

THE FEATURES OF SILICIDE THERMOELECTRICS DEVELOPMENT

Fedorov M.I., Zaitsev V.K.

Ioffe Physico-Technical Institute, Polytekhnicheskaya ul., 26, St.Petersburg, 194021, Russia
Contact author: m.fedorov@mail.ioffe.ru

Abstract. Transition metal silicides are promising materials for thermoelectric applications. All these materials have some common features. These are - complex crystal lattice, anisotropy of transport properties, wide homogeneity range, high effective mass of current carriers. A review of transport properties of these materials has been made in the paper. Special attention is paid to the anisotropy of their properties. Prospects of the increase of their thermoelectric figure of merit and possible applications have been discussed also.

Introduction.

Nowadays thermoelectricity finds new application areas. In this case the main properties of new thermoelectrics besides high figure of merit should be cheapness, accessibility, ecologically friendliness, mechanical and chemical strength. Many silicides meet these claims. Now we shall discuss only higher silicides of transition metals (Cr, Mn, Fe, Ru, Re). These silicides have many common features in their properties, so they can be discussed jointly.

Table 1. Crystal structures of silicides, which could be used in thermoelectric devices

Material	Melting point, K	Syngony	a , nm	b , nm	c , nm	α , °	Reference
CrSi ₂	1763	Hexagonal	0.4431	-	0.6364	-	[1, 2]
Mn ₄ Si ₇	1430	Tetragonal	0.5525	-	1.7463	-	[3]
FeSi ₂	1490	Orthorhombic	0.9863	0.7791	0.7833	-	[4]
Ru ₂ Si ₃	1970	Orthorhombic	1.1074	0.8957	0.5533	-	[5]
ReSi _{1.75}	2213	Triclinic	0.3138	0.3120	0.7670	89.9	[6]

Table 2. Some parameters of silicides, which could be used in thermoelectric devices.

Material	Type	ZT_{\max}	ΔS , $\mu\text{V/K}$ (T=300 K)	E_g (eV)
CrSi ₂	p	0.25[7]	48[7]	0.7[7]
MnSi _{1.7}	p	0.7[8]	99[8]	0.66[9]
FeSi ₂	n, p	0.2[10]	76[11]	0.87[12]
Ru ₂ Si ₃	n, p	0.4(n)[13]; 0.3(p)[14]	~25[15]	1.1[16]
ReSi _{1.75}	p	0.8[17]	~450[18]	0.16 [19]

General review.

Silicides as thermoelectrics were proposed by E.N.Nikitin's paper in 1958[20]. The main advantage of these thermoelectrics

is high density of states ($d \sim 10^{21} \text{cm}^{-3}$), but the current carrier mobility was found to be very low ($u \sim 10 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$). Melting point and crystal structure parameters of silicides

are shown in the table 1. As the table 1 shows all discussed thermoelectrics have the symmetry lower than cubic. Although they have different crystal structures all these structures (except CrSi_2) could be considered as slightly deformed tetragonal structure. So, it is possible to find anisotropy of transport properties in these materials. Although the anisotropy of electrical and thermal conductivity can be found often, the anisotropy of Seebeck coefficient is rare phenomenon. Table 2 shows achieved nowadays ZT of these materials, the difference of Seebeck coefficient along and across some crystallographic axis together with energy gap. As the table 2 shows all these silicides have anisotropic Seebeck coefficient. The anisotropy of transport properties produces some difficulties in manufacturing thermoelectric material for usual thermoelements, but strong anisotropy of Seebeck coefficient allows to use these materials in anisotropic thermoelements [21]. In the following sections all these materials will be discussed separately.

Chromium disilicide.

Chromium disilicide (CrSi_2) is the less studied material among 3d-transition metal silicides. Probably, it is connected with high enough melting point and not very high ZT . Now $ZT=0.25$ is achieved in undoped material. Thermoelectric properties of undoped CrSi_2 are shown in the Fig.1. Chromium disilicide has the higher value of Seebeck coefficient and electrical conductivity along hexagonal C-axis. Hence, the highest figure of merit is found in the direction along the C-axis. For the best of the author knowledge there is no papers on the systematic study of thermoelectric properties of doped chromium disilicide. CrSi_2 has significant anisotropy of Seebeck coefficient not only at room temperature but in all studied temperature interval.

