

Crystallographic study of ternary ordered skutterudite IrGe_{1.5}Se_{1.5}

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(Received 19 February 2010; accepted 13 May 2010)

The crystal structure of skutterudite-related phase IrGe_{1.5}Se_{1.5} has been refined by the Rietveld method from laboratory X-ray powder diffraction data. Refined crystallographic data for IrGe_{1.5}Se_{1.5} are $a=12.0890(2)$ Å, $c=14.8796(3)$ Å, $V=1883.23(6)$ Å³, space group $R\bar{3}$ (No. 148), $Z=24$, and $D_c=8.87$ g/cm³. Its crystal structure can be derived from the ideal skutterudite structure (CoAs₃), where Se and Ge atoms are ordered in layers perpendicular to the [111] direction of the original skutterudite cell. Weak distortions of the anion and cation sublattices were also observed. © 2010 International Centre for Diffraction Data. [DOI: 10.1154/1.3478411]

Key words: IrGe_{1.5}Se_{1.5}, X-ray powder diffraction data, Rietveld refinement, skutterudite

I. INTRODUCTION

Skutterudites (general formula MX_3 , where $M=Co, Rh$, or Ir and $X=P, As$, or Sb) have, in the past two decades, attracted much interest because of their promising thermoelectric properties (Uher, 2003). The ideal skutterudite structure (space group $Im\bar{3}$) can be considered as a severe distortion of the ReO_3 structure by tilting of the $[MX_6]$ octahedra (tilt system $a^+a^+a^+$) (Mitchell, 2002). A consequence of such tilting is the proximity of four X anions forming rectangular rings $[X_4]$ in which $X-X$ bonds occur. In addition to the binary skutterudites, ternary skutterudites also exist. These compounds can be prepared by isoelectronic substitution at the cation site M by pair of elements from 8 and 10 groups, e.g., $Fe_{0.5}Ni_{0.5}Sb_3$ (Kjekshus and Rakke, 1974), or by isoelectronic substitution on the anion site X by a pair of elements from 14 and 16 groups, e.g., $CoGe_{1.5}Te_{1.5}$ (Vaquero *et al.*, 2006). Lyons *et al.* (1978) mentioned the synthesis of IrGe_{1.5}Se_{1.5} and structural relation of this compound to the cubic skutterudite structure (space group $Im\bar{3}$). These authors also noticed the presence of weak superstructure diffractions violating the $Im\bar{3}$ symmetry in the powder diffraction pattern; however, no details were given. The crystal structure of the title phase is reported in the Linus Pauling File (2010) (collection code 461743) as being isostructural to the cubic skutterudite CoAs₃, and its calculated powder diffraction data are included in ICDD (2005). IrGe_{1.5}Se_{1.5} phase is also listed in the conference abstract of Fleurial *et al.* (1997) as a part of review of skutterudite materials.

The aim of this work is to present a Rietveld structural study of IrGe_{1.5}Se_{1.5} using conventional powder X-ray diffraction data and in particular shed the light on the ordering of Ge and Se atoms in its crystal structure.

II. EXPERIMENTAL

The IrGe_{1.5}Se_{1.5} ternary compound was synthesised from the elements by high-temperature solid-state reactions. Stoi-

chiometric amounts of 3N5-Ir (Alfa Aesar), 5N-Ge (VÚK Panenské Břežany a.s.), and 5N-Se (Alfa Aesar) were weighed in a stoichiometric ratio into graphitized quartz ampoules and after evacuation ($<10^{-2}$ Pa) the ampoules were sealed and ingoted at 1050 °C for 24 h. The ingot was consequently treated by the modified ceramic method and heated at 600 °C. Further details on this method are described in our previous paper (Navrátil *et al.*, 2007).

