JOURNAL OF SOLID STATE CHEMISTRY 30, 149–156 (1979)

Thermoelectric Properties of Chromium Sulfo-Selenides*

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Received July 17, 1978; in revised form November 25, 1978

Chromium sulfo-selenides are extrinsic semiconductors which are stable at moderately high temperatures. Low thermal conductivity and good electrical properties make these materials interesting with respect to their applications in thermoelectric technology. Preparation and thermoelectric properties of various compositions of chromium sulfo-selenides are reported.

Introduction

In the last few years there has been a great interest in transition metal chalcogenides, because of their unusual electrical and magnetic properties (*1*). Current research activities include exploration of these materials for technological applications such as solar cells, electrochemical cells, catalysts, etc. It has been known that some of the rare earth chalcogenides are good thermoelectric materials (*2*) and could be used for thermoelectric power conversion for various space applications. Since physical properties of the semiconducting transition metal chalcogenides have not been investigated for applications in thermoelectric technology and some of them are very stable at moderately high temperatures required for thermoelectric power generation, we investigated the thermoelectric properties of the semiconducting chromium sulfo-selenides. The results of preliminary investigations show them to have many characteristics required of a good thermoelectric material. We have studied the electrical resistivity, Seebeck coefficient, thermal conductivity and charge carrier mobilities of rhombohedral chromium sulfo-selenides, $Cr_2S_{3-x}Se_x$.

Experimental

Preparation of Materials

$Cr_2S_{3-x}Se_x$ ($0 \leq x \leq 1$) were prepared by reacting high-purity elements in stoichiometric quantities in evacuated silica tubes at 1000°C. The temperature of the reaction was increased slowly in order to avoid breakage of the tube due to excess pressure of the chalcogens. Small amounts of I_2 added to the reactants helped to get a homogeneous single compound. After complete reaction, the polycrystalline material was pulverized and pressed into a pellet in vacuum at 750°C for 5 hr under a pressure of 30 000 psi. The pellets were further sintered in evacuated silica tubes at 900°C for 1 week. In this way pellets with 96% theoretical density could be obtained.

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* This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract 7-100, sponsored by the National Aeronautics and Space Administration.

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0022-4596/79/110149-08$02.00/0

Printed in Great Britain

The compounds were identified and crystal lattice parameters were determined by X-ray powder diffraction. The densities of the pellets were determined by hydrostatic techniques using isopropyl alcohol.

Electrical Properties

Electrical resistivities of the different materials were measured on cylindrical pellets by a direct-current four-probe method. The pellet was mounted in an apparatus which could be used for measuring Seeback coefficient, thermal conductivity, and resistivity simultaneously at various temperatures. The details of the apparatus are given elsewhere (*3*). The whole apparatus was kept in an evacuated chamber. The electrical and thermocouple wires were positioned on the sample into precisely drilled microholes along the sample length. Good electrical and thermal contact with the sample could be achieved in this way. For resistivity measurements, correction for Seebeck voltage was done by alternating the current directions.

Hall coefficients were measured on rectangular slices of about 0.005 in. thick, cut from the pellets. Gold wires were bonded to the sample by silver conducting paste. Because of the thermal noise, an ac method was used with a PAR lock-in amplifier for signal measurements. The sample was placed in the field of an electromagnet which could be varied up to 6000 G. The Hall voltage was measured at various fields in both field directions. An alloy of Si–Ge of known doping level was used to check the accuracy of the results. No magnetoresistance was found at room temperature and no correction to the Hall voltage was necessary.

Thermal Conductivity Measurements

Thermal conductivity of the cylindrical pellet was measured using a steady state comparison method (*4*) with longitudinal heat flow. Experimental details are described elsewhere (*3*). Pyroceram cylinders were used as standards. The accuracy of our measurements (±15%) was determined using several standard materials of known thermal conductivities. The errors at higher temperatures were larger than at lower temperatures because of the radiation loss inherent in this type of measurement. The temperature gradient along the sample at the steady state conditions was measured by thermocouples placed in microholes drilled into the pellets. Sufficient time was allowed to attain temperature equilibrium before doing the measurements.

Results and Discussions

We have prepared and characterized six different compositions of the $Cr_2S_{3-x}Se_x$ alloys. A solid solution of any composition could be made between Cr_2S_3 and Cr_2Se_3 (*5*). Single crystals of these solid solutions could also be made by chemical transport reactions. The compounds were identified by X-ray powder diffraction (Table 1). The hexagonal lattice parameters a_0 and c_0 obey "Vegard's" law. c_0 values depend upon the stoichiometry of the compound, since the presence of interstitials affects these values.

