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Heat Capacity and Heat Content Measurements on Binary Compounds in the Ru–Si, Ru–Ge, and Ru–Sn Systems

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Molar heat capacities of $Ru_{0.5}Si_{0.5}$, $Ru_{0.4}Si_{0.6}$, $Ru_{0.5}Ge_{0.5}$, $Ru_{0.4}Ge_{0.6}$, $Ru_{0.4}Sn_{0.6}$, and $Ru_{0.3}Sn_{0.7}$ were determined every 10 K by differential scanning calorimetry in the temperature range from 310 to 1080 K. The present results have been fitted by a polynomial function of temperature: $C_p = a+bT-cT^{-2}$. Heat contents of the six phases have been verified by drop calorimetry. Standard enthalpies of formation are given for the studied compounds. © 1997 Academic Press

INTRODUCTION

In the course of a systematic study of binary transition–nontransition systems, we studied the Ge–Ru and Ru–Sn phase diagrams (1, 2) by differential thermal analysis, X-ray diffraction, and microprobe analysis, and we determined the enthalpies of formation of binary intermediate compounds by direct reaction calorimetry (3, 4). Ru–Si is still under investigation (5) in our laboratories and does not conform with literature results (6, 7). These systems deserve investigation because of their large implications in semiconducting materials and catalysts industry.

The aim of the present work was to determine by differential scanning calorimetry the heat capacities of $Ru_{0.5}Si_{0.5}$, $Ru_{0.4}Si_{0.6}$, $Ru_{0.5}Ge_{0.5}$, $Ru_{0.4}Ge_{0.6}$, $Ru_{0.4}Sn_{0.6}$, and $Ru_{0.3}Sn_{0.7}$ and to validate them by measuring the heat contents by drop calorimetry between room temperature and 1070 K. These measurements allowed us to calculate standard enthalpies of formation of the compounds under scrutiny using data precedently obtained (3, 4), which were referred to pure elements in their equilibrium states at the reaction temperatures. In addition, heat capacities are very sensitive to detect first- and second-order transitions.

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EXPERIMENTAL

A. Preparation of Samples and Characterization

We synthetized intermetallic phases by induction melting or direct reaction from mixed ruthenium and X powders (X being silicon, germanium, or tin) in appropriate ratios under an argon atmosphere. Table 1 gives the characteristics of the starting elements. After an annealing of 7 days at 1273 K inside silica tubes, the samples were slowly cooled to room temperature. Powder X-ray diffractions were carried out with a Philips PW1370 diffractometer and copper $K\alpha$ radiation. Compounds were checked by comparison with JCPDS references (8) or Lazy-Pulverix (9) calculations based on published crystallographical data (10–16), see Table 2. Estimated lattice parameters were in good agreement with data from literature.

B. Differential Scanning Calorimetry

Heat capacity measurements were carried out with a DSC-111 from Setaram, designed as a Calvet calorimeter, containing reference and laboratory cells surrounded by two thermal fluxmeters connected in opposite signs. The procedure of measurement has already been described (17–19). Samples weighing about 1.5 to 2.2 g were placed without crucible in the laboratory cell under an argon atmosphere. The heat capacities of binary alloys were determined every 10 K between 310 and 1080 K. The heating rate was $3\ K \cdot min^{-1}$ during 200 s, and the temperature was kept constant during 400 s. The C_p calibrations relied on compacted ruthenium powder and C_p values from the literature (20). No reactions between samples and crucibles and no appreciable weight losses were observed at the end of the calorimetric investigations.

C. Drop Calorimetry

Heat content determinations were carried out in our high temperature calorimeter. For each series of measurements,

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TABLE I
Characteristics of Components

Components	Origin	Purity	Shape	Size
Ruthenium	Metalor	99.96% min	Powder	1–25 μm
Silicon	Balzers	99.999% min	Granules[a]	1–5 mm
Germanium	Balzers	99.999% min	Granules[a]	0.7–3.5 mm
Tin	Balzers	99.9995% min	Shots	1.5–3.5 mm
Tin	Goodfellow	99.9%	Powder	< 44 μm

[a]Granules were ground to be used for powder metallurgy.

alloy samples and alumina were dropped alternatively from room temperature to 1070 K into the calorimeter crucible. Alumina allowed us to calibrate the calorimeter with help of the work of the NIST group (21).