The X-ray diffraction pattern was collected in the Bragg-Brentano geometry on an X'Pert Pro PANalytical diffractometer, equipped with an X'Celerator detector using $Cu K\alpha$ radiation. To minimize the background, the specimen of IrGe_{1.5}Se_{1.5} was placed on a flat low-background silicon wafer. Table I summarizes the experimental details for the recording of the powder diffraction pattern. The observed diffractogram of IrGe_{1.5}Se_{1.5} phase is shown in Figure 1. A full width at half maximum of $0.067^\circ 2\theta$ X-ray powder data was obtained at $14.595^\circ 2\theta$, demonstrating good crystallinity of the specimen under investigation.

TABLE I. Experimental conditions.

Instrument	PANalytical X'Pert Pro
Radiation	$Cu K\alpha_1, Cu K\alpha_2$
Monochromator	Curved graphite (002)
Detector	X'Celerator
Soller slits	0.04 rad
Divergence slit	0.25°
Antiscatter slit	0.5°
Step width	$0.02^\circ 2\theta$
Angular range	10 to $110^\circ 2\theta$
Time per step	6 s
Specimen form	Powder
Specimen particle size	Ground in agate mortar and pestle to $<15 \mu m$
Specimen holder	"Zero" background
Specimen motion	Spinning: 1 rad s^{-1}

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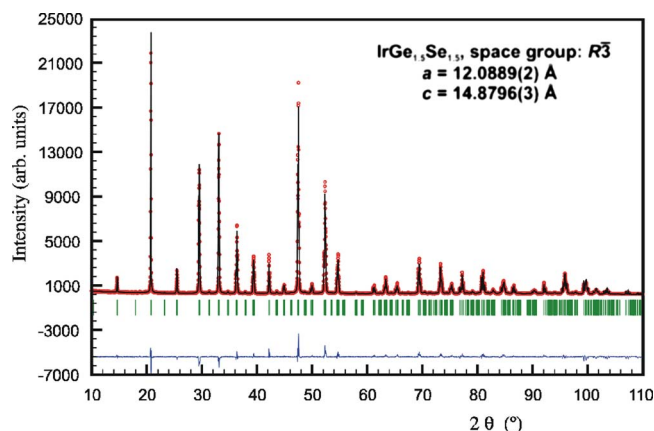


Figure 1. (Color online) Observed (circles), calculated (solid line), and difference Rietveld profiles for $\text{IrGe}_{1.5}\text{Se}_{1.5}$. The vertical bars indicate the positions of the Bragg reflections.

III. STRUCTURE REFINEMENT

The crystal structure $\text{IrGe}_{1.5}\text{Se}_{1.5}$ was refined by the Rietveld method for X-ray powder diffraction data using the FULLPROF program (Rodríguez-Carvajal, 1990). A preliminary Rietveld analysis of $\text{IrGe}_{1.5}\text{Se}_{1.5}$ using the cubic structure model for this compound included in the Linus Pauling File (2010) converged to rather high values of agreement factors ($R_p=12.3\%$, $R_{wp}=17.9\%$, and $R_B=8.68\%$). This structure model (space group $Im\bar{3}$) is isostructural to CoAs_3 (Kjekshus and Rakke, 1974), and the Ge and Se atoms randomly occupy the $24g$ position of the space group $Im\bar{3}$. Their occupancy factors were assigned according to the $\text{IrGe}_{1.5}\text{Se}_{1.5}$ composition.

However, apparent peak splitting and presence of weak superstructure reflections, which were not fitted by this cubic structural model, indicate an ordering of Ge and Se atoms. Analogous observation was made during the Rietveld refinement of $\text{IrSn}_{1.5}\text{Te}_{1.5}$ (Bos and Cava, 2007) and $\text{CoSn}_{1.5}\text{Te}_{1.5}$ (Laufek *et al.*, 2008). The structural studies of Vaqueiro *et al.* (2006, 2008) using high-resolution neutron powder diffraction on $\text{CoGe}_{1.5}\text{Te}_{1.5}$ and $M\text{Ge}_{1.5}\text{S}_{1.5}$ ($M=\text{Co}, \text{Rh}, \text{Ir}$), respectively, showed that ordering among Ge and Te (S) atoms in

TABLE II. Refined atomic coordinates for $\text{IrGe}_{1.5}\text{Se}_{1.5}$ [room temperature, space group $R\bar{3}$, $a=12.0890(2)$ Å, $c=14.8796(3)$ Å, $V=1883.23(6)$ Å³, $U_{\text{iso}}=0.0078(3)$ Å², $Z=24$, $D_x=8.87$ g/cm³, $R_p=5.53\%$, $R_{wp}=7.27\%$, and $R_B=5.98\%$].

