Synthesis and Rietveld refinement of the ternary skutterudite $RuSb_2Te$

F. Laufek[a)]
Czech Geological Survey, Geologická 6, 152 00 Praha 5, Czech Republic

J. Návrátil[b)]
Institute of Macromolecular Chemistry of the Academy of Sciences of the Czech Republic v.v.i., Heyrovsky sq. 2, 12006 Prague, Czech Republic

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The $RuSb_2Te$ compound has been synthesized and structurally characterized from powder X-ray diffraction data. $RuSb_2Te$ has the skutterudite structure, $Im\bar{3}$ symmetry, unit-cell parameter $a = 9.2665(1)$ Å, $V = 795.70(1)$ Å^3, $Z = 8$, and $D_c = 7.88$ g/cm^3. The Sb and Te atoms randomly occupy the crystallographic 24*g* position; no indications of ordering of Te and Sb atoms have been detected. © *2011 International Centre for Diffraction Data*. [DOI: 10.1154/1.3660324]

Key words: $RuSb_2Te$, X-ray powder diffraction data, Rietveld refinement, skutterudite, crystal structure

I. INTRODUCTION

Many experimental studies performed in last two decades have demonstrated that materials with the skutterudite structure (general formula MX_3 where $M = $ Co, Ir or Rh; $X = $ P, As or Sb) offer great potential for thermoelectric applications (Uher 2003; Fleurial *et al*., 1997). The crystal structure of skutterudite (space group $Im\bar{3}$) is a derivative of the perovskite structure AMX_3 and is characterized by large tilting of the $[MX_6]$ octahedra (tilt system $a^+a^+a^+$) (Mitchell, 2002). The *A*-site, occupied in the perovskite structure, is vacant.

The tilting of the octahedra results in the proximity of *X* anions forming $[X_4]$ rectangles in which the homonuclear *X*-*X* bonds occur. Besides binary skutterudites, ternary skutterudites have been also synthesized. These phases can be obtained by isoelectronic substitution either on the cation site *M* by a pair of elements from 8 and 10 groups, e.g., $Fe_{0.5}Ni_{0.5}Sb_3$ (Kjekshus and Rakke, 1974) or by analogous substitution on the anion site *X* by a pair of elements from 14 and 16 groups of the periodical system, e.g., $CoGe_{1.5}Te_{1.5}$ (Vaqueiro *et al*., 2006). The crystallographic studies of (Vaqueiro *et al*., 2006, 2010) on $AB_{1.5}Te_{1.5}$ ($A = $ Co, Rh, Ir; $B = $ Ge, Sn) ternary skutterudites showed a long-range ordering of *B* and Te atoms resulting in lowering of the symmetry from cubic to rhombohedral. The phase $RuSb_2Te$ is mentioned in the list of prospective thermoelectric materials with skutterudite structure of Fleurial *et al*. (1997), however, no detailed information concerning the crystal structure and powder diffraction data is available in the literature and in crystallographic databases [ICDD (2010), Fiz Karlsruhe and NIST (2010) and Linus Pauling File (2011)].

The aim of this work is synthesis and Rietveld structure analysis of the ternary skutterudite $RuSb_2Te$. Powder diffraction data up to 110° 2θ (Cu $K\alpha$) are reported.

II. EXPERIMENTAL

The $RuSb_2Te$ ternary compound was synthesized from individual elements by high-temperature solid-state reaction. Stoichiometric amounts of Ru (99.9%), Sb (99.999%), and Te (99.999%) were sealed into an evacuated carbon-coated silica glass tube and heated up to 1050 °C for 48 h in a furnace. After quenching into a cold-water bath, the same tube was placed into furnace and annealed at 550 °C for 120 h. After regrinding under acetone, the resultant material was pelletized and heated again at 550 °C for 120 h. The completion of the solid-state reaction of obtained powder samples was verified by powder X-ray diffraction.

Powder X-ray diffraction data of $RuSb_2Te$ were obtained in the Bragg-Brentano geometry on a Bruker D8-Advance diffractometer. Cu $K\alpha$ radiation was used. To minimize the background, the specimen of $RuSb_2Te$ was placed on a flat low-background silicon wafer. The generator was operated at 40 kV and 40 mA, respectively. The details of data collection are summarized in Table I. The observed powder diffractogram is shown in Figure 1. A full width at half maximum of 0.053° 2θ X-ray powder data was observed at 13.503° 2θ, indicating good crystallinity of the investigated specimen.

