ADVANCED THERMOELECTRIC MATERIALS 1986 IRD REPORT

TRANSITION METAL SILICIDES

TECHNICAL FINAL REPORT

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I. INTRODUCTION

Thermoelectric energy conversion has proven a reliable source of power under the demanding conditions of space. Radioisotope and nuclear reactor heat sources have been combined with devices constructed from various thermoelectric materials including chromel-alumel, bismuth telluride, lead telluride and silicon germanium. Such devices have provided many years of uninterrupted power. A thermoelectric system consists of heat source, heat rejection and conversion components each of which presents challenges and can limit device performance. The heat source and rejection systems define the ultimate limits on system weights and power. The efficiency of the converter, which represents a relatively small investment in weight in itself, determines overall system performance because regardless of the total thermal flux made available by the heat source and rejection systems, it is the converter which actually produces the electrical power.

The converter in turn is largely defined by the choice of thermoelectric materials. Many device geometries with various advantages and disadvantages are possible and have been employed, but the the thermoelectric material imposes an upper limit to device performance. State-of-the-art silicon germanium alloys, for example, impose an upper limit on conversion efficiency of about 8.6% on a device operating between 600 K and 1300 K (or about 5.6% on a device operating between 800 K and 1300 K). Actual efficiencies achieved are not much lower than this, indicating how effective current designs are at utilizing existing materials. Theoretical (Carnot) efficiency is 54% (38% for Tc=800 K) for such a device. Solid state theory provides no intrinsic reason for the low efficiency of thermoelectric materials. The margin for growth over current materials of about a factor of 6 in conversion efficiency justifies the search for improved materials.

This program seeks to identify candidate thermoelectric materials with the potential for significantly better performance compared to current silicon-germanium alloys. The following properties, in approximate order of priority, are desired:

- 1) chemical, thermal and structural stability to at least 1300 K;
- 2) low lattice thermal conductivity;
- 3) high charge carrier mobility;
- 4) dopable to both n- and p-type;
- 5) dopable to the extrinsic regime at the highest operating temperatures;
- 6) capable of good electrical and thermal connections;
- 7) fabrication by conventional methods.

The ideal material would meet all of these requirements. A promising material may fail to meet some of these requirements, but compensate by being extremely attractive in some other respects. In some cases, certain applications may place different emphasis on various requirements.

Applications with only limited life requirements may relax the stability requirement. Some applications might be sufficiently performance sensitive that non-conventional preparation methods may be considered since this is largely a cost consideration, both in terms of production of practical materials and in terms of the development time and costs.

The current program seeks materials consistent with space power applications such as the General Purpose Heat Source (GPHS) radioisotope generators and the SP-100 nuclear reactor programs. A successful materials program might well be expected to provide motivation for entirely new space power efforts based on the new materials. The SP-100 program, for example, might have been built of advanced thermoelectric materials (rather than the silicon-germanium based materials currently planned for this program) had sufficient materials development progress been achieved.

Transition metal silicides have been investigated in 1986 as potentially high figure of merit thermoelectric materials. Many silicon-rich silicides of column VII and VIII transition metals have been reported in the literature to be semiconductors. Silicides of the 3-d transition metals manganese, iron and cobalt have all been investigated to some extent. Although not without some attractive features, these materials are generally insufficiently refractory for use at 1300 K. Silicides of the 4-d and 5-d transition metal elements ruthenium, rhodium, rhenium, osmium and iridium have higher melting points and in some cases have been reported to be semiconductors, however relatively little data are available. OsSi2 in particular has been reported to have a band gap of 1.8 eV, much larger than the band gap of silicon of about 1.1 eV, and therefore should be relatively immune to the onset of intrinsic conduction at high temperatures which can limit the usefulness of an otherwise attractive material.