The good agreement of these values of heat contents compared with integrated C_p validates the differential scanning calorimetry determinations of heat capacities.

RESULTS AND DISCUSSION

A. Molar Heat Capacities

Table 3 gives the values of molar heat capacities which were measured (mean of 2 measurements) for each compound.

Our molar heat capacity measurements, polynomial fits, and weighed mean values of heat capacities of pure elements are presented in Figs. 1–6. The second-order transition $\alpha \rightarrow \beta$ of $Ru_{0.4}Ge_{0.6}$, previously revealed by crystallographic investigations (12, 16) and high temperature resistivity (24–27), is confirmed at 860 K. Concerning $Ru_{0.4}Si_{0.6}$, we noticed a possible second-order solid state transition at 620 K. It can be mentioned that thermoelectric properties of this compound change in the vicinity of this temperature (28, 29). For the four other intermediate phases, we did not detect any noticeable first- or second-order transition.

TABLE 3
Experimental Molar Heat Capacities ($J \cdot mol^{-1} \cdot K^{-1}$)

T (K)	$Ru_{0.5}Si_{0.5}$	$Ru_{0.4}Si_{0.6}$	$Ru_{0.5}Ge_{0.5}$	$Ru_{0.4}Ge_{0.6}$	$Ru_{0.4}Sn_{0.6}$	$Ru_{0.3}Sn_{0.7}$
310	22.05	21.71	24.17	23.31	24.04	25.17
320	21.91	21.88	23.77	23.15	23.71	25.13
330	22.31	22.07	24.22	23.40	24.03	25.10
340	22.16	22.14	24.04	23.23	23.77	24.96
350	22.18	22.11	24.03	23.12	23.71	24.86
360	22.35	22.19	24.32	23.30	23.92	24.85
370	22.44	22.22	24.33	23.32	23.87	24.91
380	22.43	22.27	24.33	23.22	23.82	24.83
390	22.50	22.31	24.41	23.28	23.80	24.87
400	22.58	22.42	24.46	23.34	23.85	24.89
410	22.70	22.44	24.60	23.40	23.87	24.89
420	22.81	22.42	24.69	23.49	23.91	24.90
430	22.78	22.45	24.59	23.43	23.80	24.87
440	22.85	22.49	24.70	23.48	23.82	24.91
450	22.95	22.55	24.77	23.50	23.83	25.00
460	23.03	22.63	24.87	23.56	23.86	25.01
470	23.10	22.61	24.89	23.59	23.86	25.03
480	23.17	22.69	24.89	23.67	23.86	25.05
490	23.19	22.74	24.97	23.67	23.90	25.10
500	23.29	22.80	24.99	23.62	23.83	25.19
510	23.35	22.79	25.09	23.71	23.84	25.15
520	23.43	22.84	25.17	23.80	23.94	25.22
530	23.50	22.89	25.38	23.87	24.10	25.23
540	23.49	22.92	25.33	23.81	24.03	25.27
550	23.55	22.98	25.48	23.93	24.07	25.29
560	23.61	23.03	25.49	23.89	24.10	25.32
570	23.68	23.10	25.57	23.96	24.16	25.37
580	23.82	23.11	25.70	24.04	24.22	25.38
590	23.89	23.16	25.81	24.10	24.27	25.42
600	24.00	23.15	25.95	24.15	24.38	25.42
610	24.04	23.20	25.96	24.17	24.38	25.48
620	24.10	23.20	26.03	24.23	24.37	25.51
630	24.18	23.17	26.11	24.28	24.45	25.52
640	24.22	23.18	26.16	24.27	24.45	25.58
650	24.31	23.15	26.26	24.35	24.53	25.59
660	24.36	23.16	26.33	24.38	24.54	25.69
670	24.60	23.15	26.59	24.58	24.74	25.77
680	24.65	23.21	26.63	24.64	24.82	25.85
690	24.70	23.25	26.64	24.71	24.80	25.94
700	24.82	23.26	26.72	24.73	24.88	26.03
710	24.83	23.29	26.80	24.78	24.88	26.10
720	24.94	23.32	26.85	24.83	24.90	26.18
730	25.00	23.32	26.91	24.93	24.67	26.22
740	24.95	23.27	26.93	24.95	24.92	26.25
750	24.99	23.32	27.03	25.01	24.95	26.33
760	25.02	23.34	27.09	25.04	25.00	26.40
770	25.11	23.38	27.23	25.13	25.10	26.47