Atom	Site	x	y	z
Ir(1)	6c	0	0	0.2484(5)
Ir(2)	18f	0.6670(6)	0.8316(4)	0.5828(3)
Ge(1)	18f	0.8405(9)	0.0140(8)	0.1588(4)
Ge(2)	18f	0.9380(8)	0.2090(9)	0.5601(4)
Se(1)	18f	0.9303(7)	0.2150(8)	0.0701(3)
Se(2)	18f	0.8353(8)	0.0210(7)	0.6672(4)

the skutterudite structure leads to the lowering of the symmetry from cubic (space group $Im\bar{3}$) to trigonal (space group $R\bar{3}$). The Rietveld refinement of $\text{IrGe}_{1.5}\text{Se}_{1.5}$ based on the starting $\text{IrGe}_{1.5}\text{Se}_{1.5}$ anion-ordered structure model in space group $R\bar{3}$ converged to the significantly better values of agreement factors ($R_p=5.53\%$, $R_{wp}=7.27\%$, and $R_B=5.98\%$) and accounted for all observed diffractions (see Fig. 2). The refined structural parameters of the structure $\text{IrGe}_{1.5}\text{Se}_{1.5}$ are given in Table II, and Figure 1 shows the final Rietveld plots.

Taking into account the similar X-ray scattering factors of Ge and Se atoms, the current Rietveld analysis does not provide any direct information regarding the ordering and assignment of Ge and Se atoms. The assignment of individual positions of Ge and Se atoms in the crystal structure of $\text{IrGe}_{1.5}\text{Se}_{1.5}$ was mainly based on different Ir-Se and Ir-Ge bonding distances. Despite the fact that the covalent radii of Ge and Se atoms are almost the same ($r_{\text{Ge}}=1.22$ Å, $r_{\text{Se}}=1.19$ Å) (Emsley, 1989), theoretical calculations of Partik and Lutz (1999) on skutterudite-type compounds showed that the covalent bond between the metal and germanium is much stronger than that between the metal and the chalcogen atoms. Hence, two of the four available anion positions (all in general Wyckoff position $18f$, space group $R\bar{3}$) in $\text{IrGe}_{1.5}\text{Se}_{1.5}$, which display shorter Ir-anion distances (from 2.40 to 2.42 Å), were assigned as Ge positions. Two residual anion positions showing slightly longer Ir-anion distances (from 2.47 to 2.51 Å) were assigned as Se positions. This

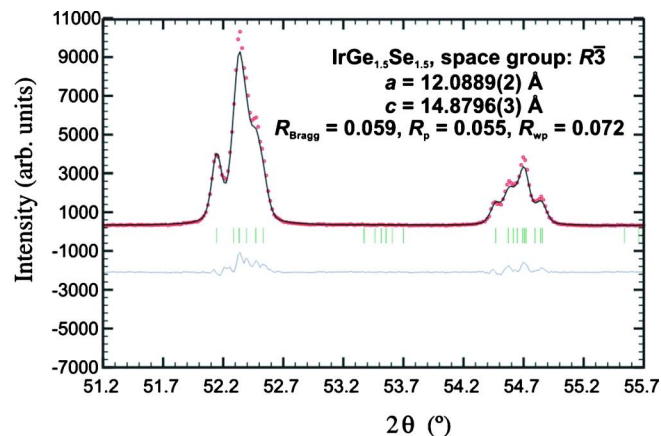
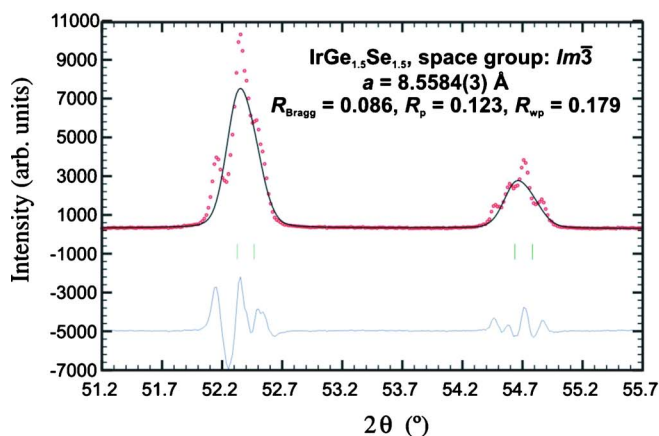


