCOGENIDES Fe_2GeTe_4 , Mn_2GeTe_4 AND Mn_2SnTe_4

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X-ray powder diffraction data for the ternary chalcogenides Fe_2GeTe_4 , Mn_2GeTe_4 and Mn_2SnTe_4 are reported. The powder patterns were obtained using $\text{CuK}\alpha$ radiation. The unit cell parameters determined by least-squares refinement for the orthorhombic space group $Pnma$ are: $a = 13.6553(6)$ Å, $b = 7.8970(3)$ Å, $c = 6.4817(2)$ Å for Fe_2GeTe_4 , $a = 13.9414(4)$ Å, $b = 8.1382(3)$ Å, $c = 6.5640(2)$ Å for Mn_2GeTe_4 , $a = 14.0203(4)$ Å, $b = 8.1468(3)$ Å, $c = 6.6075(4)$ Å for Mn_2SnTe_4 . Observed and calculated X-ray powder diffraction data are given for the titled compounds.

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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 semimagnetic semiconductors, obtained from the tetrahedrally coordinated derivatives of the II-VI binaries [2]. One of these families is $\text{II}_2\text{-IV-VI}_4$, which present interesting magnetic properties [3-5], and 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 [6]. However, a distorted spinel structure with space group $I4_1/a$ have been reported for Fe_2SnS_4 [7], and an orthorhombic structure with space group $Cmmm$ for Mn_2SnS_4 [8]. It should be noted that the olivine structure containing transition metal are known as multipurpose magnetic materials [9]. In particular, for the system with composition $\text{II}_2\text{-IV-Te}_4$ (II = Fe, Mn, IV = Ge, Sn), the telluride Fe_2GeTe_4 [10], Mn_2GeTe_4 [11] and Mn_2SnTe_4 [12] compounds have been studied and detailed structural analysis have been described in each case. High-quality powder diffraction data were obtained for these compounds during our investigation and they are reported in the present study.

2. Experimental

Samples of the ternary phases Fe_2GeTe_4 , Mn_2GeTe_4 and Mn_2SnTe_4 were synthesized by direct fusion of stoichiometric quantities of the elements in a sealed, evacuated quartz ampoule. The fusion process were 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

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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 2:1:4 ratios for each phase. For the X-ray analysis, small quantities of the samples were ground mechanically in an agate mortar and pestle. The resulting fine powders were mounted on a zero-background holder covered with a thin layer of petroleum jelly. A Philips PW-1250 powder diffractometer was used for data collection with the conditions given in Table 1. The X-ray powder diffraction data were collected at 298(1) K. The position of the peaks was established using the α_1 component. The α_2 component was stripped mathematically using the diffractometer software.

Table 1. Data collection conditions of the ternaries Mn_2GeTe_4 , Fe_2GeTe_4 and Mn_2SnTe_4

Diffractometer:	Philips PW-1250	Instrumental settings:	40kV, 25mA
Geometry:	Bragg-Brentano	Receiving slit:	0.2°
Reflection mode:	θ/θ	Scatter slit:	1.0°
Radiation:	CuK α	Range of 2 θ :	10° to 100°
Wavelength:	$\lambda = 1.5418 \text{ \AA}$	Step size:	0.02°
Monochromator:	graphite	Counting time:	15 s/step
Detector:	scintillation	External standard:	Silicon

3. Results and discussion

Figure 1 shows the resulting X-ray powder pattern for Fe_2GeTe_4 , Mn_2GeTe_4 and Mn_2SnTe_4 compounds. The 20 first measured reflections were completely indexed using the program DICVOL04 [13], which gave unique solution in orthorhombic cells. 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 these materials are isostructural with the olivine-type compound, which crystallize in the orthorhombic space group $Pnma$ (N° 62). Figure 1 shows the unit cell diagram for the olivine-type structure adopted for the tree chalcogenide compounds. The complete powder diffraction datasets (43 diffraction peaks for Fe_2GeTe_4 , 42 for Mn_2GeTe_4 and 46 for Mn_2SnTe_4) were reviewed by using the program NBS*AIDS [14], and the refined unit cell parameters given in Table 2 were obtained. This table contain the figures of merit M_N [15] and F_N [16]. Tables 3, 4 and 5 contain the observed and calculated X-ray powder diffraction data for Fe_2GeTe_4 , Mn_2GeTe_4 and Mn_2SnTe_4 , respectively.