III. STRUCTURE REFINEMENT

The crystal structure of $RuSb_2Te$ was refined using the Rietveld method for X-ray powder diffraction data by means

TABLE I. Experimental conditions.

Instrument	Bruker D8 Advance
Radiation	Cu$K\alpha$
Detector	NaTl(I) scintillation detector
Soller slits	0.035 rad
Divergence slit	1°
Anti-scatter slit	1°
Step width	0.02°
Specimen form	Powder
Specimen particle size	Ground in agate mortar and pestle to < 15 μm
Specimen holder	"Zero" background
Specimen motion	Spinning: 1 r s^{-1}

a)Author to whom correspondence should be addressed. Electronic mail: frantisek.laufek@geology.cz
b)Present address: Joint Laboratory of Solid State Chemistry of Institute of Macromolecular Chemistry of the Academy of Sciences of the Czech Republic v.v.i. and the University of Pardubice, 53210 Pardubice, Czech Republic

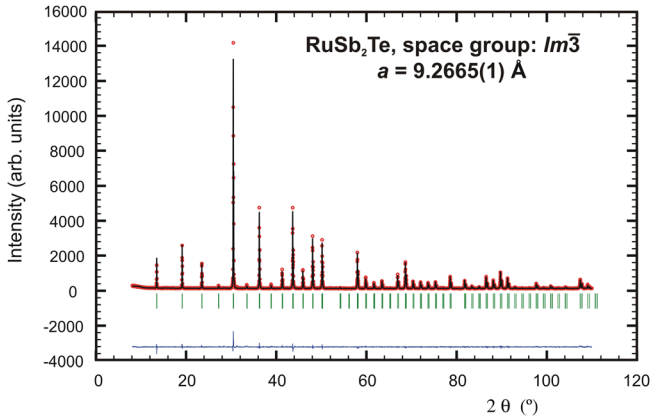

Figure 1. (Color online) Observed (circles), calculated (solid line), and difference Rietveld profiles for $RuSb_2Te$. The vertical bars indicate the positions of Bragg reflections.

of the program FULLPROF (Rodríguez-Carvajal, 1990). All peaks in the powder diffraction pattern were indexed on a cubic body-centred cell analogous to $CoSb_3$ (Kjekshus and Rakke, 1974). Consequently, the crystal structure of $CoSb_3$ was used as a starting structural model in the Rietveld refinement.

The refined parameters include those describing peak shape and width, peak asymmetry (two parameters), unit-cell parameters and fractional coordinates. The pseudo-Voigt function was used to model the line shape of the diffraction profiles. The background was determined by linear interpolation between consecutive breakpoints in the diffraction pattern.

The convergence criterion, ε, forcing the termination of the refinement when parameter shifts $< \varepsilon \times \sigma$, was set to 0.1. In total, 13 parameters were refined. The Sb and Te randomly occupy the 24*g* position in the $Im\bar{3}$ space group; their occupancy factors were assigned according to the $RuSb_2Te$ chemical composition (i.e., 0.67 and 0.33 for Sb and Te, respectively). The final cycles of refinement converged to the satisfactory values of agreement factors: $R_p = 4.69\%$, $R_{wp} = 6.30\%$, $R_B = 3.68\%$, and $\chi^2 = 1.05$).

It is worth noting that a relatively large group of anion-ordered ternary skutterudites $MX_{1.5}Y_{1.5}$ with $R\bar{3}$ symmetry has been described [e.g., $IrGe_{1.5}Se_{1.5}$ (Laufek and Navrátil, 2010), $RhGe_{1.5}Se_{1.5}$ (Liang *et al.*, 2011), $CoSn_{1.5}Te_{1.5}$ (Laufek *et al.*, 2008)]. The refinement of $RuSb_2Te$ based on the anion-ordered structure model of $CoSn_{1.5}Te_{1.5}$ (space group $R\bar{3}$) was also attempted. Although this refinement resulted in approximately the same values of profile agreement parameters ($R_p = 4.77\%$, $R_{wp} = 6.34\%$, $R_B = 5.63\%$,

TABLE II. Refined parameters for $RuSb_2Te$ [room temperature, space group $Im\bar{3}$, $a = 9.2665(1)$ Å, $V = 795.70(1)$ Å^3, $Z = 8$, $D_c = 7.88$ g/cm^3, $R_p = 4.69\%$, $R_{wp} = 6.30\%$, and $R_B = 3.68\%$). The displacement parameters of Sb and Te were constrained to be equal in the Rietveld refinement.