Thermal Conductivity

Thermal conductivities of various chromium sulfo-selenides, at different temperatures, are given in Figs. 1 and 2.

TABLE I

HEXAGONAL LATTICE PARAMETERS OF POLYCRYSTALLINE CHROMIUM SULFO-SELENIDES

Composition	a_0 (Å)	c_0 (Å)
Cr_2S_3	5.951	16.69
$Cr_2S_{2.4}Se_{0.6}$	6.012	16.90
$Cr_2S_{2.1}Se_{0.9}$	6.043	16.95
$Cr_2S_{1.5}Se_{1.5}$	6.097	17.10
$Cr_2S_{0.6}Se_{2.4}$	6.192	17.25
Cr_2Se_3	6.247	17.36

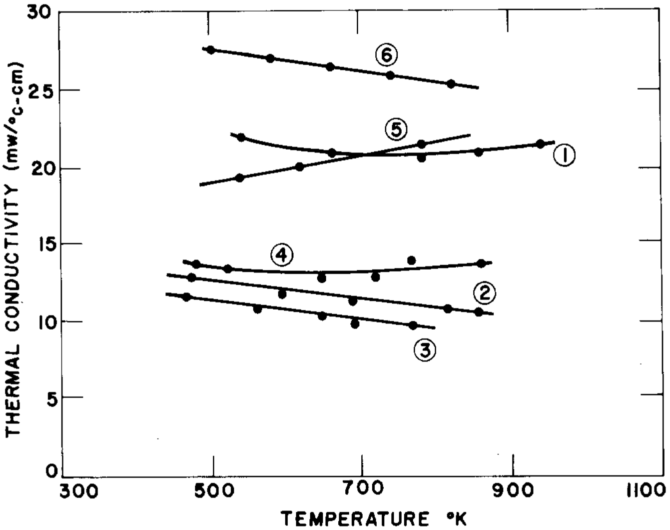

FIG. 1. Temperature dependence of the thermal conductivities of various $Cr_2S_{3-x}Se_x$ solid solutions. (The numbers in the figure refer to sample numbers in Table II.)

Thermal conductivities of chromium sulfide and selenide are higher than the solid solutions. This is expected due to the increased phonon scattering as inhomogeneities in atomic ordering are introduced by anionic substitution. Reduction of thermal conductivity by alloying, first proposed by Ioffe (*6*), has been done in several cases to increase the figure of merit of a thermoelectric material. The thermal conductivity values are in the range of 10 to 25 mW/cm-°C; such low values are quite close to those of some of the

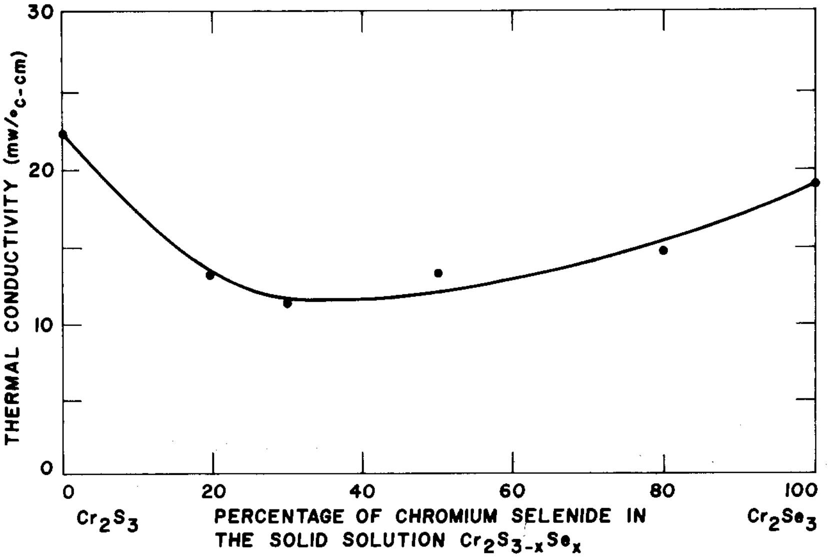

FIG. 2. Room temperature thermal conductivities of $Cr_2S_{3-x}Se_x$ solid solutions as a function of the composition.