The crystal structure of OsSi2 is reported to be the same as ss-FeSi2, known to be a fairly attractive thermoelectric. The heavier osmium compound is expected to have a lower thermal conductivity and similar electronic properties and therefore may be a better thermoelectric and also useful at higher temperatures, due to it's higher melting point. Interestingly, RuSi2 has not been reported although it must exist if the osmium and iron compounds both exist. Similar arguments can be made for other transition The bonding in many of these crystal structures leads to a metal silicides. tetrahedral environment around the silicon atoms suggesting an electronic structure similar to that in silicon may occur. The heavier transition elements and more complex crystal structures suggest these materials might have lower thermal conductivities than silicon. These general properties coupled with the greater chemical flexibility to tailor material properties afforded by the binary compounds, compared with alloys of elements alone

such as Si-Ge alloys, is very promising for materials development activities.

II EXPERIMENTAL DETAILS

Eleven samples were prepared by direct reaction from the elements. Stoichiometric amounts of -325 mesh powders were mixed until uniform, as indicated by visual inspection. Approximately five grams of powder were loaded into a split graphite mold, 0.5" in diameter. The graphite mold and pistons were treated with boron nitride to act as a mold release. The powders were heated in vacuum to a temperature about 100 K less than the anticipated melting temperature of the compound. 10 kpsi was applied for 30 minutes, the pressure released and the compact ejected from the die. Furnace power was then removed and the sample allowed to cool. X-ray diffraction measurement were performed on eight samples and compared to literature x-ray diffraction patterns.

This sample preparation procedure has the advantage of being quick and simple and has produced some excellent samples. As a semiconductor preparation technique, however, the approach is quite crude. Contamination from container walls, incomplete reaction and loss of charge material can result in alteration of stoichiometry perhaps with disastrous effects on transport properties, particularly the Seebeck coefficient and the electrical resistivity. As a survey technique this approach has proven satisfactory, however improvements are recommended for the following phase of effort.

Hall effect measurements were attempted on all samples prepared using a Van de Pauws technique developed for use on SiGe alloys. In most cases high, non-ohmic contact resistances interfered with accurate determinations. While this type of measurement complication is not uncommon and often fairly

readily solved, sample quality was not generally good enough to justify special efforts to obtain accurate mobility measurements.

Thermal diffusivity performed from 200 C to 1000 C on seven samples using a Theta Industries laser flash diffusivity apparatus. Thermal conductivity was calculated using the measured thermal diffusivity and density and heat capacity calculated using the Debye theory. The heat capacity two samples, one of which was SiGe, was measured using a Perkin Elmer differential scanning calorimeter (DSC) and found to agree with the calculated Debye heat capacity to within 10%. The heat capacity is a bulk, thermodynamic quantity and the Debye value is usually fairly reliable at high temperatures. The use of calculated values of heat capacity in the determination of the thermal conductivity probably does not introduce more than about a 20% error in the thermal conductivity, which is sufficient for surveys of this kind. Relative values of the thermal conductivities are probably more reliable than this. Differential thermal analysis was also performed on one sample.

The high temperature electrical resistivity was determined on two samples using a special fixture designed to handle small samples. The fixture suspends a 0.5" diameter samples between four thermocouples equally spaced around the perimeter of the sample. Using one neighboring pair of leads as current probes and the second pair as voltage probes, the electrical resistivity may be determined. The thermocouples are held in place by tungsten springs in a sapphire fixture. Originally intended to allow the determination of the Seebeck coefficient in addition to the electrical resistivity, test runs on SiGe indicated large errors in the Seebeck determination. Analysis of the data obtained in these test runs indicate the main source of error was a temperature drop across the joint of the thermocouples. Estimates indicate this error might have been reduced to

the 10%-15% range in some cases, but probably not better than this. The essential problem is that the heat flux which supplies the temperature gradient must, in this geometry, flow through the thermocouples. A better geometry would hold the sample in such a way that very little heat flows through the thermocouple itself, which requires some auxiliary support system. This feature will be incorporated in the next version of the Seebeck measuring experiment.

