

# THERMOELECTRIC PROPERTIES OF SELENIDE SPINELS

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## ABSTRACT

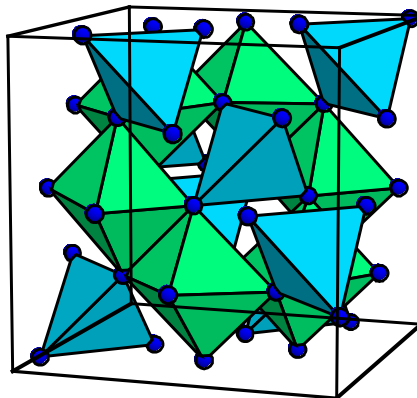
Many compounds with the spinel structure type have been analyzed for their thermoelectric properties. Published data was used to augment experimental results presented here and to select promising thermoelectric spinels. Compounds studied here include  $\text{Cu}_{0.5}\text{Al}_{0.5}\text{Cr}_2\text{Se}_4$ ,  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Cr}_2\text{Se}_4$ ,  $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{Se}_4$ , and  $\text{CuIr}_2\text{Se}_4$ . Many exhibit low lattice thermal conductivity of about 20 mW/cmK, independent of temperature. Preliminary results are given for two series of compounds that were selected for further study:  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  and  $\text{Zn}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ .

## INTRODUCTION

The growth of commercial applications of thermoelectric devices depends primarily on increasing the figure of merit,  $ZT$ , for thermoelectric materials. The figure of merit is defined as  $ZT = \alpha^2 \sigma T / \lambda$ , where  $\alpha$  is the Seebeck coefficient,  $\sigma$  the electrical conductivity,  $\lambda$  the thermal conductivity, and  $T$  is the absolute temperature. Materials with a large  $\alpha^2 \sigma$  value, or power factor, are usually heavily doped semiconductors, such as  $\text{Bi}_2\text{Te}_3$ . The thermal conductivity of semiconductors is usually dominated by phonon or lattice thermal conductivity. Thus, one method for finding new, advanced thermoelectric materials is to search for semiconductors with low lattice thermal conductivity.

In this paper we evaluate compounds based on the Spinel structure with general composition  $\text{A}_1\text{B}_2\text{X}_4$  where A and B are transition metals and X is a chalcogen, primarily Se. Previous work on such compounds [1] have shown that a range of metals and insulators exist with this structure type.

The structure of Spinel (Figure 1) consists of cubic close packed chalcogen atoms with metal B atoms in half the octahedral holes and metal A atoms in 1/8 of the tetrahedral holes. There can be significant mixing of the different metal atoms on the two metal sites. As suggested by Spitzer [2] the relatively high coordination number of the B atoms in this structure may favor low lattice thermal conductivity. The large cubic unit cells (about  $10\text{\AA}$ ) full of vacant octahedral holes should reduce the lattice thermal conductivity by increasing the scattering of phonons. The multi-valley electronic structure associated with such cubic compounds can be expected to enhance the thermopower.



**Figure 1. Illustration of the Spinel unit cell (e.g.  $\text{ZnCr}_2\text{Se}_4$ ) showing Se atoms as spheres Cr atoms (not shown) at the center of the shaded octahedra and Zn atoms (not shown) at the center of the shaded tetrahedra. The cubic unit cell is indicated.**

There are approximately 300 known Spinel with X = Se or S. Many of these compounds have X = Se compounds with 3-d transition metals for A and B atoms (Figure 2), and constitute most of the samples in this investigation. Many oxide spinels have been studied for their magnetic properties but are not suitable for thermoelectric applications because they are too insulating. Only a few of the known spinel sulfides are metals or heavily doped semiconductors; such compounds based on the sulfides of V, Co, Fe or Ni, are somewhat unstable in the spinel structure, preferring the Cr<sub>3</sub>S<sub>4</sub>-type at high temperature and pressure[3].

Several of the known AB<sub>2</sub>S<sub>4</sub> sulfides with the Cr<sub>3</sub>S<sub>4</sub>-type structure are high temperature/pressure polymorphs of compounds with the Spinel structure at room temperature and pressure. Known compounds with X = Te are metals with low thermopower ( $\alpha$ ) (Table 1).

The Cr<sub>3</sub>S<sub>4</sub>-type selenides are attractive for thermoelectric applications not only because they may have low thermal conductivity as suggested above, but they also exhibit a range of electronic properties – from metals to semiconductors. Precise, heavy doping of the semiconductor is critical to obtain optimal power factor for both n- and p-type materials. Proven thermoelectric materials such as filled Skutterudites and Zn<sub>4</sub>Sb<sub>3</sub> are often difficult to dope to the optimal n- or p-type carrier concentration. An advantage of the A<sub>x</sub>B<sub>3-x</sub>X<sub>4</sub> compounds is the chemical versatility of the structure, allowing continuous doping from metal to n- and p- type semiconductor.