Table (2) Refined unit cell parameters and figures of merit obtained for the tree materials

	a (Å)	b (Å)	c (Å)	V (Å ³)	M_{20} [15]	F_{30} [16]
Fe_2GeTe_4	13.6553(6)	7.8970(3)	6.4817(2)	698.96(3)	56.3	31.5 (0.0042, 228)
Mn_2GeTe_4	13.9414(4)	8.1382(3)	6.5640(2)	744.74(3)	50.9	38.1 (0.0042, 189)
Mn_2SnTe_4	14.0203(4)	8.1468(3)	6.6075(4)	754.72(4)	48.8	38.3 (0.0039, 202)

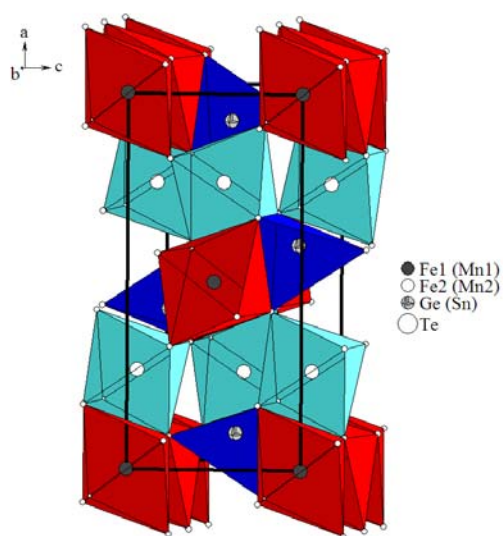
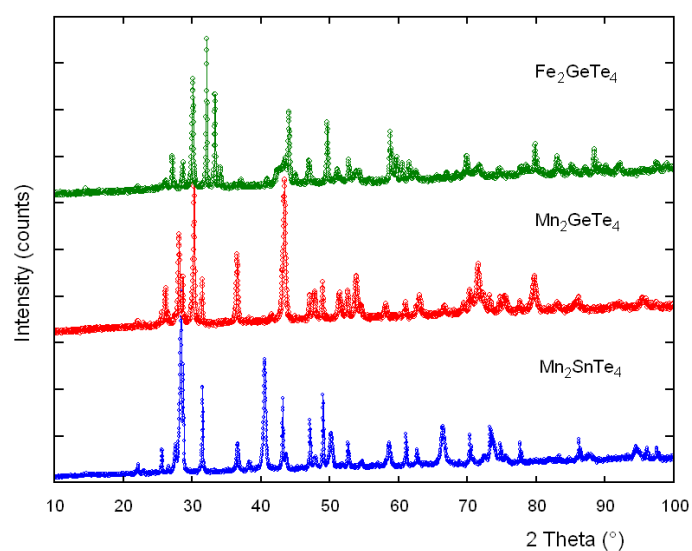


Fig. (1) X-ray powder patterns of the ternaries Fe_2GeTe_4 , Mn_2GeTe_4 and Mn_2SnTe_4 and the unit cell diagram of the olivine-type compounds.

Table (3) X-ray powder diffraction data of Fe_2GeTe_4 ($\lambda = 1.5418 \text{ \AA}$)

$2\theta_{\text{obs}}$ (°)	d_{obs} (Å)	$(I/I_0)_{\text{obs}}$	h	k	l	$2\theta_{\text{cal}}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
21.987	4.0390	3.4	2	1	1	21.986	4.0393	-0.002
26.045	3.4182	5.0	2	2	0	26.046	3.4181	0.001
			4	0	0	26.079	3.4138	
27.215	3.2739	19.8	1	2	1	27.216	3.2737	0.001
28.468	3.1326	16.8	4	1	0	28.459	3.1336	-0.009
			1	1	2	30.499	2.9284	
30.506	2.9278	72.8	2	0	2	30.506	2.9278	0.000
31.690	2.8210	100.0	4	1	1	31.689	2.8212	-0.002
33.039	2.7089	61.9	3	2	1	33.031	2.7096	-0.008
33.928	2.6399	12.5	3	0	2	33.926	2.6400	-0.001
36.817	2.4391	4.5	0	3	1	36.821	2.4389	0.004