Atom	Site	*x*	*y*	*z*	Occ.	B_{iso} [Å^2]
Ru	8*c*	1/4	1/4	1/4	1	0.24(3)
Sb	24*g*	0	0.1545(2)	0.3359(2)	0.67	0.34(2)
Te	24*g*	0	0.1545(2)	0.3359(2)	0.33	0.34(2)

TABLE III. Powder diffraction data for $RuSb_2Te$. Reflections with I_{calc} and $I_{obs} < 1\%$ are not shown in the table.

h	*k*	*l*	$2\theta_{obs}$(°)	d_{obs}(Å)	I_{obs}	$2\theta_{calc}$(°)	d_{calc}(Å)	I_{calc}	$2\theta_{obs}$ - $2\theta_{calc}$
1	1	0	13.506	6.5507	9	13.503	6.5522	9	0.003
2	0	0	19.146	4.6318	18	19.140	4.6333	18	0.006
2	1	1	23.501	3.7824	12	23.497	3.7831	12	0.004
1	3	0	30.484	2.9300	119	30.481	2.9303	20	0.003
3	1	0				30.481	2.9303	100	
3	2	1	36.246	2.4764	43	36.243	2.4766	43	0.003
4	0	0	38.845	2.3165	2	38.842	2.3166	2	0.003
3	3	0	41.306	2.1839	11	41.303	2.1841	9	0.003
4	1	1				41.303	2.1841	1	
2	4	0	43.647	2.0721	47	43.648	2.0720	30	−0.001
4	2	0				43.648	2.0720	17	
3	3	2	45.898	1.9756	12	45.897	1.9756	11	0.001
4	2	2	48.066	1.8914	33	48.063	1.8915	32	0.003
1	5	0	50.155	1.8174	33	50.158	1.8173	2	−0.003
3	4	1				50.158	1.8173	25	
4	3	1				50.158	1.8173	3	
3	5	0	57.986	1.5892	25	57.987	1.5892	9	−0.001
4	3	3				57.987	1.5892	10	
5	3	0				57.987	1.5892	6	
6	0	0	59.838	1.5444	8	59.837	1.5444	7	0.001
5	3	2	61.649	1.5033	4	61.652	1.5032	3	−0.003
2	6	0	63.433	1.4652	6	63.437	1.4651	2	−0.004
6	2	0				63.437	1.4651	3	
6	2	2	66.925	1.3970	11	66.927	1.3970	10	−0.002
3	6	1	68.641	1.3662	22	68.638	1.3663	3	0.003
6	3	1				68.638	1.3663	17	
4	4	4	70.324	1.3376	6	70.329	1.3375	6	−0.005
4	5	3	72.001	1.3105	5	72.002	1.3105	4	−0.001
5	4	3				72.002	1.3105	1	
4	6	0	73.658	1.2850	5	73.660	1.2850	3	−0.002
6	4	0				73.660	1.2850	2	
2	7	1	75.305	1.2610	6	75.303	1.2610	1	0.002
6	3	3				75.303	1.2610	4	
7	2	1				75.303	1.2610	1	
3	7	0	78.559	1.2167	11	78.556	1.2167	9	0.003
7	3	0				78.556	1.2167	1	
5	6	1	81.767	1.1769	1	81.771	1.1768	1	−0.004
7	3	2			7	81.771	1.1768	7	
2	8	0				86.548	1.1237	1	
6	4	4	86.544	1.1238	12	86.548	1.1237	7	−0.004
8	2	0				86.548	1.1237	3	
5	6	3	88.127	1.1076	8	88.133	1.1076	5	−0.006
6	5	3				88.133	1.1076	3	
6	6	0	89.711	1.0921	18	89.717	1.0921	15	−0.006
8	2	2				89.717	1.0921	3	
3	8	1	91.298	1.0772	11	91.301	1.0772	2	−0.003
4	7	3				91.301	1.0772	7	
7	4	3				91.301	1.0772	1	
7	5	0				91.301	1.0772	1	
h	*k*	*l*	$2\theta_{obs}$(°)	d_{obs}(Å)	I_{obs}	$2\theta_{calc}$(°)	d_{calc}(Å)	I_{calc}	$2\theta_{obs}$ - $2\theta_{calc}$
1	9	0	97.656	1.0233	5	97.659	1.0233	1	−0.003
9	1	0				97.659	1.0233	4	
9	2	1	100.869	0.9992	2	100.868	0.9992	2	0.001
3	9	2	107.404	0.9558	13	107.405	0.9558	2	−0.001
6	7	3				107.405	0.9558	1	
7	6	3				107.405	0.9558	10	
9	3	2				107.405	0.9558	1	
8	4	4	109.068	0.9458	4	109.072	0.9458	4	−0.004