Figure 2. (Color online) Details of the two Rietveld fits for $\text{IrGe}_{1.5}\text{Se}_{1.5}$ showing the peak splitting. The left and right parts of Figure 2 show refinement based on disordered CoAs_3 (space group $Im\bar{3}$) and on the anion-ordered $\text{CoGe}_{1.5}\text{Te}_{1.5}$ (space group $R\bar{3}$) structure models, respectively. The observed reflections are completely fitted in the anion-ordered $\text{IrGe}_{1.5}\text{Se}_{1.5}$ structure model.

TABLE III. Selected interatomic distances (Å) for IrGe_{1.5}Se_{1.5} and those for IrGe_{1.5}S_{1.5} (Vaqueiro *et al.*, 2008; X=S or Se).

		IrGe _{1.5} Se _{1.5}	IrGe _{1.5} S _{1.5}
Ir(1)	Ge(1)	3 × 2.42(1)	3 × 2.407(5)
	X(2)	3 × 2.47(1)	3 × 2.38(1)
Ir(2)	Ge(2)	2.40(1)	2.389(5)
	Ge(2)	2.403(8)	2.381(4)
	Ge(1)	2.408(8)	2.375(6)
	X(1)	2.498(7)	2.378(9)
	X(1)	2.50(1)	2.461(9)
	X(2)	2.510(7)	2.41(1)

distribution of Ge and Se atoms in the crystal structure of IrGe_{1.5}Se_{1.5} is further supported by its comparison with its isostructural ternary skutterudite IrGe_{1.5}S_{1.5} (Vaqueiro *et al.*, 2008). Table III presents a comparison of selected bond distances for IrGe_{1.5}Se_{1.5} and IrGe_{1.5}S_{1.5} (Vaqueiro *et al.*, 2008). As is evident from Table III, the Ir-Ge distances are approximately the same in both compounds, while Ir-Se distances are significantly larger than corresponding Ir-S distances in IrGe_{1.5}S_{1.5}. This can be explained by the lower covalent radius of S ($r_S=1.04$ Å) with respect to the covalent radius of Se ($r_{Se}=1.19$ Å) (Emsley, 1989).

On other hand, the possibility that a certain degree of mixing of Ge and Se atoms occurs in the structure of IrGe_{1.5}Se_{1.5} cannot be ruled out. Nevertheless, apparent peak splitting and presence of weak superstructure diffractions suggest that essential amounts of Ge and Se atoms are on different crystallographic positions.

Despite the other satisfactory agreement parameters, the overall goodness of fit (χ^2) calculated by FULLPROF was 3.1, which is rather poor. According to Toby (2006), such high values of χ^2 can occur when the diffraction data are collected with very high precision (i.e., with very good counting statistics) and the misfit between observed and calculated patterns becomes very large when compared with uncertainties in the measured intensities. In these cases, the more reasonable χ^2 can be calculated using the R_{wp} value of a structureless Le Bail fit (Le Bail *et al.*, 1988) to the same data, contrary to the conventional R_{exp} . In this case, the R_{wp} of the Le Bail fit was 5.9%, yielding a χ^2 using $R_{exp}=R_{wp}(\text{Le Bail})$ of 1.54. Similar observation was described by Whitfield *et al.* (2007) during the refinement of the mineral jadarite.