## Experimental

The thermoelectric properties of many sulfur and selenide spinel compounds reported in the literature [1] were used to narrow the search. For insulating compositions, which would need to be heavily doped for thermoelectric applications, the most useful of this information for thermoelectric considerations is the apparent band gap and carrier mobility. These data are summarized in Table 1.

The metallic spinels, such as CuCr<sub>2</sub>S<sub>4</sub>, can be used to dope or alloy with related semiconducting spinels. The solid solution Fe<sub>x</sub>Cu<sub>1-x</sub>Cr<sub>2</sub>S<sub>4</sub> changes from a p-type semimetal to n-type, and then back to p-type as  $x$  is increased[4]. The maximum room temperature power factor for this system is about 1  $\mu$ W/cmK<sup>2</sup>.

Most of the known selenide spinels contain Cr as the B atom, and a +2 element such as Zn or Cd as the A atom. The other elements that can go on the B site are mostly rare earth group elements and Al which will make less chemically stable spinels with a strongly ionic character (large band gap insulators). CuIr<sub>2</sub>Se<sub>4</sub> is both a metal and a pressure induced semiconductor, and as such may have interesting thermoelectric properties [5]. Various doped chromium selenide spinel semiconductors have been made by doping with about one percent of a +1 or +3 element on the A<sup>+2</sup> site, such as with CdCr<sub>2</sub>Se<sub>4</sub> [6, 7] or HgCr<sub>2</sub>Se<sub>4</sub> [8] where a RT power factor of about 1  $\mu$ W/cmK<sup>2</sup> was found [9]. CuCr<sub>2</sub>Se<sub>4</sub> like its S counterpart is metallic and can be used not only to dope but also alloy with the insulating chromium spinels such as Cd<sub>x</sub>Cu<sub>1-x</sub>Cr<sub>2</sub>Se<sub>4</sub>[10] (maximum RT power factor 10<sup>-4</sup>  $\mu$ W/cmK<sup>2</sup>) and Ga<sub>x</sub>Cu<sub>1-x</sub>Cr<sub>2</sub>Se<sub>4</sub>[11]. Such solid solutions are often not

Known Selenide Spinel

$A^{+2}B_2^{+3}Se_4$

1																	2			
H																	He			
3	4													5	6	7	8	9	10	
Li	Be													B	C	N	O	F	Ne	
11	12													13	14	15	16	17	18	19
Na	Mg													Al	Si	P	S	Cl	Ar	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86			
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn			
		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71				
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				

**Figure 2. Elements known to make A<sub>1</sub>B<sub>2</sub>Se<sub>4</sub> compounds with the spinel structure type, where A elements are horizontally hatched and B elements vertically hatched.**

completely miscible, forming two spinel phases with different crystallographic cells [12, 13] particularly when the two types of A ions differ in size.

**Table 1. Room Temperature thermoelectric properties of S or Se spinel compounds reported in the literature [1, 5, 14, 15]. I indicates insulating.**

Composition	Resistivity m $\Omega$ cm	Seebeck $\mu$ V/K	$\Delta E_{\text{optical}}$ eV	$\Delta E_{\text{resistivity}}$ eV	Mobility cm <sup>2</sup> /Vs
FeCr <sub>2</sub> S <sub>4</sub>	I	-		0.02 - 0.2	0.3
CoCr <sub>2</sub> S <sub>4</sub>	I	-		0.01 - 0.3	0.2
MnCr <sub>2</sub> S <sub>4</sub>	I	-		0.1 - 0.3	
ZnCr <sub>2</sub> S <sub>4</sub>	I	-		0.6	
CdCr <sub>2</sub> S <sub>4</sub>	I	-	1.6	0.2-0.6	
HgCr <sub>2</sub> S <sub>4</sub>	I	-	1.4	0.4 - 2	
Ni <sub>0.5</sub> Co <sub>0.5</sub> Cr <sub>2</sub> S <sub>4</sub>	200	60		0 - 0.12	1
CuCr <sub>2</sub> S <sub>4</sub>	0.9	16		0.03	
CuV <sub>2</sub> S <sub>4</sub>	0.6	5			
CuTi <sub>2</sub> S <sub>4</sub>	0.4	-12			
CuCo <sub>2</sub> S <sub>4</sub>	0.4	13			
NiCo <sub>2</sub> S <sub>4</sub>	0.8	-18			
CoNi <sub>2</sub> S <sub>4</sub>	0.4	-2			
Co <sub>3</sub> S <sub>4</sub>	0.3	5			
ZnCr <sub>2</sub> Se <sub>4</sub>	I	-	1.3	0.3	5
CdCr <sub>2</sub> Se <sub>4</sub>	I	-	1.3	0.2 - 0.6	50
HgCr <sub>2</sub> Se <sub>4</sub>	I	-	0.84	0.4 - 2	30
CuCr <sub>2</sub> Se <sub>4</sub>	0.1	16			<10
CuIr <sub>2</sub> Se <sub>4</sub>	5				

Using these previous results, we prepared compositions that looked promising for thermoelectric applications and/or where thermoelectric data was missing.