41.087	2.1949	4.2	3	2	2	41.093	2.1947	0.005
42.559	2.1224	15.0	5	2	1	42.560	2.1223	0.002
43.908	2.0603	47.2	1	1	3	43.911	2.0601	0.003
			2	0	3	43.916	2.0599	
			4	2	2	44.838	2.0197	
44.852	2.0190	6.3	5	1	2	44.853	2.0190	0.001
46.487	1.9518	15.5	3	0	3	46.485	1.9518	-0.001
49.893	1.8262	40.4	2	2	3	49.891	1.8263	-0.003
			4	0	3	49.910	1.8257	
51.330	1.7784	8.4	4	1	3	51.320	1.7787	-0.010
52.402	1.7445	13.8	3	4	1	52.406	1.7444	0.004
53.650	1.7069	6.3	8	0	0	53.648	1.7069	-0.002
54.359	1.6863	6.8	0	4	2	54.367	1.6860	0.007
58.851	1.5678	32.1	3	3	3	58.849	1.5679	-0.002
			6	0	3	58.887	1.5669	
59.751	1.5463	15.9	2	1	4	59.760	1.5461	0.009
60.611	1.5264	10.6	3	0	4	60.605	1.5266	-0.006
61.334	1.5102	11.7	8	0	2	61.330	1.5102	-0.004
62.571	1.4832	3.2	8	1	2	62.565	1.4834	-0.006
67.117	1.3934	4.5	5	0	4	67.106	1.3936	-0.010
69.839	1.3456	13.0	10	1	0	69.841	1.3456	0.001
71.762	1.3142	7.4	5	2	4	71.765	1.3141	0.003
74.770	1.2686	2.1	7	3	3	74.766	1.2687	-0.004
			8	2	3	74.785	1.2684	
			1	2	5	77.793	1.2267	
77.808	1.2265	4.9	9	1	3	77.799	1.2266	-0.009
78.439	1.2182	4.8	9	3	2	78.443	1.2181	0.004
78.713	1.2146	3.4	1	6	2	78.714	1.2146	0.001
79.834	1.2004	19.1	2	6	2	79.828	1.2004	-0.006
80.534	1.1917	2.5	10	3	1	80.551	1.1915	0.016
			0	3	5	82.954	1.1630	
83.008	1.1623	12.0	8	1	4	83.003	1.1624	-0.005
			8	5	0	83.277	1.1593	
83.279	1.1592	8.7	11	0	2	83.278	1.1593	-0.002
85.147	1.1385	6.2	5	4	4	85.147	1.1385	0.001
87.368	1.1152	4.2	6	1	5	87.375	1.1151	0.007
88.232	1.1065	16.7	10	4	1	88.224	1.1066	-0.008
			11	3	1	88.250	1.1063	
			8	5	2	89.765	1.0915	
89.791	1.0913	3.0	3	6	3	89.795	1.0912	0.004
91.557	1.0748	3.6	6	6	2	91.548	1.0749	-0.008
			5	3	5	92.087	1.0700	
92.109	1.0698	6.1	7	1	5	92.116	1.0697	0.007
97.613	1.0236	5.7	8	1	5	97.607	1.0237	-0.006
98.630	1.0158	4.3	3	2	6	98.635	1.0157	0.005

Table (4) X-ray powder diffraction data of Mn_2GeTe_4 ($\lambda = 1.5418 \text{ \AA}$)