TABLE 2
Crystal Structures and Lattice Parameters (nm) of the Intermediate Phases

Phases	Space group	Structure	Isotype	*a*	*b*	*c*	Refs.
RuSi	*Pm3m*	Cubic	CsCl	0.470061			(10)
RuSi	*P*213	Cubic	FeSi	0.291250			(10)
Ru_2Si_3	*Pbcn*	Orthorhombic	Ru_2Ge_3	1.1057	0.8934	0.5533	(11–13)
RuGe	*P*213	Cubic	FeSi	0.48449			(14)
Ru_2Ge_3	*Pbcn*	Orthorhombic	Ru_2Ge_3	1.1436	0.928	0.5716	(11, 12, 15)
$Ru_2Ge_3\beta$	*P*-4*c*2	Tetragonal	Ru_2Sn_3	0.573911		0.995217	(12)
Ru_2Sn_3	*P*-4*c*2	*Tetragonal*	Ru_2Sn_3	0.6178		0.9916	(12)
Ru_3Sn_7	*Im3m*	Cubic	Ru_3Sn_7	0.9351			(16)

TABLE 3—*Continued*

T (K)	$Ru_{0.5}Si_{0.5}$	$Ru_{0.4}Si_{0.6}$	$Ru_{0.5}Ge_{0.5}$	$Ru_{0.4}Ge_{0.6}$	$Ru_{0.4}Sn_{0.6}$	$Ru_{0.3}Sn_{0.7}$
780	25.14	23.43	27.29	25.18	25.16	26.52
790	25.17	23.49	27.36	25.23	25.20	26.60
800	25.18	23.58	27.47	25.31	25.26	26.61
810	25.26	23.65	27.54	25.45	25.27	26.69
820	25.32	23.67	27.66	25.53	25.37	26.75
830	25.37	23.76	27.72	25.67	25.42	26.78
840	25.44	23.76	27.84	25.89	25.44	26.82
850	25.42	23.88	27.86	25.95	25.47	26.90
860	25.51	23.98	27.99	24.76	25.50	27.06
870	25.56	24.04	28.05	24.66	25.57	27.12
880	25.59	24.16	28.05	24.61	25.61	27.17
890	25.54	24.22	28.13	24.60	25.64	27.20
900	25.76	24.27	28.34	24.80	25.79	27.31
910	25.72	24.40	28.40	24.77	25.86	27.39
920	25.80	24.46	28.51	24.74	25.92	27.46
930	25.89	24.62	28.61	24.87	26.02	27.62
940	25.96	24.72	28.78	24.99	26.11	27.69
950	25.90	24.81	28.71	24.94	26.03	27.69
960	26.02	24.84	28.82	25.02	26.16	27.88
970	25.97	25.01	28.75	24.98	26.07	27.91
980	25.99	25.07	28.95	25.04	26.21	28.03
990	26.27	25.14	29.28	25.34	26.53	28.18
1000	26.30	25.23	29.38	25.34	26.60	28.20
1010	26.16	25.28	29.19	25.26	26.40	28.29
1020	26.19	25.44	29.40	25.28	26.48	28.34
1030	26.26	25.50	29.43	25.37	26.51	28.43
1040	26.36	25.58	29.45	25.41	26.61	28.43
1050	26.23	25.65	29.46	25.47	26.50	28.57
1060	26.30	25.74	29.45	25.55	26.53	28.65
1070	26.35	25.92	29.53	25.58	26.55	28.89
1080	26.40	25.85	29.54	25.67	26.60	28.88

Note. The values of the molar heat capacities were fitted according to the general form: $C_p = a + bT - cT^{-2}$ (22, 23). Table 4 gives the polynomial coefficients for the six phases.