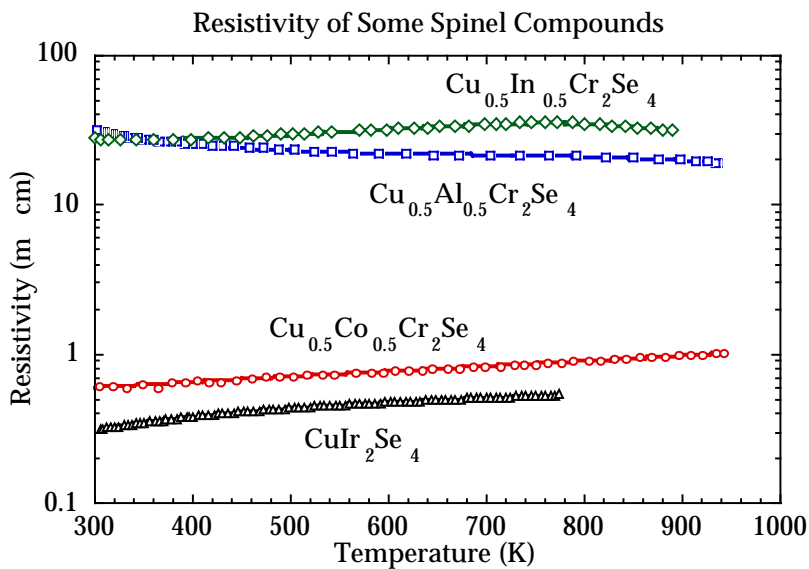
Polycrystalline samples were prepared by mixing and reacting elemental powders in evacuated silica ampoules for several days at 700° - 800° C. The samples were analyzed by x-ray diffractometry to confirm the crystalline structure. The powders were then hot-pressed in graphite dies into dense samples, 3 mm long and 12 mm in diameter. The hot-pressing was conducted at a pressure of 1400 kg/cm<sup>2</sup> and at a temperature of 700° - 800° C for about 2 hours under argon atmosphere. The density of the samples was calculated from the measured weight and dimensions and was found to be greater than 90% of the theoretical density for all samples.

The samples were also characterized by microprobe analysis which was performed using a JEOL JXA-733 electron superprobe. The Al and In concentration in the samples of Cu<sub>0.5</sub>In<sub>0.5</sub>Cr<sub>2</sub>Se<sub>4</sub> and Cu<sub>0.5</sub>Al<sub>0.5</sub>Cr<sub>2</sub>Se<sub>4</sub> were not uniform. The CuIr<sub>2</sub>Se<sub>4</sub> contained some (~10%) IrSe<sub>2</sub> secondary phase. The elemental concentrations determined from microprobe analysis for Ga<sub>x</sub>Cu<sub>1-x</sub>Cr<sub>2</sub>Se<sub>4</sub> were within a few atomic percent of the expected values.

**Table 2. Room temperature thermoelectric properties from this study. I indicates insulating. FM indicates Ferromagnetic.**

Composition	Resistivity m $\Omega$ cm	Seebeck $\mu$ V/K	Thermal Conductivity mW/cmK	Mobility cm <sup>2</sup> /Vs
FeCr <sub>2</sub> Se <sub>4</sub>	$2 \times 10^4$	400	28	0.1
ZnCr <sub>2</sub> Se <sub>4</sub>	I	-	31	2
CdCr <sub>2</sub> Se <sub>4</sub>	I	-	30	<5
Cu <sub>0.5</sub> Al <sub>0.5</sub> Cr <sub>2</sub> Se <sub>4</sub>	30	100	16	6
Cu <sub>0.5</sub> In <sub>0.5</sub> Cr <sub>2</sub> Se <sub>4</sub>	30	300	20	16
Cu <sub>0.5</sub> Co <sub>0.5</sub> Cr <sub>2</sub> Se <sub>4</sub>	0.6	30	25	10
CuSnCrSe <sub>4</sub>	10	100	20	5
CuCr <sub>2</sub> Se <sub>4</sub>	0.28	25	37	FM
CuIr <sub>2</sub> Se <sub>4</sub>	0.3	3		-2