III RESULTS

Table 1 summarizes the samples prepared in 1986. Some of the physical properties of these samples are summarized in Table 2. Since no attempt was made to dope samples, a wide range of Seebeck coefficient values were typically observed within a given sample, depending on the point at which the probe contacted the sample. The range of observed Seebeck values are given in Table 2. We will first discuss those samples which contain neither Ru nor Os. The phase diagrams of the Ir-Si and Rh-Si systems have not been reported, but a variety of crystal structure types have been reported. Three silicon rich Ir-Si compounds, Ir3Si5, IrSi2 and IrSi3, and two silico rich Rh-Si compounds, Rh2Si3, RhSi2 have been reported. At least some of these can be expected to be fairly large band gap semiconductors.

Two samples prepared in this study, 59 with nominal composition Ir3Si5 and 60 with nominal composition Rh3Si5, resulted in very complex x-ray diffraction patterns representing more than one phase. In both cases considerable loss pressure was observed during the hot pressing and large amounts of material extruded through the dies. This behavior suggests the presence of a relatively low melting point phase in each case. These systems will require an approximate determination of the phase diagrams, at least in the silicon-rich region, before significant progress can be made.

The Ir-Si sample exhibited p-type Seebeck values, some of which were as large as 287 uV/K, indicative of the semiconducting nature of at least some of the sample. The Seebeck values for the Rh-Si sample were uniformly small and negative and the resistivity was quite small, indicating the metallic nature of this sample. While more extensive study is certainly recommended, no further work on the Ir-Si or Rh-Si systems was pursued in this study.

CrSi2 and ReSi2 have been reported in the literature as semiconductors and one sample of CrSi2, 50, and two samples of ReSi2, 61 and 63, were prepared. Large Seebeck coefficient and carrier mobility values were observed (see Table 2), which indicates reasonable electrical properties may be possible in these materials. The thermal conductivity, calculated using the measured thermal diffusivity and density with a heat capacity value calculated from the Debye model (see Table 2), is shown for CrSi2 and ReSi2 in Figure 1. The thermal conductivity of these two samples is significantly higher than SiGe, also shown in Figure 1. Literature values reported for the same compounds suggest thermal conductivity values comparable to SiGe are possible, so these compounds are also probably worth further investigation.

While the Cr, Re, Ir and Rh silicides are all semiconductors with the potential for significantly improved figure of merit values, the Os-Si and Rh-Si systems appear more promising at this time. Three Ru-Si samples, 55 Ru2Si3, 56 RuSi2 and 64 RuSi1.8Ge0.2 and two Os-Si samples, 58 Os2Si OsSi2, were prepared in this study. X-ray diffraction indicated all of these samples were predominantly of the Ru2Si3-type crystal structure, which appears to be fairly stable. While OsSi2 exists, none of these samples were of predominantly this phase, although sample 58 may have traces of this compound in it as indicated by the x-ray diffraction pattern. The thermal conductivity values of these samples (see Figures 1 and 2) are lower than

SiGe at high temperatures.

The RuSi2 sample exhibits a remarkably low thermal conductivity, as low as 0.012 W/cm-K, more than a factor of 3 below that of SiGe. The reason for the especially low thermal conductivity in this particular sample is not clear at this time and should be studied more closely. Since doping and alloying are expected to lower the thermal conductivity even further, these materials appear quite attractive from the point of view of thermal conductivity, compared to SiGe. Figure 3 shows the electrical resistivity of Ru2Si3 and Os2Si3 as prepared and measured in this study. comparison, a sample of undoped SiGe is also shown in this figure. temperature slope indicates the band gap of the sample and these are also shown in Figure 3. While Ru2Si3 and Os2Si3 have somewhat smaller band gaps (0.71 eV and 0.88 eV, respectively) than SiGe (1.19 eV), they are still large enough to be useful at high temperatures. Although room temperature mobility values were not determined due to inadequacy of the existing apparatus, the similarity of the resistivity data in the intrinsic regime indicates similar carrier mobilities to SiGe. Large positive and negative Seebeck coefficient values were also observed at room temperature suggesting the electron and hole mobilities are similar.