The refined parameters include those describing peak shape and width, peak asymmetry, unit-cell parameters, and fractional coordinates. Finally, 25 parameters were refined. Isotropic displacement parameters were constrained to be equal for all atoms. The pseudo-Voigt function was used to generate the line shape of the diffraction peaks. The background was determined by linear interpolation between consecutive breakpoints in the pattern. The convergence criterion, ϵ , forcing the termination of the refinement when parameter shifts $< \epsilon \times \sigma$ was set to 0.1. The refined 2θ zero error of $0.030(1)^\circ$ matches very well the zero shift of about $0.038^\circ 2\theta$ which was determined from a linear interpolation function deduced from the LaB₆ external standard.

IV. RESULTS AND DISCUSSION

The powder diffraction data are listed in Table IV. The observed values of diffraction positions, d spacing, and intensities were extracted by the program XFIT (Coelho and Cheary, 1997), employing the split Pearson VII profile function. The $2\theta_{obs}$ and d_{obs} were corrected for the zero-point shift of $0.030^\circ 2\theta$. The powder data presented here for IrGe_{1.5}Se_{1.5} differ from ICDD (2005) in presence of weak superstructure reflections, indicating ordering of Ge and Se atoms (see structure refinement). The most obvious superstructure reflections are (hkl , $^\circ 2\theta$, I_{calc}) 208 (52.145, 22), 428, 6 to 28 (69.273, 15), and 006 (36.189, 9).

The crystal structure of the title phase is isostructural with IrSn_{1.5}Te_{1.5} (Bos and Cava, 2007), CoGe_{1.5}Te_{1.5} (Vaqueiro *et al.*, 2006), CoSn_{1.5}Se_{1.5} (Laufek *et al.*, 2009), and IrGe_{1.5}S_{1.5} (Vaqueiro *et al.*, 2008). As was proposed by Vaqueiro *et al.* (2006) and Partik *et al.* (1996), crystal structures of these phases can be derived from the cubic skutterudite structure MX_3 ($M=Co, Rh, \text{ or } Ir; X=P, As, \text{ or } Sb$), where Ge (Sn) and Te (Se) atoms show long-range ordering in planes perpendicular to the [111] direction of the original cubic cell. As a consequence of ordering, the symmetry is lowered from cubic to trigonal. However, the $a^+a^+a^+$ tilt system of octahedra of parent skutterudite structure is preserved. In the crystal structure of IrGe_{1.5}Se_{1.5}, each Ir atom is octahedrally coordinated by three Ge and three Se atoms. The Ge and Se atoms are arranged in a *facial* configuration. The [IrGe₃Se₃] octahedra share all six corners with adjacent octahedra, forming perovskitelike three-dimensional network [Figure 3(a)]. The cubic structure model of IrGe_{1.5}Se_{1.5} included in Linus Pauling File (2010) has the same crystallographic data as the CoAs₃ skutterudite structure (Kjekshus and Rakke, 1974). This cubic model apparently represents an average crystal structure of IrGe_{1.5}Se_{1.5} prepared by the method described in this paper and does not take into account the ordering of Ge and Se atoms (see above).