Samples in the form of disks (typically a 1.0 mm thick, 12 mm diameter slice) were cut from the cylinders using a diamond saw for electrical and thermal transport property measurements. Temperature dependence of electrical resistivity, Hall effect, Seebeck coefficient, thermal diffusivity and heat capacity measurements were conducted on selected samples between 80 and 800K. The resistivity and Hall effect were measured using the method of Van der Pauw [16]. The carrier density was calculated from the Hall coefficient, assuming a scattering factor of 1.0 in a single carrier scheme, by  $n = 1/R_H e$ , where  $n$  is the density of holes or electrons, and  $e$  is the electron charge. The Hall mobility ( $\mu_H$ ) was calculated from the Hall coefficient and the resistivity values by  $\mu_H = R_H/\rho$ . The normal Hall effect, however, is often compounded by the anomalous Hall effect because of ferromagnetism in many of the compounds. Therefore it is often difficult to estimate the Hall mobility or carrier concentration. The Seebeck coefficient ( $\alpha$ ) was measured with a high temperature light pulse technique [17]. Room temperature thermal conductivity was measured using the comparison method [18]. High temperature heat capacity and thermal diffusivity were measured using a flash diffusivity technique [19]. The thermal conductivity ( $\lambda$ ) was calculated from the experimental density, heat capacity, and thermal diffusivity values.



**Figure 3. Electrical Resistivity of some Spinel compounds.**

## Results and Discussion

The Spinel selenides and sulfides exhibit a wide variety of electronic properties (Tables 1 and 2). Some,  $\text{CuIr}_2\text{Se}_4$  and  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Cr}_2\text{Se}_4$  for example, are metals having room temperature resistivity ( $\rho$ ) from about  $10^{-4}$  to  $10^{-3}$   $\Omega\text{cm}$ . Others, such as the alloys  $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{Se}_4$  and  $\text{Cu}_{0.5}\text{Al}_{0.5}\text{Cr}_2\text{Se}_4$ , are semimetals or very low band gap semiconductors with high carrier concentrations. Spinel having a stable +2 A atom, are usually insulators or high band gap ( $\sim 1$  eV optical gap) semiconductors. These semiconductors can then be doped n- or p-type [6-10]. Measurements of the resistivity and thermopower as a function of temperature frequently contain discontinuities and hysteresis (hysteretic samples not shown), which may be due to magnetic or structural changes, or even loss of S or Se at high temperatures.

Exchange split  $\text{Cr}^{+3}$  in octahedral coordination will have 3 electrons to completely fill the majority spin  $T_{2g}$  orbital (or subsequent band); thus  $\text{Cr}^{+3}$  may not provide metallic carriers. This is certainly the case for the insulating chromium spinels in Tables 1 and 2. The doping or alloying on the A site should produce doped semiconductors or metals. However, significant alloying on the A site may result in a polaron semiconductor instead of a metal due to the localization effects of the distant dopant atoms. Such behavior is more clearly demonstrated in the related defect NiAs-type  $\text{ACr}_2\text{Se}_4$  chromium selenides [3, 20].

The resistivity due to small polaron hopping conduction has only a slightly different temperature dependence ( $T\exp(E_a/kT)$ ) than that expected of a semiconductor ( $\mu^{-1}\exp(E_a/kT)$  where the mobility  $\mu$  is proportional to  $T^{-3/2}$  for many semiconductors). Both forms are dominated by an exponential with characteristic energy  $E_a$ . For the materials described here the resistivity data is not sufficiently well described by either of the exact forms to determine the transport mechanism. Nevertheless, band semiconductor transport characteristically has carriers with high mobility and low concentration while small polarons have high concentration and low mobility. Thus, the data suggests that these materials have polaron conductivity.