Fig. 1 along with the thermoelectric properties along C-axis (Seebeck coefficient - S_{\parallel} , electrical conductivity - σ_{\parallel} , thermal conductivity - κ_{\parallel} , thermoelectric figure of merit - ZT_{\parallel}) shows its anisotropic properties (Difference of the Seebeck coefficient along

and across C-axis - $S_{\parallel}-S_{\perp}$, the ratios of the conductivities: electrical - $\sigma_{\perp}/\sigma_{\parallel}$ and thermal - $\kappa_{\parallel}/\kappa_{\perp}$, anisotropic thermoelectric figure of merit - ZT_a)

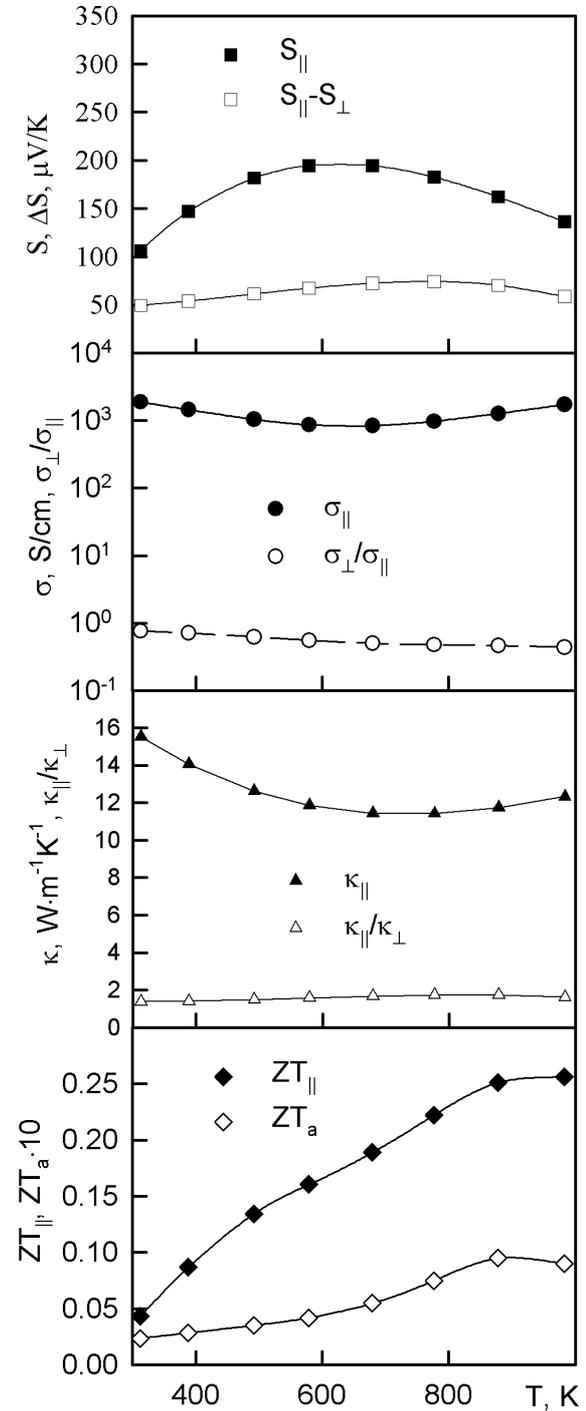


Fig.1 Thermoelectric properties of CrSi_2 along hexagonal C-axis and the anisotropy of its thermoelectric properties. According to the data of [7].

ZT_a is the thermoelectric figure of merit of anisotropic crystal when the principal

axis (C) is directed at 45° to the directions of thermal (Q) and electrical (I) fluxes (fig.2). In this case according to the Ref [22], ZT_a can be written as:

$$ZT_a = \frac{(S_{\parallel} - S_{\perp})^2 \sigma_{\parallel} / \kappa_{\parallel}}{(1 + \kappa_{\perp} / \kappa_{\parallel})(1 + \sigma_{\parallel} / \sigma_{\perp})} \quad (1)$$

As a rule, anisotropic figure of merit is lower than the usual figure of merit in the optimum direction. It does not imply the useless of the anisotropic thermoelectric generator. The advantage of anisotropic thermoelectric generator is a possibility of production high voltage on the load only with connection only cold sides of the crystals.

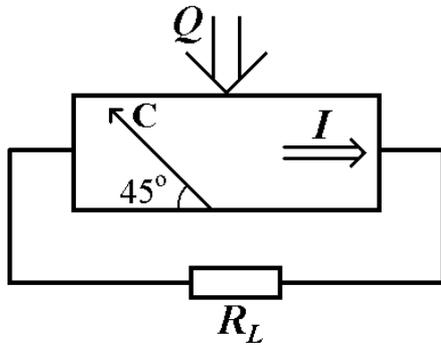


Figure 2. A scheme of anisotropic thermoelement.