B. Enthalpy Increments

Integration of the C_p functions between room temperature (298.15 K) and T gives the following formulae

$$H(T) - H(298.15\,\mathrm{K}) = a(T - 298.15) + b/2 \times 10^{-3}(T^2 - 298.15^2) + c \times 10^6(1/T - 1/298.15).$$

TABLE 4
Polynomial Coefficients of $C_p = a + bT - cT^{-2}$ ($J \cdot mol^{-1} \cdot K^{-1}$)

Phases	Temperature range (K)	a ($J \cdot mol^{-1} \cdot K^{-1}$)	b ($J \cdot mol^{-1} \cdot K^{-2}$)	c ($J \cdot mol^{-1} \cdot K$)
$Ru_{0.5}Si_{0.5}$	310–1080	21.1	$5.18 \times 10^{-}$	0.1×10^6
$Ru_{0.4}Si_{0.6}$	310–620	21.5	3.01×10^{-3}	0.1×10^6
	620–1080	9.7	13.49×10^{-3}	-2.0×10^6
$Ru_{0.5}Ge_{0.5}$	310–1080	20.4	6.63×10^{-3}	-0.1×10^6
$Ru_{0.4}Ge_{0.6}$	310–860	19.1	7.44×10^{-3}	-0.2×10^6
	860–1080	17.8	6.59×10^{-3}	-0.8×10^6
$Ru_{0.4}Sn_{0.6}$	310–1080	20.3	5.85×10^{-3}	-0.2×10^6
$Ru_{0.3}Sn_{0.7}$	310–1080	19.4	8.37×10^{-3}	-0.4×10^6

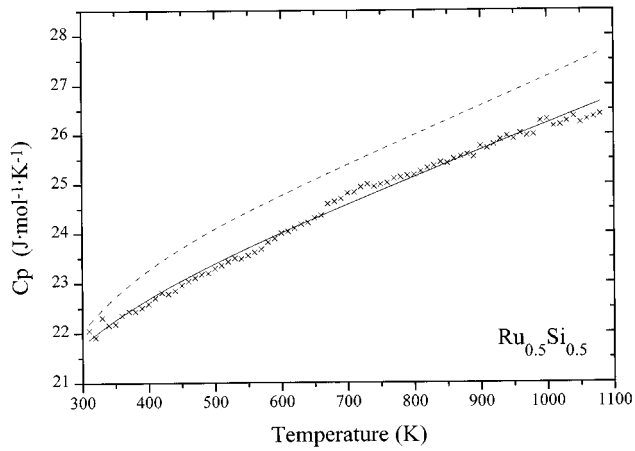

FIG. 1. Molar heat capacities of $Ru_{0.5}Si_{0.5}$ vs temperature; ×, experimental points; —, polynomial fit; - - -, $0.5C_p(Ru) + 0.5C_p(Si)$ according to (20).

Table 5 gives the enthalpy increments of the six phases versus temperature.