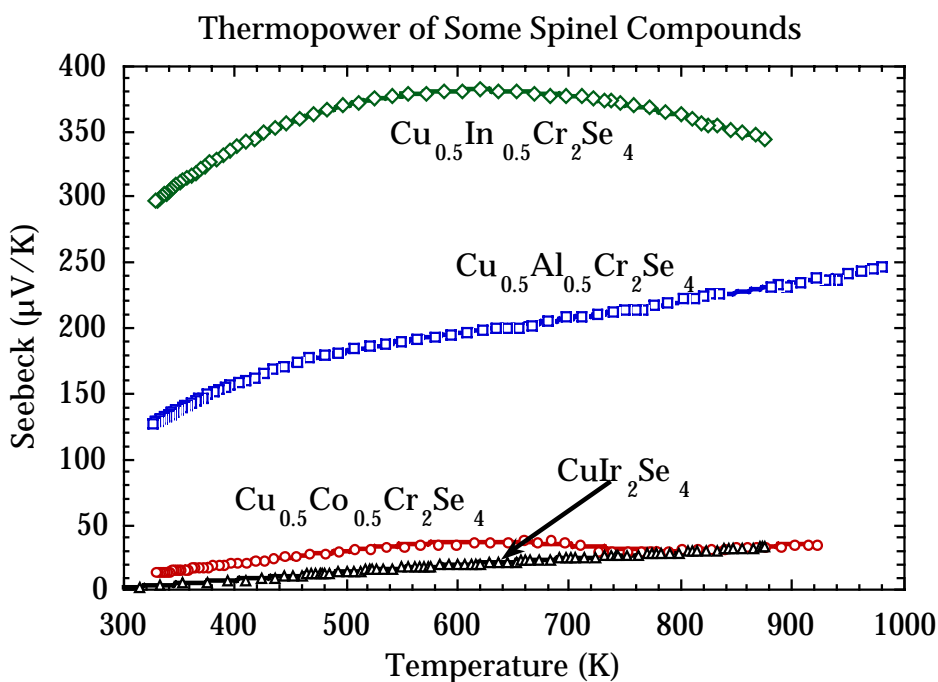
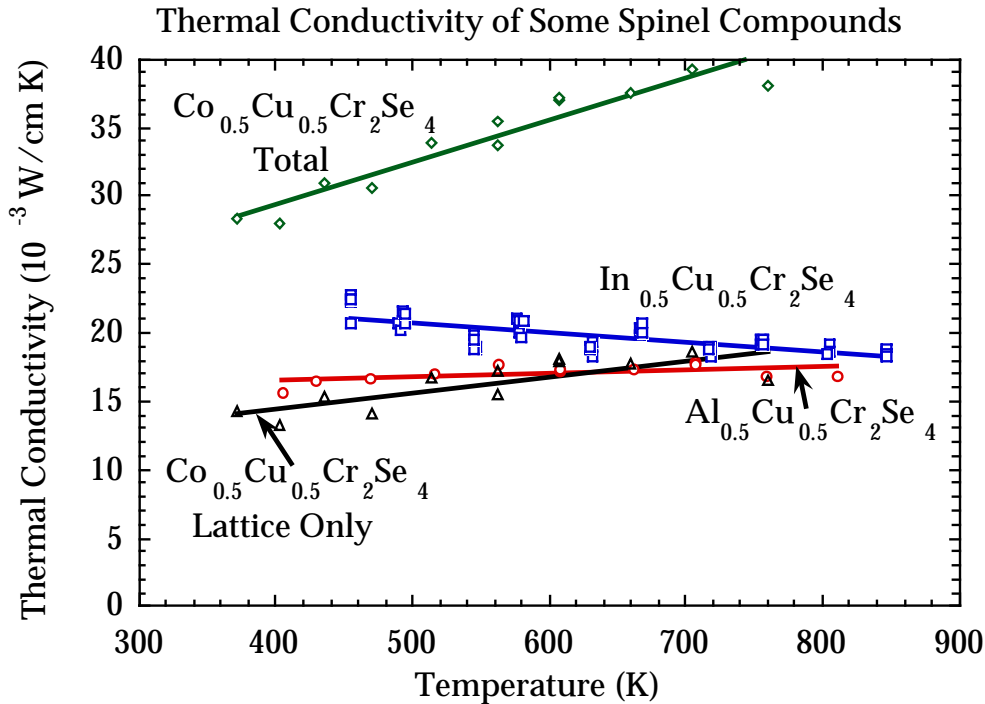


Figure 4. Thermopower of some Spinel compounds.



**Figure 5. Thermal Conductivity of some Spinel compounds.**

The thermopower of some of the spinel compounds studied is shown in Figure 4. The low resistivity samples have metallic like thermopowers that are small and linear. The higher resistivity samples can have large thermopowers like conventional semiconductors, even though transport is probably by small polarons.

The thermal conductivity  $\lambda$  is given by the sum of the electronic  $\lambda_E$  and lattice contribution  $\lambda_L$ .  $\lambda_E$  is directly related to the electronic conductivity:  $\lambda_E = L\sigma T$ , where  $L$  is the Lorenz factor. The Lorenz factor used is that typical for metals ( $2.4 \times 10^{-8} \text{ J}^2/\text{K}^2\text{C}^2$ ). The measured thermal conductivity of some spinel compounds is shown in Figure 5. The electronic contribution of the high resistivity samples ( $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{Se}_4$  and  $\text{Cu}_{0.5}\text{Al}_{0.5}\text{Cr}_2\text{Se}_4$ ) is not significant ( $< 1 \text{ mW/cm K}$ ) so the measured values are due to the lattice contribution.