III. CONCLUSIONS AND FUTURE PLANS

This program has shown that the ruthenium and osmium silicides are low thermal conductivity, band-type semiconductors similar to SiGe, with band gaps sufficiently large to limit excessive intrinsic behavior at the highest temperatures. Alloying with germanium and doping with boron and phosphorus, can be expected to result in high figure of merit materials, just as similar techniques applied to pure silicon resulted in the SiGe alloys in use today. The us

III. CONCLUSIONS AND FUTURE PLANS

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The current investigation must be supplemented by doping and alloying experiments. More importantly, development of high temperature Seebeck measurement techniques suitable to small samples must be completed before any reliable performance evaluations can be made. Future plans consist of

the following activities:

- 1) complete development of high temperature Seebeck measurement capability suitable to small sample sizes;
- 2) investigate sample preparation techniques including arc-melting, zone-melting and annealing to improve sample homogeneity;
- 3) investigate the use of boron and phosphorous as doping agents to control the carrier concentration and optimize the electrical properties; and
- 4) investigate alloys of the compounds Ru2Si3, Os2Si3 and the germanium analogs to control the thermal conductivity and optimize the figure of merit.

FIGURE CAPTIONS

FIGURE 1: Thermal conductivity of several transition metal silicides prepared in this study. SiGe is shown for comparison.

FIGURE 2: Thermal conductivity of Ru2Si3-type samples as a function of temperature. SiGe is shown for comparison.

FIGURE 3: Electrical Resistivity as a function of inverse temperature for undoped samples of Ru2Si3, Os2Si3, and SiGe.

Table 2: Physical properties of some silicon base compounds.
Calculated values are based on the crystal structure identified in the
X-ray diffraction work summarized in Table 1.

Sample Number	Nominal Composition	per	# Formula Units per Unit Cell	Weight	Density Ideal	Density Measured	•	k Coe High	Conc.		Blectric yResistiv		Debye	Cp Debye	Measur	Minimum Thermal Conductivity
				grans	g/cc	g/cc	uV/K	uV/K	10B20/c	ccm2/V-s	mohm-em	A3	J/K-cm3	J/K-g	J/K-g	W/cm-K
	Si	1	8	28.09	2.30	2.33			·····			161.90	2.05	0.888	0.976	
	Si0.8Ge0.2	1	8	36.99	3.00	3.00						163.86		0.674		0.041
	Cr8i2	3	4	108.17	5.75	5.07	102		6.65	12.7	0.740 *	124.95	3.98	0.691		0.087
	Ru2Si3	5	2	287.66	6.99	7.61	-256	201				136.70		0.433	*****	
	RuSi2	5	2	287.66	6.99	6.84	-30	54			11.62 *	136.70	2 / -7-	0.433		0.012
	Ru2Si3					7.06	-158	164					3.03			0.027
	0s28i3	5	2	464.66	11.08	10.80	20	232			10240	139.32		0.268		0.031
59	Ir38i5				in the least of the second	10.45	3.4	287					70.7	******		
60	Rh3815				\$ 1 Per 1	7.81	-3.7	-0.7			0.202					*1
61	ReSi2	3	2	242.37	10.71	9.39			0.105	54.03	11.03 *	75.13	3.31	0.309		
62	0s8i2	5	2	464.66	11.08	8.52	200	289				139.32	100	0.268		
63	ReSi2	3	2	242.37	10.71	6.68	112	176				75.13	3.31	7		0.128
64	RuSil.8Ge0.2	5	2	287.66	7.01						18320	136.33		0.433		0.025

^{* -} Literature Values

Table 1: Transition metal silicides prepared by reaction sintering.