C. Determination of Standard Enthalpies of Formation of the Compounds

In previous works (3, 4), we presented our calorimetric results about enthalpies of formation of RuX (X = Si, Ge, and Sn) compounds at high temperature. Enthalpies of formation have been obtained by direct reaction calorimetry and were refered to the pure elemental components in their equilibrium states at the reaction temperature. The present C_p measurements allow us to determine the enthalpy increments of the compounds between room temperature and calorimeter temperature and then to compute the

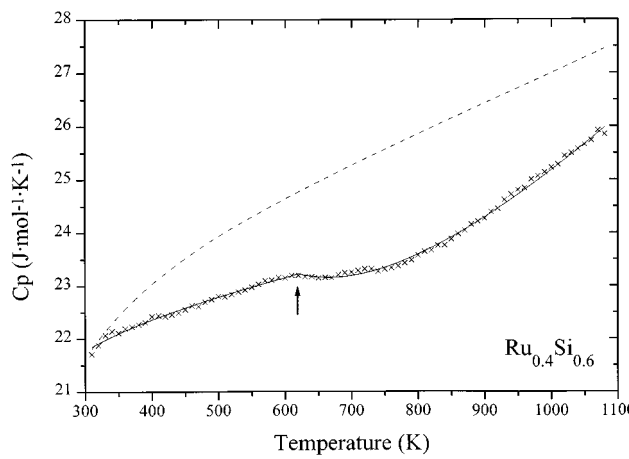

FIG. 2. Molar heat capacities of $Ru_{0.4}Si_{0.6}$ vs temperature; ×, experimental points; —, polynomial fit; - - -, $0.4C_p(Ru) + 0.6C_p(Si)$ according to (20); ↑, possible solid state transformation (28, 29).

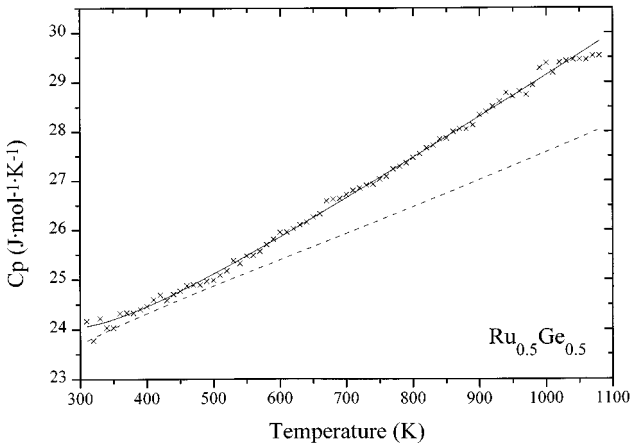

FIG. 3. Molar heat capacities of $Ru_{0.5}Ge_{0.5}$ vs temperature; ×, experimental points; —, polynomial fit; - - -, $0.5C_p(Ru) + 0.5C_p(Ge)$ according to (20).

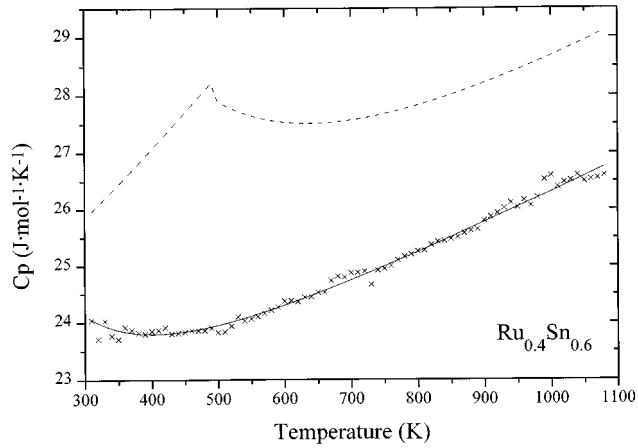

FIG. 5. Molar heat capacities of $Ru_{0.4}Sn_{0.6}$ vs temperature;, ×, experimental points; —, polynomial fit; —, $0.4C_p(Ru) + 0.6C_p(Sn)$ according to (20).