The lattice thermal conductivity is relatively independent of temperature (Figure 7) indicating multiple scattering processes. Low, temperature independent thermal conductivity is found in complex structures such as glasses. Common crystalline materials have large lattice thermal conductivity that is proportional to  $1/T$  at high temperatures [21]. The quaternary spinel compounds should have lower lattice thermal conductivity because of additional alloy scattering.

The power factor and therefore figure of merit is relatively low for most of these compounds. These materials should have carriers with high effective masses ( $m^*/m \sim 4$ ), that improve the thermoelectric properties, but the very low mobility of these carriers cancels any improvement. Typical thermoelectric materials have Hall mobilities greater than  $10 \text{ cm}^2/\text{Vs}$ , whereas the materials in Table 2 have mobilities at least 10 times less. This may be due to the hopping method of transport, the increased electron scattering from the transition metal magnetic moments (magnon scattering) or due to the lower covalency of these materials as compared to conventional thermoelectric semiconductors.

The spinels with the most promising thermoelectric properties are derivatives of  $\text{CuCr}_2\text{Se}_4$ . Our next task is to select a representative series of compounds to study that may give good

thermoelectric properties with optimal doping or alloying. The series of compounds  $\text{Fe}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$  [4] and  $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  [10] have been studied in the composition ranges appropriate for thermoelectric materials with some promising results. The compounds  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  [11] should be semiconducting at  $x = 1/2$  assuming Ga is +3 and Cu is +1. The alloys should produce both p- and n-type compositions, depending on whether  $x < 1/2$  or  $x > 1/2$  respectively. We found that the related series  $\text{In}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  makes two phase samples with the major phase being  $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{Se}_4$ . A previous study of  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  [11] did not investigate bulk samples in the composition range useful for thermoelectrics. Thus we chose to examine the series  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ .

The other series of samples being studied is  $\text{Zn}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ . The parent compound  $\text{ZnCr}_2\text{Se}_4$  undergoes magnetic ordering at low temperature. From band structure calculations [22] it was suggested that in the ordered state the magnon scattering will no longer hinder the mobility, but will still have the high effective mass carriers with large thermopower.