As was mentioned by Mitchell (2002) and Vaqueiro *et al.* (2008), the skutterudite structure can be derived from the perovskite structure ABX_3 by omission of A atoms and tilting of the octahedra (tilt system $a^+a^+a^+$). According to O'Keeffe and Hyde (1977), the tilt angle (φ) can be calculated from $M-X-M$ angle using a relationship

$$\cos(M-X-M) = 1 - \frac{2(2 \cos \varphi + 1)^2}{9}$$

Using this equation and the average Ir-X-Ir angle for IrGe_{1.5}S_{1.5} (Vaqueiro *et al.*, 2008), IrGe_{1.5}Se_{1.5} (this work), and IrSn_{1.5}Te_{1.5} (Bos and Cava, 2007), we have estimated the tilt angles for above mentioned phases to be 37.0° , 35.6° , and 33.4° . These values of tilt angles are in accordance with general trend observed in skutterudites; for a given cation (i.e., Ir), the tilt angle (φ) decreases with increasing size of the anions (Mitchell, 2002). The empty A site, which is located at the centre of the octahedral cluster [IrGe₃Se₃]₈, has approximately icosahedral coordination. However, contrary to the binary skutterudites, the icosahedral coordination is slightly distorted. The distances from hypothetical filler atom A to the Ge and Se atoms would have values of 3.10 and 3.26 Å, respectively.

Analogically to the binary skutterudites, the Ge and Se atoms form two crystallographically distinct four-membered

TABLE IV. Powder data for IrGe_{1.5}Se_{1.5}. Reflections with I_{calc} and $I_{\text{obs}} < 1\%$ are not shown in I_{calc} , which are obtained by using the structural parameters from the Rietveld refinement.