$2\theta_{\text{obs}} (\text{^\circ})$	$d_{\text{obs}} (\text{\AA})$	$(I/I_0)_{\text{obs}}$	h	k	l	$2\theta_{\text{cal}} (\text{^\circ})$	$d_{\text{cal}} (\text{\AA})$	$\Delta 2\theta (\text{^\circ})$
21.825	4.0688	4.2	0	2	0	21.823	4.0691	-0.001
25.541	3.4846	8.0	4	0	0	25.535	3.4853	-0.006

25.891	3.4383	23.2	3	1	1	25.894	3.4378	0.004
26.530	3.3568	7.4	1	2	1	26.531	3.3567	0.001
27.908	3.1941	53.6	1	0	2	27.903	3.1947	-0.005
28.790	3.0983	28.3	2	2	1	28.792	3.0981	0.002
			1	1	2	30.023	2.9738	
30.072	2.9691	100.0	2	0	2	30.069	2.9694	-0.003
31.040	2.8786	27.5	4	1	1	31.034	2.8792	-0.006
36.578	2.4545	43.2	4	2	1	36.571	2.4550	-0.006
38.720	2.3235	2.8	6	0	0	38.719	2.3236	-0.001
41.573	2.1704	4.2	5	2	1	41.568	2.1707	-0.005
			1	1	3	43.270	2.0891	
43.301	2.0877	90.3	2	0	3	43.304	2.0876	0.002
47.080	1.9286	15.6	6	2	1	47.077	1.9287	-0.004
47.930	1.8963	17.7	6	0	2	47.928	1.8964	-0.002
49.004	1.8573	23.8	2	2	3	49.000	1.8574	-0.004
			7	1	1	49.050	1.8556	
51.280	1.7800	15.5	3	2	3	51.278	1.7801	-0.002
52.460	1.7427	17.6	8	0	0	52.462	1.7427	0.002
			0	3	3	53.779	1.7031	
53.801	1.7024	26.6	7	0	2	53.793	1.7027	-0.008
54.641	1.6782	7.5	2	4	2	54.636	1.6784	-0.005
58.144	1.5852	8.9	5	2	3	58.139	1.5853	-0.005
			2	5	0	58.151	1.5850	
60.894	1.5200	10.1	3	1	4	60.888	1.5201	-0.006
			1	2	4	61.210	1.5129	
61.233	1.5124	5.4	8	1	2	61.236	1.5123	0.003
			6	2	3	62.567	1.4833	
62.600	1.4826	6.3	9	1	1	62.610	1.4824	0.010
			1	4	3	62.653	1.4815	
62.975	1.4747	6.7	4	5	0	62.972	1.4747	-0.003
63.060	1.4729	12.0	7	0	3	63.063	1.4728	0.003
66.714	1.4008	5.1	9	0	2	66.713	1.4009	-0.001
			2	4	5	69.863	1.3452	
69.870	1.3451	5.5	10	1	1	69.876	1.3450	0.006
70.259	1.3386	11.7	8	3	2	70.252	1.3387	-0.007
70.689	1.3315	8.2	2	6	0	70.695	1.3314	0.006
71.542	1.3177	26.5	9	3	1	71.536	1.3178	-0.007
73.285	1.2906	9.4	1	1	5	73.292	1.2905	0.007
			5	2	0	73.316	1.2901	73.316
74.837	1.2676	9.6	10	1	2	74.845	1.2675	0.008
			1	11	1	77.535	1.2301	
77.561	1.2298	5.3	2	2	5	77.559	1.2298	-0.002
77.648	1.2286	2.6	4	0	5	77.652	1.2285	0.004
79.726	1.2017	21.4	6	3	4	79.726	1.2017	0.001
84.703	1.1433	1.8	5	6	2	84.707	1.1433	0.004
			5	6	0	84.736	1.1430	
			5	5	2	84.996	1.1402	
85.002	1.1401	3.1	2	5	4	85.006	1.1400	0.004
			1	2	7	85.977	1.1296	
85.984	1.1296	8.5	10	2	3	85.987	1.1295	0.003
89.381	1.0952	2.4	12	0	2	89.385	1.0952	0.004
92.041	1.0704	3.9	8	6	0	92.046	1.0704	0.005
96.141	1.0353	2.6	4	1	6	96.143	1.0353	0.002