The anisotropic thermoelectric power (when $R_L = \infty$) can be written as:

$$E = 1/2(S_{\parallel} - S_{\perp}) \cdot \Delta T \cdot l / d \quad (2)$$

where l is the length of the crystal along the electrical current direction, and d is the length of the crystal along the thermal flux direction (thickness). Taking into account that $\Delta T = Qd / (l \cdot h) / \kappa_{45}$, where κ_{45} is thermal conductivity along thermal flux and h is the length of the crystal in the perpendicular to the scheme plain direction, one can obtain:

$$E = 1/2(S_{\parallel} - S_{\perp}) Q / h / \kappa_{45} \quad (3)$$

and

$$E/Q = 1/2(S_{\parallel} - S_{\perp}) / h / \kappa_{45} \quad (4)$$

Hence, the more narrow the crystal, the higher the voltage, which can be produced from the same value of thermal flux.

Higher Manganese Silicide

The main feature of higher manganese silicide (HMS) is a number of crystal structures in the region of its existence ($\text{MnSi}_{1.7-1.75}$). All the structures are tetragonal ones with general formula $\text{Mn}_n\text{Si}_{2n-m}$.

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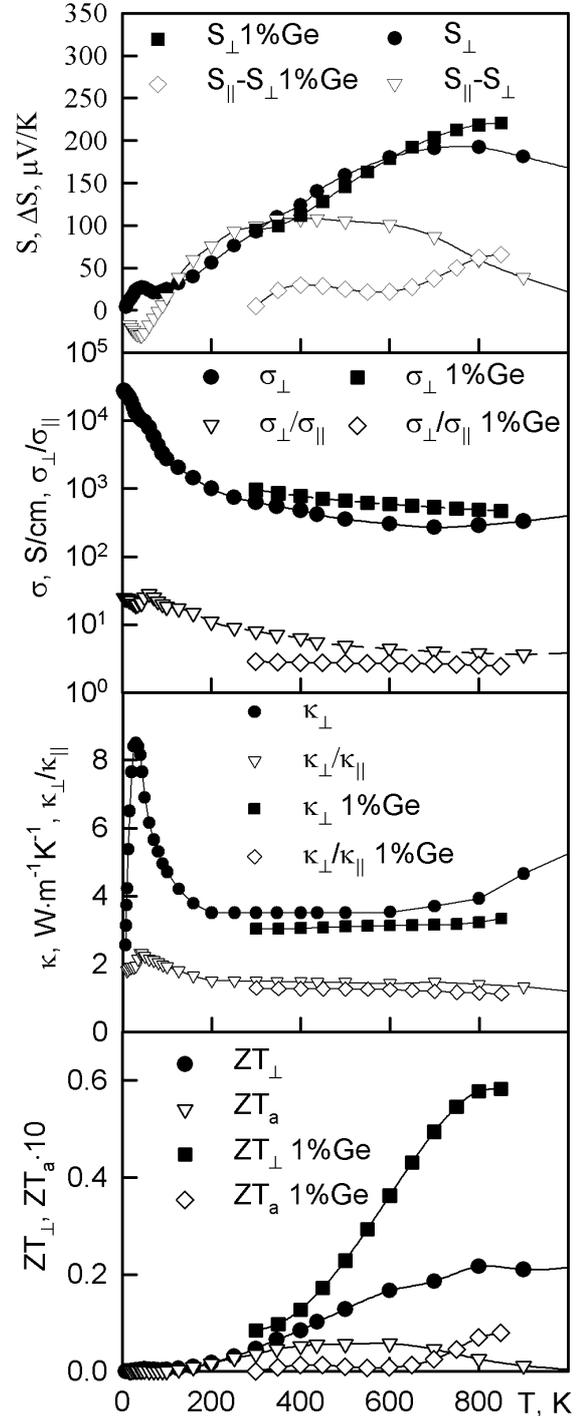


Figure 3. Thermoelectric properties of HMS (pure and doped with 1%Ge) across tetragonal C-axis and the anisotropy of its thermoelectric properties.

Another feature is that a second phase precipitates are created at directed crystallization from the melt. These precipitates do

not spoil “single crystal structure”. The precipitates are the planes oriented orthogonally to the tetragonal axis. All blocks of HMS phase are oriented in the same directions, so in neutron diffraction study such a sample is seen as a single crystal with narrow peaks. Similarly to CrSi₂ HMS has significant anisotropy of Seebeck coefficient that allows to use it in anisotropic thermoelectric generators or IR-receivers. Maximum anisotropic figure of merit is $8 \cdot 10^{-3}$. Contrary to chromium disilicide, pure HMS has the highest thermoelectric figure of merit across the axis of the highest order (tetragonal).