$h k l$	$2\theta_{\text{obs}}$ (deg)	d_{obs} (Å)	I_{obs}	$2\theta_{\text{calc}}$ (deg)	d_{calc} (Å)	I_{calc}	$h k l$	$2\theta_{\text{obs}}$ (deg)	d_{obs} (Å)	I_{obs}	$2\theta_{\text{calc}}$ (deg)	d_{calc} (Å)	I_{obs}			
0 1 2	14.622	6.0532	7	14.595	6.0643	3	1 6 4	63.369	1.4666	7	63.341	1.4671	2			
1 1 0				14.643	6.0445	3	7 -6 4				63.341	1.4761	2			
2 0 2				20.735	4.2802	100	20.736				4.2801	100	0 7 2	63.382	1.4663	2
1 0 4	25.384	3.5060	3	25.382	3.5062	3	5 3 2	65.113	1.4314	2	63.382	1.4663	2			
1 2 2	25.481	3.4928	7	25.475	3.4936	3	0 2 10				65.121	1.4313	2			
3 -2 2				25.475	3.4936	3	0 6 6				65.337	1.4271	2			
3 0 0				25.504	4.4897	3	2 6 2	65.447	1.4249	5						
0 2 4	29.439	3.0316	40	29.430	3.0325	42	8 -6 2	69.272	1.3553	15	65.445	1.4250	2			
2 2 0	29.525	3.0230	40	29.532	3.0223	42	4 2 8				69.279	1.3552	6			
2 1 4	33.080	2.7058	78	33.023	2.7103	7	6 -2 8				69.279	1.3552	7			
3 -1 4				33.023	2.7103	39	6 2 4	69.441	1.3524	15	69.437	1.3525	8			
3 1 2				33.090	2.7050	41	8 -2 4				69.437	1.3525	6			
4 -1 2	33.090	2.7050	7	4 0 10	73.083	1.2937	7									
0 0 6	36.189	2.4801	9	36.192	2.6969	10	4 4 6	73.302	1.2904	15	73.096	1.2935	7			
0 4 2	36.356	2.4691	32	36.358	2.4690	31	8 -4 6				73.301	1.2904	7			
2 -1 6	39.228	2.2947	7	39.235	2.2943	7	8 0 2				73.403	1.2889	7			
4 -3 4	39.348	2.2880	7	39.332	2.2889	7	5 -2 10	75.019	1.2651	2	75.031	1.2649	2			
2 3 2	39.402	2.2850	12	39.390	2.2857	7	5 4 4				75.298	1.2611	2			
4 1 0				39.409	2.2846	6	7 2 2				75.322	1.2607	4			
4 0 4				42.184	2.1405	11	42.182	2.1406	16	0 0 12	76.809	1.2400	4			
0 3 6	44.802	2.0213	3	44.798	2.0215	3	0 8 4	77.214	1.2345	14	77.213	1.2345	12			
3 3 0	44.94	2.0154	3	44.954	2.0148	3	2 4 10				80.744	1.1892	6			
2 2 6	47.373	1.9174	71	47.381	1.9171	39	6 -4 10				80.736	1.1893	11			
4 -2 6				47.381	1.9171	29	6 4 2	81.037	1.1856	12	80.744	1.1892	5			
4 2 2				47.514	1.9121	29	6 -4 10				81.042	1.1856	6			
6 -2 2	47.514	1.9121	39	3 6 6	82.822	1.1645	1									
0 1 8	49.755	1.8311	2	49.749	1.8313	2	9 -6 6	82.812	1.1647	2	82.822	1.1645	1			
0 5 4	49.974	1.8236	6	49.942	1.8247	2	9 0 0				82.934	1.1633	1			
1 5 2				49.990	1.8230	2	2 2 12				84.355	1.1472	4	84.362	1.1472	2
6 -5 2				49.990	1.8230	2	4 -2 12	84.362	1.1472	2						
2 0 8	52.145	1.7526	22	52.146	1.7526	22	2 6 8	84.608	1.1445	1						
2 4 4	52.329	1.7469	67	52.332	1.7468	21	8 -6 8	84.609	1.1444	3	84.608	1.1445	3			
6 -4 4				52.332	1.7468	22	4 6 4				84.756	1.1428	2			
6 0 0				52.394	1.7449	22	10 -6 4				84.762	1.1428	4			
1 2 8	54.453	1.6837	6	54.467	1.6833	6	2 8 0	84.812	1.1422	4	84.805	1.1423	1			
3 -2 8				54.467	1.6833	1	8 2 0				84.805	1.1423	2			
1 4 6				54.572	1.6803	6	4 3 10				86.362	1.1257	4			
4 1 6	54.577	1.6801	7	54.572	1.6803	1	10 -3 4	86.617	1.1230	4	86.622	1.1229	3			
5 -4 6				54.572	1.6803	1	5 -1 12				89.945	1.0899	1			
3 4 2				54.692	1.6769	1	8 0 8				92.056	1.0703	8			
7 -4 2	54.706	1.6765	15	54.692	1.6769	6	2 0 14	95.373	1.0417	4	95.386	1.0416	4			
2 5 0				54.707	1.6765	6	6 2 10				95.665	1.0393	6	95.681	1.0391	2
5 2 0				54.708	1.6764	1	8 -2 10							95.681	1.0391	4
0 4 8	61.072	1.5161	3	61.071	1.5161	3	2 8 6	95.878	1.0375	4						
4 4 0	61.299	1.5110	4	61.294	1.5111	3	8 2 6	95.889	1.0374	13	95.878	1.0375	3			
1 0 10	63.035	1.4735	2	63.052	1.4732	2	10 -8 6				95.878	1.0375	4			
2 3 8	63.154	1.4710	2	63.176	1.4706	1	10 -2 6				95.878	1.0375	2			
5 -3 8				63.176	1.4706	2	0 10 2	95.967	1.0368	4						
							$h k l$	$2\theta_{\text{obs}}$ (deg)	d_{obs} (Å)	I_{obs}	$2\theta_{\text{calc}}$ (deg)	d_{calc} (Å)	I_{calc}			
							6 4 8	99.288	1.0108	9	99.300	1.0107	8			
							10 -4 8				99.300	1.0107	2			
							0 6 12				99.300	1.0107	8			
							6 0 12	99.288	1.0108	9	99.300	1.0107	2			
							6 4 8				99.548	1.0089	2			
							10 -4 8				99.536	1.0090	4			
							6 6 0	99.755	1.0074	7	99.747	1.0074	8			
							3 1 14				101.048	0.9979	2	101.029	0.9981	2

TABLE IV. (Continued.)