97.295	1.0261	2.9	12	0	3	97.294	1.0261	-0.001
			5	5	4	97.340	1.0257	

Table (5) X-ray powder diffraction data of Mn_2SnTe_4 ($\lambda = 1.5418 \text{ \AA}$)

$2\theta_{\text{obs}}$ (°)	d_{obs} (Å)	$(I/I_0)_{\text{obs}}$	h	k	l	$2\theta_{\text{cal}}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
21.805	4.0724	6.0	0	2	0	21.800	4.0734	-0.005
25.767	3.4545	13.8	3	1	1	25.761	3.4553	-0.007
26.460	3.3656	2.6	1	2	1	26.456	3.3660	-0.004
			0	0	2	26.964	3.3038	
27.677	3.2202	10.6	4	1	0	27.682	3.2197	0.005
27.723	3.2150	100.0	1	0	2	27.717	3.2157	-0.006
28.694	3.1084	58.3	2	2	1	28.698	3.1080	0.004
32.123	2.7840	48.8	3	2	1	32.115	2.7847	-0.008
36.474	2.4613	15.8	5	1	1	36.483	2.4607	0.009
40.751	2.2123	63.2	3	3	1	40.748	2.2124	-0.003
			1	1	3	42.989	2.1021	
43.011	2.1011	40.4	2	0	3	43.008	2.1012	-0.002
43.583	2.0748	8.8	1	3	2	43.585	2.0748	0.002
47.102	1.9277	28.0	1	4	1	47.099	1.9278	-0.003
47.320	1.9193	13.7	1	2	3	47.324	1.9192	0.004
47.629	1.9076	6.3	6	0	2	47.625	1.9078	-0.004
49.003	1.8573	40.9	6	1	2	48.997	1.8575	-0.006
50.671	1.8000	18.1	4	3	2	50.669	1.8001	-0.003
52.731	1.7344	13.6	7	2	1	52.733	1.7344	0.002
			0	4	2	52.754	1.7337	
53.950	1.6981	2.0	1	3	3	53.952	1.6980	0.002
56.004	1.6406	1.7	1	0	4	56.005	1.6405	0.001
57.174	1.6097	2.2	8	2	0	57.169	1.6099	-0.005
			6	1	3	58.654	1.5726	
58.676	1.5721	13.2	1	5	1	58.679	1.5720	0.003
61.061	1.5162	18.7	9	0	1	61.061	1.5162	0.000
62.841	1.4775	9.6	4	5	0	62.841	1.4775	0.000
65.652	1.4209	4.2	9	2	1	65.647	1.4210	-0.005
			5	1	4	66.649	1.4020	
66.653	1.4020	21.2	10	0	0	66.649	1.4020	-0.004
67.394	1.3883	2.3	9	1	2	67.390	1.3884	-0.005
69.877	1.3450	17.0	8	3	2	69.876	1.3450	-0.001
70.379	1.3366	10.2	6	5	0	70.383	1.3365	0.004
70.604	1.3329	4.0	2	6	0	70.595	1.3330	-0.009
72.622	1.3007	3.3	7	3	3	72.620	1.3008	-0.002
73.276	1.2907	19.0	10	0	2	73.283	1.2906	0.007
74.936	1.2662	9.0	4	6	0	74.941	1.2661	0.005
77.769	1.2270	12.2	4	5	3	77.768	1.2270	0.000
77.974	1.2243	6.7	10	3	1	77.978	1.2242	0.004
			8	3	3	77.985	1.2241	
78.580	1.2163	1.6	7	2	4	78.588	1.2162	0.008
			9	4	1	78.590	1.2162	
83.323	1.1587	3.3	9	4	2	83.322	1.1588	-0.001
			6	5	3	84.771	1.1426	
84.783	1.1425	3.6	1	7	1	84.793	1.1424	0.010