well-known thermoelectric materials such as $(Bi/Sb)_2Te_3$ and some rare earth selenides and are considerably lower than those of silicon–germanium alloys which are presently used for thermoelectric power generation in space applications (*7*, *8*). The major contribution to the total thermal conductivity is from the lattice alone, since these samples did not have high electrical conductivities. The low lattice thermal conductivity could be attributed to the nature of the crystal structure. Cr_2X_3 crystallized with the NiAs-type structure with ordered defects (*9*). When all the octahedral holes within the hexagonal close-packed anion lattice are filled, a NiAs-type structure is formed. In Cr_2X_3, one half of the octahedral holes in alternate cation layers are empty, creating ordered cation vacancies. Due to the existence of these vacancies, Cr_2X_3 has a tendency to form nonstoichiometric compounds, $Cr_{2+x}X_3$, at higher temperatures. Nonstoichiometric $Cr_{2+x}X_3$ could be represented as $(Cr_x^{+2}Cr_{2-2x/3}^{+3}/\square)Se^{-2}$, where $\square$ represents inherent lattice vacancies. Since these materials have ordered lattice defects in alternate chromium atom planes lying perpendicular to the *a*-axis, and lattice defects are known to reduce the thermal conductivity significantly due to scattering by defects, the inherent crystalline defects in these materials contribute a major factor to the low thermal conductivities of these materials. Even though these measurements were carried out on sintered hot-pressed pellets with porosities of less than 5% measurements on single crystals will be of interest because of the anisotropic nature of these crystals. The excess chromium atoms contribute electrons to the conduction band. We have purposely prepared $Cr_{2.04}S_3$ and measured its physical properties. The thermal conductivity of $Cr_{2.04}S_3$ is slightly higher than that of the near stoichiometric compound, probably due to smaller numbers of defects and also due to larger electronic contribution to the thermal conductivity. In order to understand the influence of charge carrier concentration and the influence of defects, we are studying the properties of the materials where part of the defects are replaced by Ca and Mg. Adjustments to the carrier concentration can be easily achieved by such substitutions.

Electrical Properties

Electrical and magnetic properties of Cr_2S_3 have been studied by earlier workers (*10*). The electrical resistivity and Seebeck coefficients of different chromium sulfoselenides at various temperatures are plotted in Figs. 3 and 4, respectively. These results are in good agreement with earlier work (*10*). Both *p*-type and *n*-type Cr_2S_3 have been reported depending upon the stoichiometry. Excess chromium atoms give *n*-type and excess Se or S atoms give *p*-type polarity. All of the samples which we prepared showed *n*-type characteristics. *p*-type material with excess Se or S became *n*-type after annealing at high temperature, probably due to loss of sulfur or selenium.

The electrical resistivity of Cr_2S_3 decreases with increasing temperature, within the temperature interval of our study, with an activation energy of $\simeq 0.05$ eV. Selenium-substituted compounds showed smaller excitation energies. Cr_2S_3 and $Cr_2S_{3-x}Se_x$ behave as extrinsic semiconductors. The behavior of electrical resisitivity of pure Cr_2S_3 with increase of temperature is in good agreement with the results of earlier workers (*10*). The charge carriers in the conduction band are produced by excitation of the electrons from the donor levels which are present as a result of nonstoichiometry. The band gap between the valence and conduction band in these materials are not known. Electronegativity considerations should suggest that the band gaps should increase from selenides to sulfides. The increase of Seebeck coefficient with increase of temperature is characteristic of extrinsic

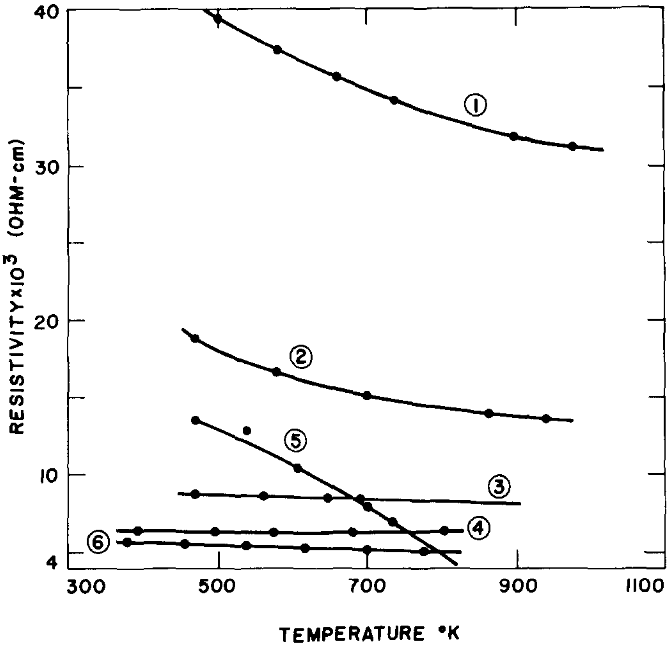

Fig. 3. Temperature dependence of the electrical resistivities of various $Cr_2S_{3-x}Se_x$ solid solutions.