Sample Number	Nominal Composition	XRD Major Phase	Comments
50	CrSi2	CrSi2	Incongruent melting indicated in DTA
55	Ru2Si3	Ru2Si3	Trace of second phase indicated by metallograph
56	RuSi2	Ru28i3	No second phase detected
57	Ru28i3		· · · · · · · · · · · · · · · · · · ·
58	0s28i3	0s2Si3	No second phase detected
59	Ir38i5	Multiphase	Significant material loss during pressing
60	Rh3Si5		Most material lost during pressing
61	ReSi2	ReSi2	Si (trace)
62	08812	0s2Si3	a
63	ReSi2		
	RuSil.8Ge0.2	Ru2Si3	No second phase detected

a - A trace of second phase detected. Possibly OsSi2, but not 8i

Table XXX: CANDIDATE TRANSITION METAL SILICIDES FOR THERMOBLECTRIC APPLICATIONS EXTREME VALUES OF THERMOBLECTRIC PROPERTIES SUMMARIZED FROM LITERATURE REFERENCES

C			mpound Name	Diagram Source	Nearest Ge Compound Known	Stabi Range	lity (1)	Thermal Conductivity	Resistivit	Seebeck	Gap		
<i>t</i>	>	1	CrSi2	2,2	Cr11Ge19	1 475	v	101	0 001	80010			
	,					1475		424	0.334		1.31	20.0	•
1			ReSi	2,2	ReGe	1880			0.3515	351		18.7	15
ţ	>				Re3Ge7	1980	C	555	25	1741	0.121	435.0	15
1		4	FeSi	2,2	FeGe	1410	C	981	0.261	91	0.051		
		5	a-FeSi2	1,2	PeGe2	1220	C	1221	0.451	251	0.81		6, 15, 16
		6	b-FeSi2	1,2	FeGe2	986		3619	6671	20016	****		19
	>		Ru2Si3		-	1800			0011	20010	1.025		18
			0s2Si3	•	0sGe2						1.000		
1				•	OsGe2	1730			1020	38020	1.820		18,24
				-,23	-	1.00			1000	90050	1.040		
			RhSi2		_								
				•									
				•	Ir3Ge7						1.025		
				-	Ir3Ge7			4617	0.6817	4517			24
	>				Ir3Ge7	>1500	M						
		15	a-LaSi2	-,2	-	1600	PI		0.231	-51	0.191	0.6	
		16	b-LaSi2	-,2	-	1520	M		Semi?1				
		17	USi3		-					2917			

C=Congruent melting
Pr=Peritectic-reaction melting
M=Melting (no indication of type)
PD=Peritectoid decomposition
PI=Polymorphic inversion

References

- 1. G.V. Samsonov and I.M. Vinitskii, "Handbook of Refractory Compounds," Plenum, NY (1980).
- 2. W.G. Moffatt, "The Handbook of Binary Phase Diagrams," Genium Publishing, Schenectady, NY (1984).
- 3. S.P. Murarka, J. Vac. Sci. Tech., 17(4), 775 (1980).
- 4. B.N. Nikitin, Sov. Phys.-Solid State 2(11), 2389 (1961).
- 5. V.S. Neshpor and G.V. Samsonov, Izvestiya Akademii Nauk SSSr, Neorganicheskie Materialy, 1(5), 655 (1965).
- 6. R.N. Nikitin, Sov. Phys.-Tech. Phys 3, 23 (1958).
- 12. S.E. Mayer and A.I. Mlavsky, "Properties of Blemental and Compound Semiconductors," ed. by H.C. Gatos, (1960).
- 14. In Crylic, Cr-Si System
- 15. V.S. Neshpor and V.L. Yupko, In Russian 2(14), 55 (1957)
- 16. In Crylic, p.141 (1957)
- 17. C.F. Krolick, "Thermoelecticty: Report on the State-of-the-Art," MBL Research and Development Report 205/64, U.S. Navy Marin
- 18. I. Engstrom, Acta Chemica Scandinavia 24, 2117 (1970).
- 19. J. Hesse, Z. Metallkde, 60, 652 (1969)
- 20. K. Mason and G. Muller-Vogt, J. Crystal Growth 63, 34 (1983).
- 21. N.G. Ageev, "Phase Diagrams of Metallic Systems," Viniti Press, Institute for Scientific Information (1959-1979).
- 23. R.P. Blliot, "Constitution of Binary Alloys, First Supplement," McGraw Hill (1965)
- 24. J.H. Buddery and A.J.R. Welch, Nature, 67, 362 (1951).
- 25. F.M. d'Heurle, R.D. Frampton and B.A. Irene, Hao Jiang and C.S. Petersson, Appl. Phys. Lett. 47(11), 1170 (1985).