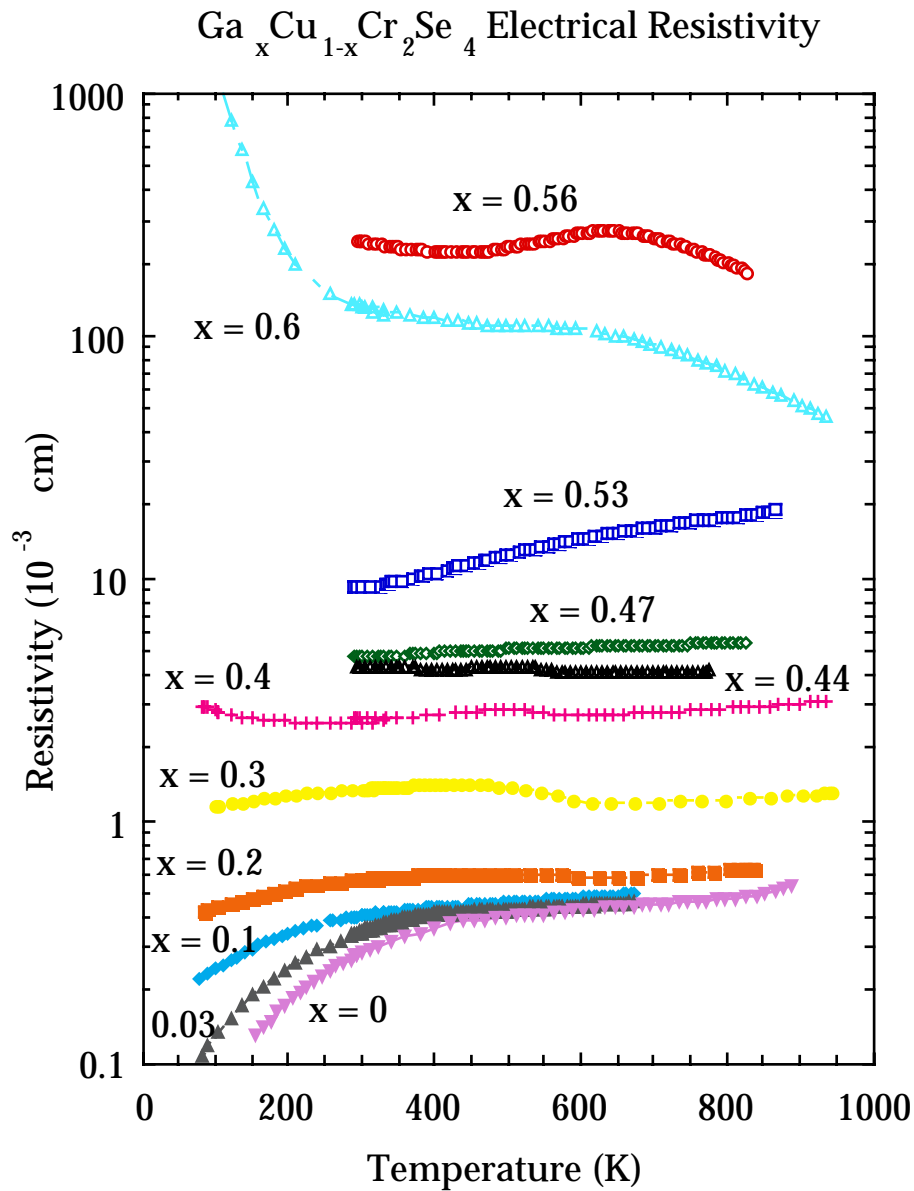


Figure 6. Electrical resistivity of  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  for various  $x$ .

The resistivity of  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  for various  $x$  is shown in Figure 6. There is a change in slope at the ferromagnetic curie temperature in samples with small  $x$ . This transition temperature decreases from 435K for  $x = 0$  to about 375K for  $x = 0.1$ . There is another transition observable in the resistivity between 475K and 525K for  $0.2 < x < 0.5$ . This other transition appears to broaden and move to even higher temperature for  $x > 0.5$ .

The thermopower of  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  for various  $x$  is shown in Figure 7. As expected, the p-type range extends up to approximately  $x < 0.5$ , gradually changing from a p-type metal with linear Seebeck coefficient to a p-type semiconductor with a peaked Seebeck coefficient. The n-type region, however, is small because the spinel structure is not stable for  $x$  above about 0.6. The room temperature thermoelectric properties are shown in Figure 8, highlighting the metal-insulator transition and p-type to n-type transition at around  $x = 0.55$ .

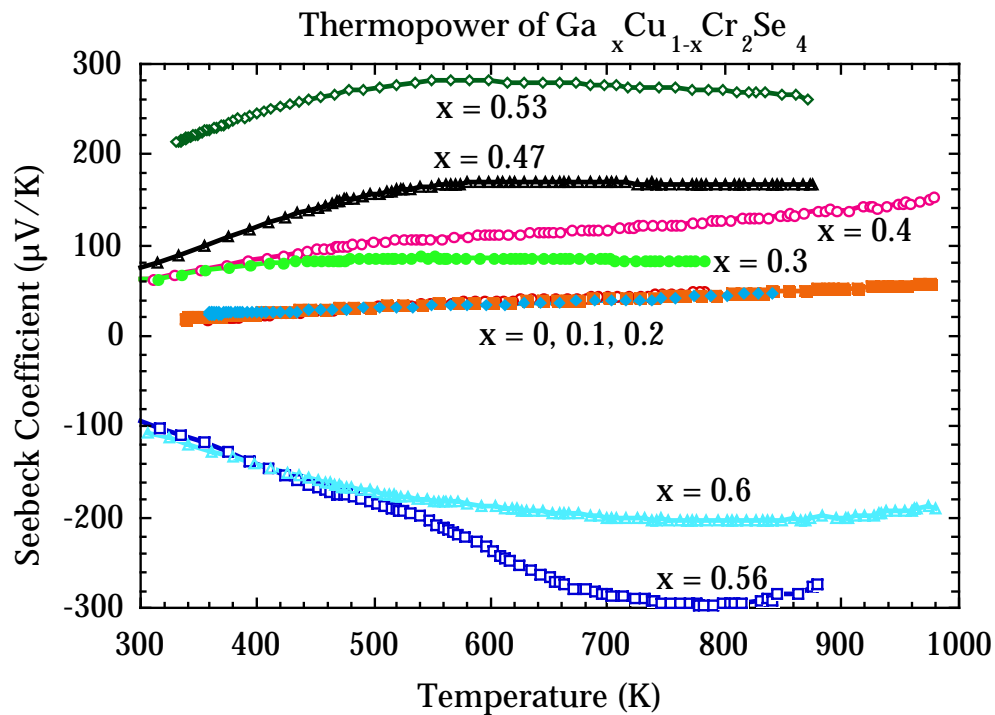
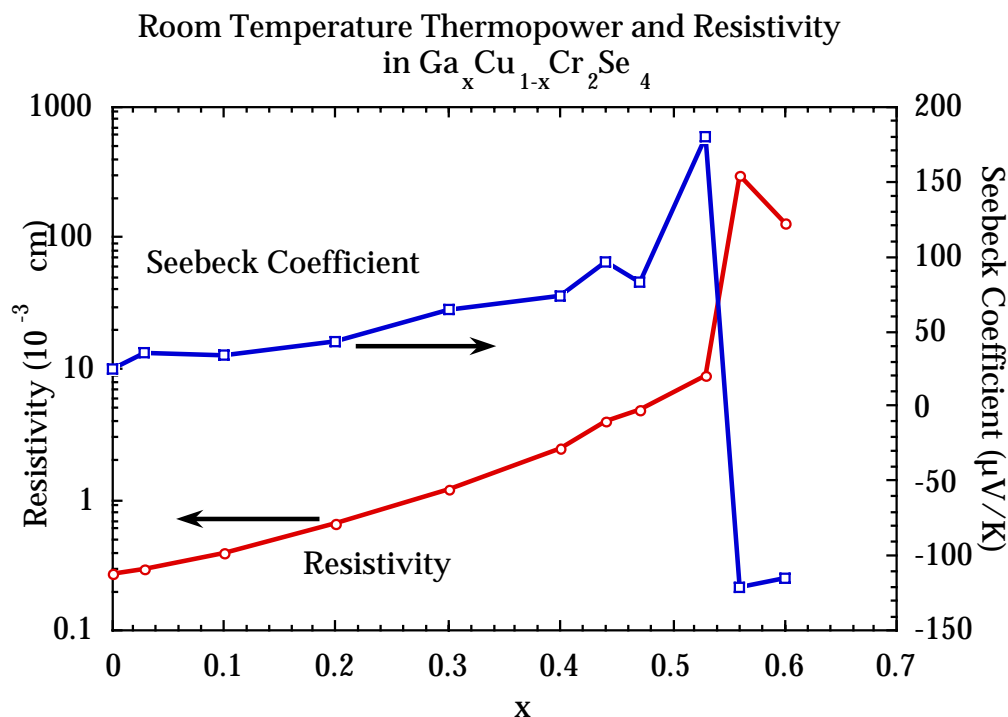