Fig.3 shows thermoelectric properties of pure HMS across tetragonal C-axis and the anisotropy of its thermoelectric properties.

Thermal conductivity of HMS based solid solutions is restricted by those of pure MnSi_{1.7}. Thermal conductivity of all solid solutions is higher than that of pure HMS along C-axis and lower than that across C-axis. Because of this fact only the modification of energy spectrum of current carriers allows to increase thermoelectric figure of merit. Optimization of the composition of HMS allows to improve its thermoelectric properties. Optimized HMS was not produced as a single crystal. The highest figure of merit is obtained in the samples where the tetragonal axes oriented practically in the same direction. Fig. 3 shows also the same parameters of HMS doped with 1%Ge. As one can see the Ge doping essentially increases the figure of merit across C-axis and decreases the anisotropy of thermoelectric properties.

Iron disilicide

Iron disilicide is one of the cheapest thermoelectrics. Since Ware and McNeil proposed to use it in thermoelectric devices [23] very many papers devoted to the study of this material have been published.

There are two phases of higher iron silicide: α -phase – metal, which has tetragonal structure and is stable at $T > 1210$ K. The composition of α -phase is FeSi_{-2.4}. β -phase – semiconductor of orthorhombic structure which is stable at $T < 1210$ K. This phase

corresponds to stoichiometric iron disilicide (FeSi₂).

Because of the existence of the two phases the production of single crystals from the melt is practically impossible. Up to now all single crystals of β -FeSi₂ have been produced by chemical transport [4, 24]. These crystals are very small and the study of the anisotropy of transport properties is very difficult. Up to now only Seebeck coefficient anisotropy at room temperature was studied [11].

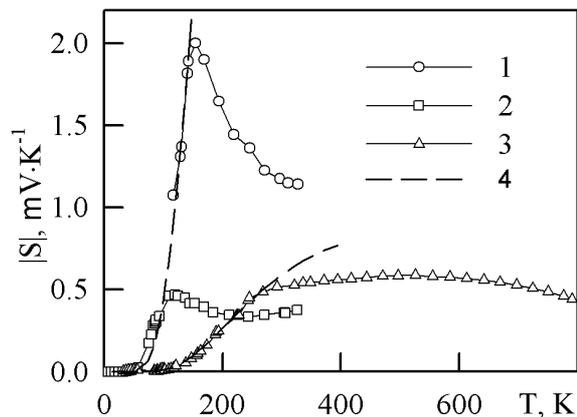


Figure 4. Absolute value of Seebeck coefficient of some β -FeSi₂ samples: 1: undoped, high purity Fe [25]; 2: $<0.7\%Co>$ [24]; 3: $<1\%Mn>$ [26]; 1,2 – single crystals, 3 - polycrystalline samples. Dashed lines (4) – approximation according to the formula $S_{ph} = S_0(\Theta/T)^{(3/2)}e^{-\Theta/T}$ [27].

The principal feature of the majority of Seebeck coefficient measurements is a sharp growth of absolute value of Seebeck coefficient at $100 < T < 300$ K (fig.4). This growth corresponds to the temperature of optical phonons excitation, so it allowed to suggest that such a growth is connected with the drag of current carriers by optical phonons. There is no direct confirmation of this effect, but the theory of this effect [27] shows good agreement with experimental data (fig.4). We can estimate possible value of thermoelectric figure of merit [26]. Our estimation shows that one can receive thermoelectric figure of merit $Z \sim 15 \times 10^{-3} K^{-1}$. At the temperature of maximum Seebeck coefficient $T=200$ K, dimensionless figure of merit can achieve the value $ZT \sim 3$.

Ruthenium silicide Ru_2Si_3

The following two silicides have not one of important advantages of silicides – they are not cheap. Nevertheless they could be used in some applications and, moreover the study of their physical properties can give very important contribution to the physics of thermoelectrics.

Ruthenium sesqui-silicide Ru_2Si_3 similarly to FeSi_2 has a phase transition at ~ 1240 K [28]. Both phases are semiconductors. $\alpha\text{-Ru}_2\text{Si}_3$ (low-temperature phase) has orthorhombic structure, whereas $\beta\text{-Ru}_2\text{Si}_3$ (high-temperature phase) has tetragonal structure. Similarly to HMS Ru_2Si_3 crystals have plate-like precipitates. Their orientation is not determined reliably. Probably, similarly to HMS it is connected with crystal growth rate [29].