$h k l$	$2\theta_{\text{obs}}$ (deg)	d_{obs} (Å)	I_{obs}	$2\theta_{\text{calc}}$ (deg)	d_{calc} (Å)	I_{calc}	$h k l$	$2\theta_{\text{obs}}$ (deg)	d_{obs} (Å)	I_{obs}	$2\theta_{\text{calc}}$ (deg)	d_{calc} (Å)	I_{obs}
							3 7 8						
							1 -7 6	101.424	0.9952	3	101.441	0.9951	2
							0 4 14	102.922	0.9848	2	102.931	0.9847	2
							0 8 10	103.229	0.9827	2	103.233	0.9827	2
							4 8 2				103.536	0.9806	2
							12 -8 2	103.539	0.9806	3	103.536	0.9806	2
							4 4 12				106.949	0.9586	2
							8 -4 12	106.942	0.9586	2	106.949	0.9586	1
							8 4 4				107.360	0.9560	1
							12 -4 4	107.357	0.9560	2	107.360	0.9560	1

rings $[\text{Ge}_2\text{Se}_2]$, in which the Se and Ge atoms are in transpositions to each other. The Ge-Se distances within the rings [Figures 3(b) and 3(c)] are more or less comparable with those observed in binary germanium selenides, e.g., GeSe (from 2.51 to 2.59 Å) (Dutta and Jeffrey, 1965) or Ge_4Se_9 (from 2.32 to 2.48 Å) (Fjellvag *et al.*, 2001). Contrary to the rectangular shape of $[\text{As}_4]$ rings found in the structure of CoAs_3 (Kjekshus and Rakke, 1974), the $[\text{Ge}_2\text{Se}_2]$ rings in the $\text{IrGe}_{1.5}\text{Se}_{1.5}$ structure are more distorted [Figure 3(c)]. The ratio of X - X distances is 1.03 for the CoAs_3 structure, while for $\text{IrGe}_{1.5}\text{Se}_{1.5}$ this ratio ranges from 1.07 to 1.08, indicating the weak distortion of the anion lattice.

ACKNOWLEDGMENTS

This study was supported by internal project of Czech Geological Survey (Project No. 332300) and P108/10/1315. The kind help of Vojtěch Vlček (University of Bayreuth) with X-ray diffraction measurement is highly acknowledged.

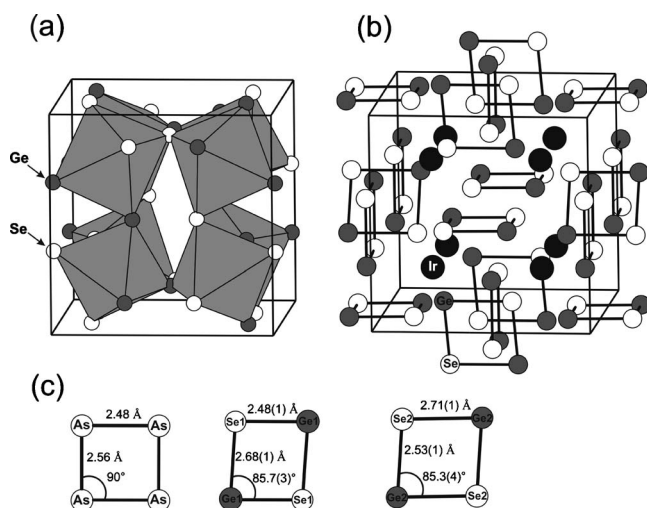


Figure 3. (a) Polyhedral and (b) ball-and-stick representation of the $\text{IrGe}_{1.5}\text{Se}_{1.5}$ structure emphasising the corner sharing arrangement of the $[\text{IrGe}_3\text{Se}_3]$ octahedra (rhombohedral setting). (c) Comparison of four-membered $[\text{As}_4]$ and $[\text{Ge}_2\text{Se}_2]$ rings found in the CoAs_3 (Kjekshus and Rakke, 1974) and $\text{IrGe}_{1.5}\text{Se}_{1.5}$ structures, respectively.

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