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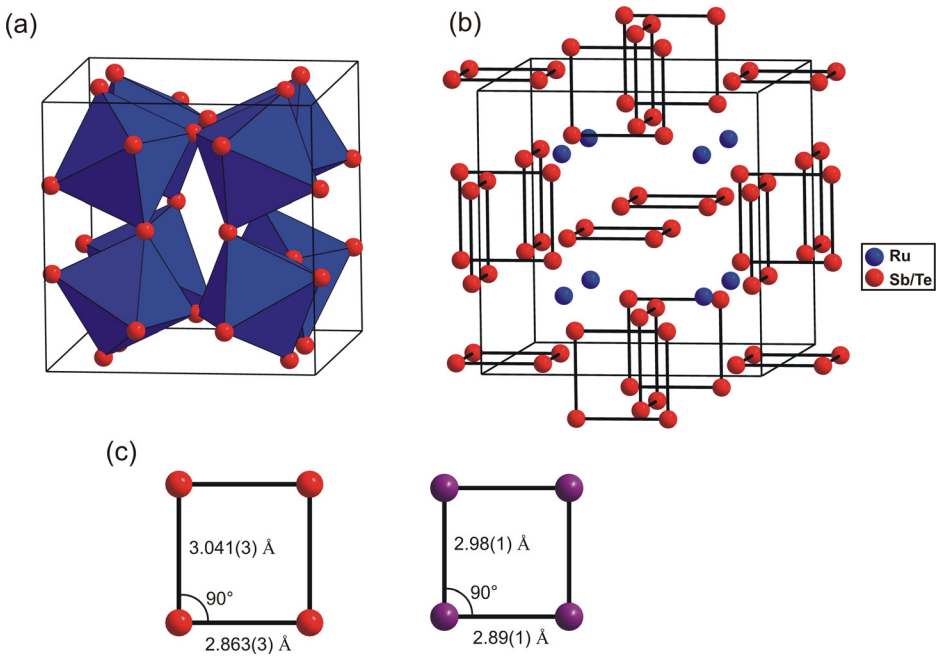

Figure 2. (Color online) (a) Polyhedral and (b) ball-and-stick representation of the $RuSb_2Te$ structure showing the corner sharing arrangement of the $[Ru(Sb/Te)_6]$ octahedra. (c) Comparison of four-member $[(Sb/Te)_4]$ and $[Sb_4]$ rings found in the $RuSb_2Te$ and $CoSb_3$ (Kjekshus and Rakke, 1974) structures, respectively.

and $\chi^2 = 0.94$ for 23 refined parameters) as for disordered structure ($Im\bar{3}$, see above), it failed to reach convergence. Moreover, the application of Platon ADDSYM Program (Spek 1988, 2003) to identify the missing symmetry elements to this structure (space group $R\bar{3}$) indicated missing symmetry elements. Therefore, the proper symmetry of the $RuSb_2Te$ structure should be $Im\bar{3}$.

To support this conclusion, powder diffraction patterns for ordered and disordered structural models of $RuSb_2Te$ were calculated. The POWDERCELL 2.4.program (Kraus and Nolze, 2000) was used for the calculations. Although the scattering factors of Sb and Te for X-rays (Cu $K\alpha$ radiation) are very similar, a comparison of these two calculated patterns has showed that weak superstructure diffractions indicating the structural ordering can be detected by conventional powder X-ray diffraction. However, neither superstructure reflections nor peak splitting was observed for $RuSb_2Te$.

The experimental conditions of diffraction-data collection are given in Table I, and Table II shows refined structural parameters for $RuSb_2Te$. The final Rietveld plot is depicted in Figure 1.

IV. RESULTS AND DISCUSSION

The powder diffraction data are listed in Table III. 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 refined zero-point shift of 0.013° 2θ.