85.071	1.1393	2.8	12	1	1	85.084	1.1392	0.012
			6	1	5	85.103	1.1390	
			2	7	1	85.834	1.1312	
86.337	1.1259	12.0	3	5	4	86.338	1.1258	0.001
			4	3	5	86.384	1.1254	
87.871	1.1101	3.6	9	5	1	87.884	1.1100	0.013
			1	2	6	93.208	1.0600	
93.227	1.0599	1.6	10	1	4	93.231	1.0598	0.005
94.456	1.0493	7.1	10	5	1	94.460	1.0493	0.005
			8	5	3	94.467	1.0492	
94.851	1.0460	5.4	1	6	4	94.847	1.0460	-0.004
			9	3	4	94.859	1.0459	
			4	1	6	95.328	1.0420	
95.345	1.0419	3.6	6	7	0	95.356	1.0418	0.011
96.315	1.0339	6.5	10	2	4	96.315	1.0339	0.000
			13	0	2	97.404	1.0252	
97.441	1.0249	7.0	5	0	6	97.430	1.0250	-0.011
			2	7	3	98.324	1.0181	

4. Conclusion

The main purpose of this work has been the presentation of X-ray powder diffraction data for the ternary chalcogenide compounds Fe_2GeTe_4 , Mn_2GeTe_4 and Mn_2SnTe_4 .

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References

- [1] J.K. Furdyna, J. Kossut, in: R.K. Willardson, A.C. Beer (Eds.), *Diluted Magnetic Semiconductors, Semiconductors and Semimetals*, vol. 25, Academic Press, New York, (1988).
- [2] E. Parthé, in: J. H. Westbrook, R. L. Fleischer (Eds.), *Intermetallic Compounds, Principles and Applications*, Vol. 1, John Wiley & Sons, Chichester, UK, (1995).
- [3] M. Quintero, M. Morocoima, E. Quintero, D. Ferrer, D. Caldera, N. Marchan, P. Bocaranda, G.E. Delgado. *Rev. Mex. Fis.* **S53**, 154-157(2007).
- [4] M. Quintero, D. Ferrer, D. Caldera, E. Moreno, E. Quintero, M. Morocoima, P. Grima, P. Bocaranda, G.E. Delgado, J.A. Henao. *J. Alloys Compd.* **469**, 4 (2009).
- [5] M. Quintero, E. Quintero, D. Caldera, E. Moreno, M. Morocoima, P. Grima, D. Ferrer, N. Marchan, P. Bocaranda, G.E. Delgado, J.A. Henao, M.A. Macías, J.L. Pinto, C. A. Ponce. *J. Mag. Mag. Mater.* **321**, 295-299 (2009).
- [6] H. Vincent, E.F. Bertaut, W.H. Baur, R.D. Shannon. *Acta Cryst.* **B32**, 1749 (1976).
- [7] J.C. Jumas, E. Philippot, M. Maurin. *Acta Cryst.* **B33**, 3850 (1977).
- [8] M. Wintenberger, J.C. Jumas. *Acta Cryst.* **B36**, 1993 (1980).
- [9] G. Lamarche, F. Lamarche, A.M. Lamarche. *Physica B***194-196**, 219 (1994).
- [10] G.E. Delgado, L. Betancourt, A.J. Mora, J.E. Contreras, P. Grima-Gallardo, M. Quintero. Submitted to *Bull. Mater. Sci.*
- [11] G.E. Delgado, L. Betancourt, A.J. Mora, J.E. Contreras, P. Grima-Gallardo, M. Quintero. *Av. Quim.* **4**, 7 (2009).
- [12] G.E. Delgado, A.J. Mora, J.E. Contreras, L. Betancourt. *Bull. Mater. Sci.* In press.

- [13] A. Boultif, D. Louër. *J. Appl. Cryst.* **37**, 724 (2004).
- [14] A.D. Mighell, C.R. Hubbard, J.K. Stalick. NBS*AIDS: A Fortran Program for Crystallographic Data Evaluation, NBS Technical Note 1141 (1981).
- [15] P.M. de Wolff. *J. Appl. Cryst.* **1**, 108 (1968).
- [16] G.S. Smith, R.L. Snyder. *J. Appl. Cryst.* **12**, 60 (1979).