Full set of thermoelectric properties was measured by Simkin et. al [15] for the crystals having domain structure. All domains had the same orientation of [010] axis, but the orientations [100] and [001] had been intermixed. Fig.5 shows thermoelectric properties of these crystals [15]. High enough values of figure of merit for doped Ru_2Si_3 have been presented in a number of papers [13, 14, 16, 30, 31]. Practically all of them have elements of extrapolation for ZT calculation, because the data obtained from different samples were used. Nevertheless, systematic study of this material has not fulfilled yet.

Rhenium silicide ($\text{ReSi}_{1.75}$)

For long time higher rhenium silicide have been considered as stoichiometric disilicide ReSi_2 with - tetragonal structure (space group $I4/mmm$, $a = 0.3131$; $c = 0.7676$ nm [32]). Now it is shown, that it is defect disilicide and its real composition is $\text{ReSi}_{1.75}$. Its crystal structure should be described as triclinic with the parameters shown in the table 1. One can see that this structure is slightly deformed tetragonal structure.

According to [17, 18] the thermoelectric properties of $\text{ReSi}_{1.75}$ are highly anisotropic. Its electrical conduction is of n-type when measured along [001] while it is of p-type

when measured along [100] [18]. The value of Seebeck coefficient is very high along [001] ($250\text{-}300$ $\mu\text{V/K}$). As a result, a very high value of dimensionless figure of merit (ZT) of 0.7 is achieved at 1073 K when measured along [001] [17]. ZT value is even increased to 0.8 with a small amount of Mo addition.

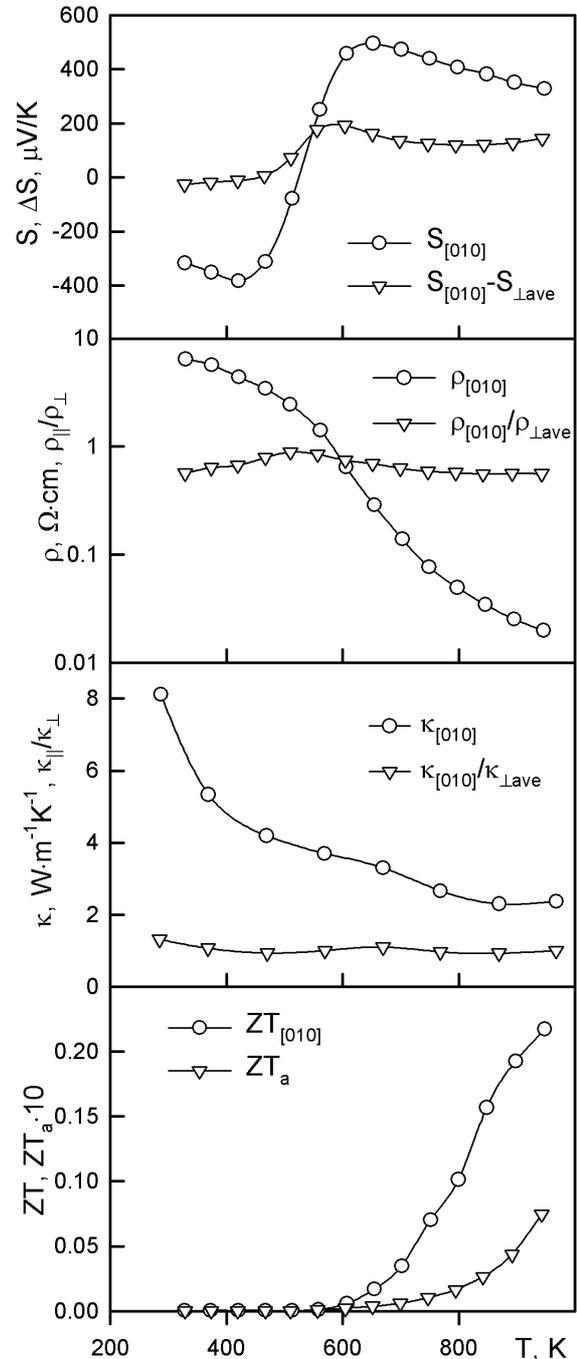


Figure 5. Thermoelectric properties of Ru_2Si_3 in the direction [010] and its anisotropic properties according to the data of [15].

Conclusion

Silicides are promising thermoelectrics, some of them show high thermoelectric figure of merit. Higher transition metal silicides show unusual transport properties, that can be useful in the search of new thermoelectrics. All these materials probably can be used for the creation of anisotropic thermoelements. Following study of the physics of silicides could open new ways for thermoelectrics improvement.

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