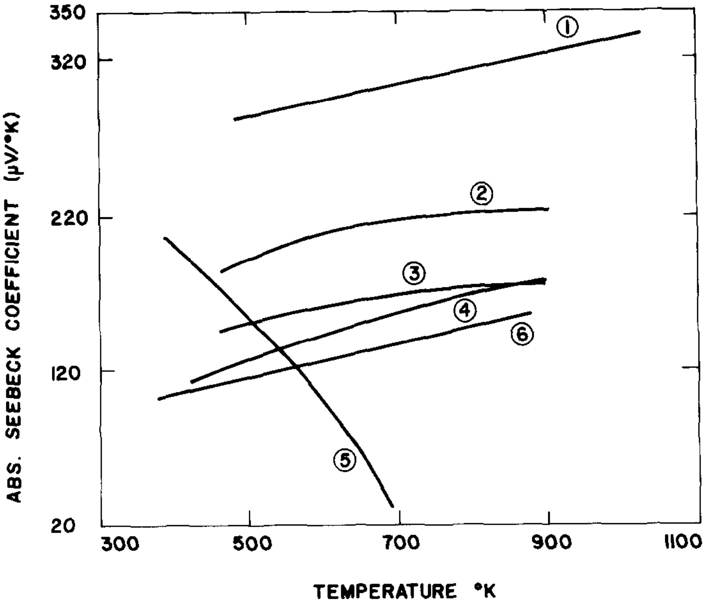

Fig. 4. Seebeck coefficients of different $Cr_2S_{3-x}Se_x$ samples as a function of temperature.

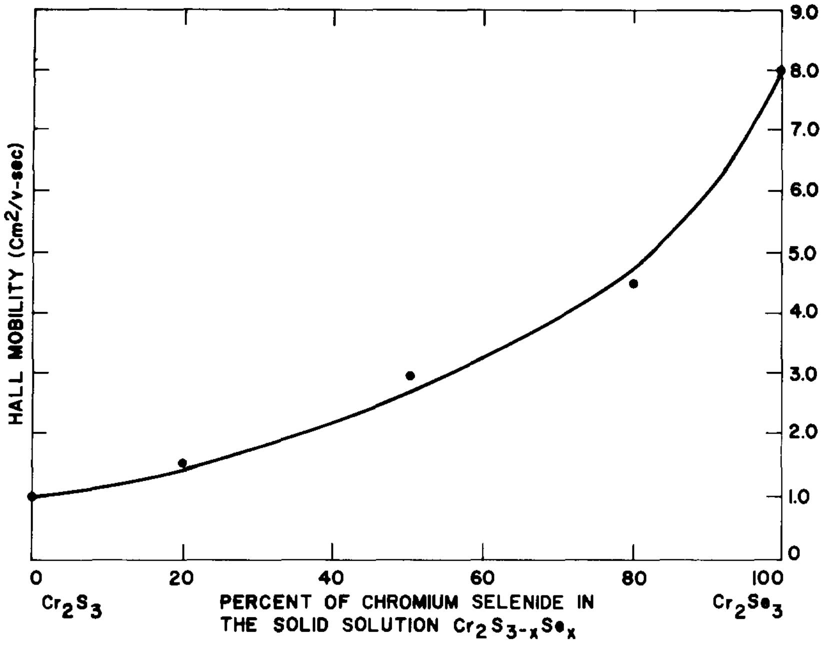

FIG. 5. Hall mobilities at room temperature of different $Cr_2S_{3-x}Se_x$ alloys.

semiconductors. In extrinsic semiconductors, Seebeck's coefficient increases linearly with [log $RT^{3/2}$], where R is the Hall coefficient. Pure Cr_2Se_3 becomes intrinisc at much lower temperatures and the resistivity data give an activation energy of approximately 0.3 eV.