standard $\Delta_f H$, starting from the following equations with $T_0 = 298.15$ K and T = calorimeter temperature,

$$(1-x)\mathrm{Ru}(T_0) + (x)X(T_0) \Rightarrow (1-x)\mathrm{Ru}(T) + (x)X(T), \quad [1]$$

increments of enthalpy of Ru and X between T and T_0, tabulated in (20);

$$(1-x)\mathrm{Ru}(T_0) + (x)X(T_0) \Rightarrow \mathrm{Ru}_{(1-x)}X_{(x)}(T_0), \quad [2]$$

enthalpy of formation of $Ru_{(1-x)}X_{(x)}$ at T_0, standard enthalpy of formation;

$$\mathrm{Ru}_{(1-x)}X_{(x)}(T_0) \Rightarrow \mathrm{Ru}_{(1-x)}X_{(x)}(T), \quad [3]$$

increments of enthalpy of $Ru_{(1-x)}X_{(x)}$ between T and T_0, expressed in Table 5;

$$(1-x)\mathrm{Ru}(T) + (x)X(T) \Rightarrow \mathrm{Ru}_{(1-x)}X_{(x)}(T), \quad [4]$$

enthalpy of formation of $Ru_{(1-x)}X_{(x)}$ at T, measured in (3, 4);

we obtain Eq. [2] = Eq. [4] + Eq. [1] − Eq. [3].

CONCLUSION

In this paper, we give first results concerning the molar heat capacities of the $\langle RuX \rangle$ (X = Si, Ge, and Sn) intermediate phases. Direct comparison with other experimental

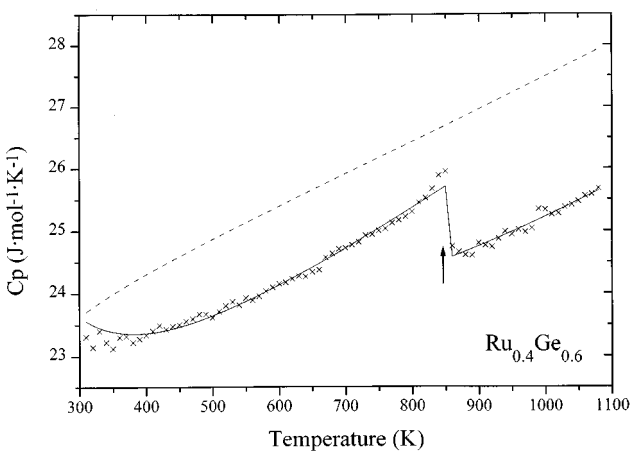

FIG. 4. Molar heat capacities of $Ru_{0.4}Ge_{0.6}$ vs temperature; ×, experimental points; —, polynomial fit; - - -, $0.4C_p(Ru) + 0.6C_p(Ge)$ according to (20); ↑, second-order transition according to (12, 15, 24–27).

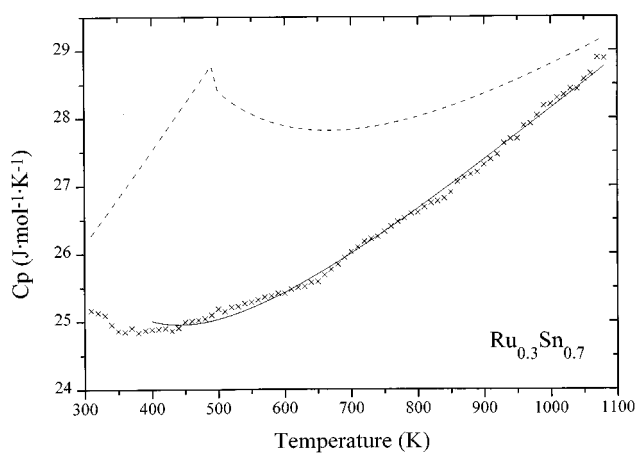

FIG. 6. Molar heat capacities of $Ru_{0.3}Sn_{0.7}$ vs temperature; ×, experimental points; —, polynomial fit; - - -, $0.3C_p(Ru) + 0.75C_p(Sn)$ according to (20).