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Ν'n	.Compound	Dhago	Magnost	^Φ o#n		Laua	•		Crystal	Lowe	atlauna	e Wial	ont a	nd Con		Estina		n Unll		U o D o	flicture M D
NO		Diagram	Ge	Stabi]	lity	Bute	cic		Structure	eTher	mallect	rical	eebe	ckap	Concentr	aMobil	itof	Reference	Con	stant	
		Source (Si,Ge)	Compound	Kange (C)	(1)			s / n \	Ref1,4,1						(estima 020/ccm2		Merit nn/w	104	om 3	10	Conversion (C)
		(nrige)		(0)		(0)	1	ajvj		IE#/C	醒一口八口下。	CKRTC	. U V / L	.C ¥ 1	O E O I C CHE A	1 4-91A	VV/ A	104	CHA	70	(0)
		2,2	Mg2Ge			945.	53	Si2	CaF2		Semi1						6	Activate	d1	C	
2	Ca2Si	1,2	Ca2Ge	910					PbC12				1.91							Pr	
3	Ca2Si	1,2	Ca2Ge	910	Pr				Cubic										Y	1 Pr	
4	CaSi	1,2	CaGe	1245	C				TlI											C	
5	CaSi2	1,2	CaGe2	1020	$\mathbf{p_r}$				CaSi2(I)											Pr	
6	CaSi2	1,2	CaGe2	1020					CaSi2(II)										Pr	
7	8r28i	1,2	Sr2Ge	1010	M															M	
		1,2	SrGe	1140	C				TlI											C	
9	Sr28i3	?							a-ThSi2												
10	SrSi2	1,2	SrGe2	1150	C				SrSi2											C	
11	BaSi	1,2	BaGe	840	$\mathbf{p_r}$				TlI											$_{\tt Pr}$	
		1,2	BaGe2	1180					AlB2	15.5	1251	6001	0.48	1		0.931				C	
		1,2	BaGe2	1180	C				BaSi2											C	
		2,2	CrGe								0.121				1 -0.4			-0.461		Pr	1550
		2,2	Cr11Ge19								0.334		1.31	9.31	20.0	2.857	6,14	66.51		M	1550
	a-MoSi2					1414	98	Si2	CrSi2	4851	0.0225	-31		49.21	60.0	0.001		12.71		PI	1980
	b-MoSi2	2,21		2030					MoSi2											M	
		1,2	W2Ge3	2160	C	1440	99	Si3	CrSi2		0.0135	0.21		0.741	6700.0			8411		C	2165
		•	W2Ge3						MoSi2												
		2,22							PeSi		0.251	1021					6,13,15			C	
	Mn118i19			1152					Mn118i19							0.000			Y	2 C	
	Mn4Si7								Mn4Si7	2510		1047				0.238					
		?,22				1142					1.836						6,13,15				
		2,2							FeSi		0.3515			9.51	18.7		15	65.41		Pr	
		•	Re3Ge7			1380	90	Si2		555					435.0			87001		C	1980
		•	PeGe	1410	C				FeSi		0.261	91	0.05	1-1561	-1.5	0.003	6,15	-41	Y	2 C	
	Fe8i1.15			4000					Lebeauite												
	a-FeSi2	•	FeGe2			1208	73	Si3	a-PeSi2								6,15,16			C	1220
	b-FeSi2	1,2	FeGeZ	986		4055		~	b-FeSi2	3619	6671	20016		-2100	1	0.500		-0.31		PD	
	Ru2Si3			1800					Ru2Si3				1.02	6			18				1800
	0s2Si3)Ru28i3								18,24				
		-,-		1730)b-FeSi2		1020	38020	1.82	0							1730
	0sSi2.4			1 4 7 0		1357	90	812()OsGe2	1 1 4 4	0 0001						•		_		
		1,2	CoGe	1460		1105	0.0	a · a			0.0861		1	-3611		1.780		-1.731	Y		1460
			CoGe2	1326		1190	23	813		3801	0.011	-377		2471	18.0	0.260	6,15	2.531			1326
	Rh4815	•							Rh4Si5												
	Rh3Si4								Rh3Si4												
	Rh2Si3																				
		-,23							DI IGIF												
		-,-							Rh4Si5												
	Ir3Si4								Rh3Si4				1 88	e							
	Ir38i5								Mana = 1 2 = 2				1.02	0							
	Ir2Si3	-	Tages						Monoclini		A 6010	4517					9.4				
		•	Ir3Ge7	1500	u				No 2 4 -	4017	0.6817	1164					24			LF.	11500
		-,- - 2	,	1500					Na3As		A 991	g 1	Λ 1Λ	1 6171	n e			1 [1		M n t	>1500
	a-LaSi2	•		-160					a-ThSi2		0.231	-91	U.19	1-41/1	0.6			-1.51		PΙ	
	b-LaSi2	-,4		1520	FI				a-GdSi2	120	Semi?1	9017								M	
41	USi3								Cu3Au	190	0.2517	4311									