The $RuSb_2Te$ crystallizes in the skutterudite-type structure. Its atomic architecture is shown in Figure 2. In this structure, each Ru atom is surrounded by six Sb/Te atoms showing a weakly distorted octahedral arrangement. The $[Ru(Sb/Te)_6]$ octahedra share all six corners forming a perovskite-like three dimensional framework. Table IV shows a comparison of selected bond distance and bond angles for isostructural compounds $RuSb_2Te$ and $CoSb_3$ (Kjekshus and Rakke, 1974). As can be seen from Table IV, the Ru-Sb/Te bond distance is slightly longer than the corresponding Co-Sb bond distance in $CoSb_3$. Neglecting the small difference in the covalent radii of Sb ($r_{Sb} = 1.41$ Å) and Te ($r_{Te} = 1.37$ Å) (Emsley, 1989), this can be explained by the considerably lower covalent radius of Co ($r_{Co} = 1.16$ Å) with respect to that of Ru ($r_{Ru} = 1.24$ Å) (Emsley, 1989).

As was noted by Mitchell (2002) and Vaqueiro *et al.* (2008), the skutterudite structure can be derived from the perovskite structure ABX_3 by omission of the A atom and by tilting of the BX_6 octahedra (tilt system $a^+a^+a^+$). The tilt angle (φ) can be calculated from the unit-cell parameter a and the Ru-(Sb/Te) bond distance according to a relationship given by O'Keefe and Hyde (1977)

$$\cos(\varphi) = \frac{3a}{8d} - 0.5$$

Using this expression, we have calculated the values of 33.5° and 32.4° for $RuSb_2Te$ (this work) and $CoSb_3$ (Kjekshus and Rakke, 1974), respectively. Once again

TABLE IV. Selected interatomic distances and bond angles for $RuSb_2Te$ and $CoSb_3$ (Kjekshus and Rakke, 1974).

	$RuSb_2Te$	$CoSb_3$
Distances (Å)		
M–X	6 ×2.605(2)	6 ×2.520(9)
X–X	2.863(3)	2.89(1)
	3.041(3)	2.98(1)
Angles (°)		
X–M–X	6 × 85.787(1)	6 × 85.323(4)
X–M–X	6 × 94.213(1)	6 × 94.768(4)
M–X–M	125.61(7)	127.3(3)
X–X–X	90.00	90.00

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neglecting the small difference in the covalent radii of Sb and Te (see above), these values of tilt angles are in accordance with a general trend observed in skutterudites: for a given anion the tilt angle (φ) increases with increasing size of the cation (Mitchell, 2002).

Because of the tilting of [Ru(Sb/Te)$_6$] octahedra according to $a^+a^+a^+$ tilt system, the Sb/Te atoms form the four-membered rings [(Sb/Te)$_4$] of rectangular shape. These rings are a hallmark of the skutterudite crystal structure. As is indicated in Figure 2(c), the short [2.863(3) Å] and long [3.041(3) Å] (Sb/Te)-(Sb/Te) bond distances alternate within the [(Sb/Te)$_4$] rings in the $RuSb_2Te$ crystal structure. These distances are more or less comparable with Sb-Sb distance of 2.869(1) Å and Te-Te distance of 2.863(5) Å found in the crystal structures of marcasite-type phases $RuTe_2$ (Koehler, 1997) and $RuSb_2$ (Kjekshus *et al*. 1977), respectively. In comparison to [Sb_4] rings found in the $CoSb_3$ structure (Kjekshus and Rakke, 1974), the Sb/Te rings show slightly more deviation from squared shape to rectangular (Figure 2(c)). The ratio of two Sb-Sb distances is 1.03 for $CoSb_3$ structure, whereas for $RuSb_2Te$ structure the ratio of two (Sb/Te)-(Sb/Te) distances has a value of 1.06.

The $RuSb_2Te$ phase does not show any indication of structural ordering of Sb and Te atoms. It is worth noting that the structural ordering of anions was only observed in ternary skutterudites with $MY_{1.5}X_{1.5}$ stoichiometry (M = Co, Ir, and Rh; X = Ge and Sn; Y = S, Se, and Te), i.e., with anion ratio of 1:1. The $RuSb_2Te$ phase shows a different ratio of anions, i.e., 1:2, and consequently crystallizes in a cubic disordered structure.

It should be also noted that the description of the skutterudites using ionic formula $M_4{}^{3+}[X_4]_3{}^{4-}$ is only formal. For example, in the $RuSb_2Te$ compound, the electronegativities of Ru, Sb, and Te are almost comparable (Pauling electronegativities: Ru 2.2, Te 2.1, and Sb 2.05), which indicates that the strict division of atoms into electropositive cations and electronegative anions is not valid. Hence, the covalent radii should be used in bond lengths considerations. Further details about bonding and band structure calculations on skutterudite-type compounds can be found in the work of Partik and Lutz (1999).

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