The electron mobilities at room temperature of different $Cr_2S_{3-x}Se_x$ compounds are shown in Fig. 5. The accuracy of Hall coefficient measurements were tested using standard silicon–germanium alloys of known mobility. Also, our mobility values are in good agreement with the values reported for Cr_2S_3 (*8*). Hall effect measurements on single crystals are required in both *a* and *c* crystal axis directions. The mobilities are rather small compared to those of good thermoelectric materials. The mobility is gradually increased as sulfur is gradually substituted by selenium. This is reasonable since selenium is a bigger and more polarizable atom then sulfur and the covalent nature of the Cr–X bond is increased with selenium substitution. The large charge carrier concentrations in these materials suggest the possibility of large numbers of ionic Cr3+ scattering centers and mobility might be higher for lower concentrations of charge carriers. The mobility of Cr_2S_3 at 300°K has been reported (*8*) to be 4 cm^2/V-sec at a charge carrier concentration of 6×10^{18} cm^{-3}. In addition mobility is dependent upon the nature and number of defects inherent in these materials.

Both the number of vacancies and the charge carrier concentrations could be adjusted independently. The carrier concentration could be adjusted without a change in the vacancy concentration by replacing chromium ions with divalent ions such as Ca^{+2} or Mg^{+2}. By varying the values of x in $Cr_{2+x}X_3$, in the range Cr_2X_3 to Cr_3X_4, it is possible to change the vacancy concentrations. These experiments are in progress.

Figure of Merit

The figure of merit, Z, of a thermoelectric material is defined as

$$Z\frac{\alpha^2\sigma}{k},$$

where α is the Seebeck coefficient, σ is the electrical conductivity, and k is the total thermal conductivity. Since the thermoelectric power conversion efficiency of a thermoelectric material depends upon the product of the figure of merit and the temperature differential, it is necessary that the material be very stable at moderately highe temperatures with a high figure of merit. Also the band gap should be large enough that the minority carrier concentration is small at the temperature of operation. Most of the thermoelectric materials with large Z have small band gaps and are unstable at moderately high temperatures. An alloy of silicon and germanium doped with phosphorus or boron is being used currently for thermoelectric generators, because of its large band gap and high temperature stability, but its figure of merit is relatively low ($0.7\times10^{-3}\,°K^{-1}$ at 900°C). Some rare earth chalcogenides have also been reported (*2*) to have Z of approximately $0.8\times10^{-3}\,°K^{-1}$ at 1000°C but they are very susceptible to oxidation and their preparation is rather involved and needs special care with highly pure rare earth elements, which are expensive. Chromium chalcogenides have many of the properties of rare earth chalcogenides and are relatively easy to prepare.

Table II shows the figure of merit at 200 and 600°C of the various chromium chalcogenides which we prepared. $Cr_2S_{2.1}Se_{0.9}$ has a figure of merit of $0.45\times10^{-3}\,°K^{-1}$ at 900°K while Cr_2Se_3 becomes intrinsic at higher temperatures. When compared with Si–Ge alloy which has a figure of merit of 0.5×10^{-3} at 600°C, these numbers look very encouraging since these materials have not been optimized for the charge carrier concentration and for the number of defects, both of which could be adjusted, as stated earlier by alkaline earth substitution.

Acknowledgment

The author is very grateful to Professor T. H. Geballe of Stanford University for allowing him to use several of their facilities and for helpful discussions. The assistance of Mike O'Connor of Stanford University in Hall effect measurements is gratefully acknowledged.

TABLE II

THERMOELECTRIC PROPERTIES OF CHROMIUM SULFO-SELENIDES

			$T = 500°K$				$T = 870°K$			
Sample	Composition	$n_e\times10^{20}$ (cm^{-3})	α ($\mu V/°K$)	$\rho\times10^3$ (Ω-cm)	k (mW/°C-cm)	$Z\times10^3$ ($°K^{-1}$)	α ($\mu V/°K$)	$\rho\times10^3$ (Ω-cm)	k (mW/°C-cm)	$Z\times10^3$ ($°K^{-1}$)
1	Cr_2S_3	2.0	−285	39.5	22	0.09	−320	31.5	20	0.16
2	$Cr_2S_{2.4}Se_{0.6}$	2.8	−192	18.0	13	0.15	−220	13.5	10	0.36
3	$Cr_2S_{2.1}Se_{0.9}$	2.9	−150	8.8	11	0.23	−180	8.0	9.0	0.45
4	$Cr_2S_{1.5}Se_{1.5}$	3.3	−130	6.3	13	0.21	−180	6.5	14	0.36
5	Cr_2Se_3	0.6	−158	12.8	19	0.10	+30 (intrinsic)	1.0	22	—
6	$Cr_{2.04}S_3$	Unmeasured	−120	5.5	28	0.09	−160	4.8	25	0.22

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