C=Congruent melting
Pr=Peritectic-reaction melting
M=Melting (no indication of type)
PD=Peritectoid decompostion
PI=Polymorphic inversion
D=Decomposition
S=Sublimation
DS=Dissociation

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1. G.V. Samsonov and I.M. Vinitskii, "Handbook of Refractory Compounds," Plenum, NY (1980).
 2. W.G. Moffatt, "The Handbook of Binary Phase Diagrams," Genium Publishing, Schenectady, NY (1984).
 3. S.P. Murarka, J. Vac. Sci. Tech., 17(4), 775 (1980).
 4. B.N. Nikitin, Sov. Phys.-Solid State 2(11), 2389 (1961).
 5. V.S. Neshpor and G.V. Samsonov, Izvestiya Akademii Nauk SSSr, Neorganicheskie Materialy, 1(5), 655 (1965).
 6. B.N. Nikitin, Sov. Phys.-Tech. Phys 3, 23 (1958).
 7. In Crylic.
 8. W. Laskow, Notebook 122181-84 through 90.
 9. V.S. Neshpor and G.V. Samsonov, Sov. Phys.-Solid State 2, 1966 (1960).
10. W.B. Bienert and F.M. Gillen, U.S. Patent No. 3,407,037, Martin Marietta Co. (1968).
11. W.B. Bienert and B.A. Skrabek, Proc. IEE/AIAA Thermoelectric Specialists Conf., (1966)
12. S.E. Mayer and A.I. Mlavsky, "Properties of Blemental and Compound Semiconductors," ed. by H.C. Gatos, (1960).
14. In Crylic, Cr-Si System
15. V.S. Neshpor and V.L. Yupko, In Russian 2(14), 55 (1957)
16. In Crylic, p.141 (1957)
17. C.F. Krolick, "Thermoelecticty: Report on the State-of-the-Art," MBL Research and Development Report 205/64, U.S. Navy Marine Engineering L
18. I. Engstrom, Acta Chemica Scandinavia 24, 2117 (1970).
19. J. Hesse, Z. Metallkde, 60, 652 (1969)
20. K. Mason and G. Muller-Vogt, J. Crystal Growth 63, 34 (1983).
21. N.G. Ageev, "Phase Diagrams of Metallic Systems," Viniti Press, Institute for Scientific Information (1959-1979).
22. M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd Edition, McGraw-Hill (1958).
23. R.P. Elliot, "Constitution of Binary Alloys, First Supplement," McGraw Hill (1965)
24. J.H. Buddery and A.J.B. Welch, Nature, 67, 362 (1951).
25. Hans Nowotny, "Electronic Structure and Alloy Chemistry of the Transition Elements,", ed. by P.A. Beck, Interscience, NY-London, 179 (1963)
26. F.M. d'Heurle, R.D. Frampton and B.A. Irene, Hao Jiang and C.S. Petersson, Appl. Phys. Lett. 4711, 1170 (1985).
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