TABLE 5
Enthalpy Increments Versus *T*

Phases	Temperature range (K)	$H(T) - H(298.15)$ (J·mol^{-1})
$Ru_{0.5}Si_{0.5}$	310–1080	$21.1T + (2.59\times10^{-3})T^2 + (0.1\times10^6)T^{-1} - 6809$
$Ru_{0.4}Si_{0.6}$	310–620	$21.5T + (1.50\times10^{-3})T^2 + (0.1\times10^6)T^{-1} - 6739$
	620–1080	$9.7T + (6.75\times10^{-3})T^2 - 2.0\times10^6)T^{-1} + 1860$
$Ru_{0.5}Ge_{0.5}$	310–1080	$20.4T + (4.31\times10^{-3})T^2 - 0.1\times10^6)T^{-1} - 6164$
$Ru_{0.4}Ge_{0.6}$	310–860	$19.1T + (3.72\times10^{-3})T^2 - 0.2\times10^6)T^{-1} - 5329$
	860–1080	$17.8T + (3.29\times10^{-3})T^2 - 0.8\times10^6)T^{-1} - 3223$
$Ru_{0.4}Sn_{0.6}$	310–1080	$20.3T + (2.93\times10^{-3})T^2 - 0.2\times10^6)T^{-1} - 5665$
$Ru_{0.3}Sn_{0.7}$	310–1080	$19.4T + (4.18\times10^{-3})T^2 - 0.4\times10^6)T^{-1} - 4950$

TABLE 6
Comparison between Heat Contents Calculated from C_p Integrations and Measured by Drop Calorimetry

Phases	Temperature range (no. of measurements)	Sample weights (mg)	Heat contents (J·mol^{-1})	
			Masd. (SD)	Calcd.
$Ru_{0.5}Si_{0.5}$	293–1072 K (5)	35–120	19,400 (1100)	19,000
$Ru_{0.4}Si_{0.6}$	292–1072 K (5)	70–130	18,800 (350)	18,300
$Ru_{0.5}Ge_{0.5}$	292–1072 K (5)	40–90	19,710 (610)	20,800
$Ru_{0.4}Ge_{0.6}$	292–1073 K (5)	45–85	20,200 (1520)	19,100
$Ru_{0.4}Sn_{0.6}$	291–1071 K (4)	35–100	19,500 (1230)	19,400
$Ru_{0.3}Sn_{0.7}$	291–1072 K (4)	50–100	20,600 (680)	20,500

TABLE 7
Enthalpies of Formation Expressed in J·mol^{-1}

Phases	T (K) measd. (from (3, 4))	$\Delta_f H^a$ at T (K) (SD) from (3, 4)	Enthalpy increments of $(1-x)$Ru + $(x)X$ (from (20))	Enthalpy increments of $Ru_{(1-x)}X_{(x)}$ (present study)	$\Delta_f H^\circ$ (298.15 K) (our results)	$\Delta_f H^\circ$ (298.15 K) (SD) (from (30, 31))
		Eq. [4]	Eq. [1]	Eq. [3]	Eq. [2]	
$Ru_{0.5}Si_{0.5}$	1515	−57,700 (±1400)	32,400	31200	−56,500	−58,100 (±3600)
$Ru_{0.4}Si_{0.6}$	1704	−80,400 (±1000)	68,000	36,800	−49200	–
$Ru_{0.5}Ge_{0.5}$	1173	−28,700 (±1000)	22,900	23,700	−29500	−28,400 (±700)
$Ru_{0.4}Ge_{0.6}$	1173	−34,800 (±1300)	22,800	21,500	−33500	–
$Ru_{0.4}Sn_{0.6}$	1173	−28,100 (±1600)	28,500	22,000	−21600	–
$Ru_{0.3}Sn_{0.7}$	1173	−29,800 (±800)	29,400	23,300	−23700	–

Note. Our estimations of standard enthalpies of formation for the equiatomic compounds of Si and Ge are in good agreement with literature data (30, 31).

[a]Calculated with reference to pure components in their equilibrium states at the reaction temperatures.

data was impossible because literature data are missing. Standard enthalpies of formation have been calculated from previous calorimetric measurements with the heat capacities determined during this present study.

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