Figure 7. Thermopower of  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  for various  $x$ .





**Figure 8. Room temperature values of electrical resistivity and thermopower for  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ .**

The room temperature values are also plotted in Figure 9 along with other  $\text{A}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  compounds for comparison. The room temperature values for p-type  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  fall near the line of constant  $3 \mu\text{W/K}^2$  power factor, indicating that these compounds have about the same thermoelectric figure of merit at this temperature. This power factor is significantly higher than that previously reported for  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  [11] on single crystals and  $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  [13], but comparable to our preliminary results on  $\text{Zn}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ . The maximum figure of merit, shown in Figure 10, is about 0.1 for the p-type compounds, which is comparable to that found in the defect NiAs - type series of compounds  $\text{Fe}_x\text{Cr}_{3-x}\text{Se}_4$  [20].

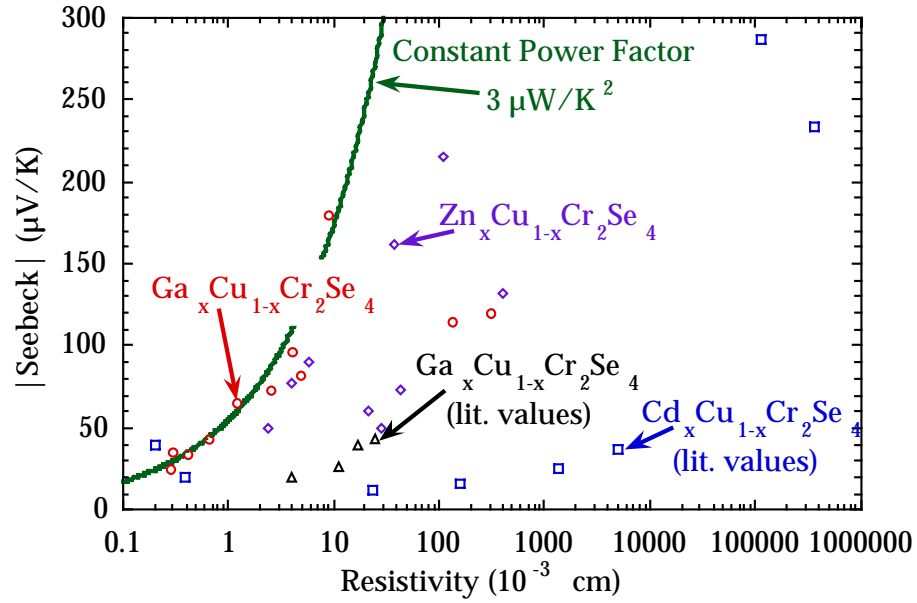


Figure 9. Room temperature values of electrical resistivity and thermopower for various  $A_xCu_{1-x}Cr_2Se_4$ . Samples with a high power factor ( $\alpha^2\sigma$ ) are to the upper left, those with a low power factor to the lower right. A iso-line of constant power factor is shown. The literature values are obtained from [11, 13].

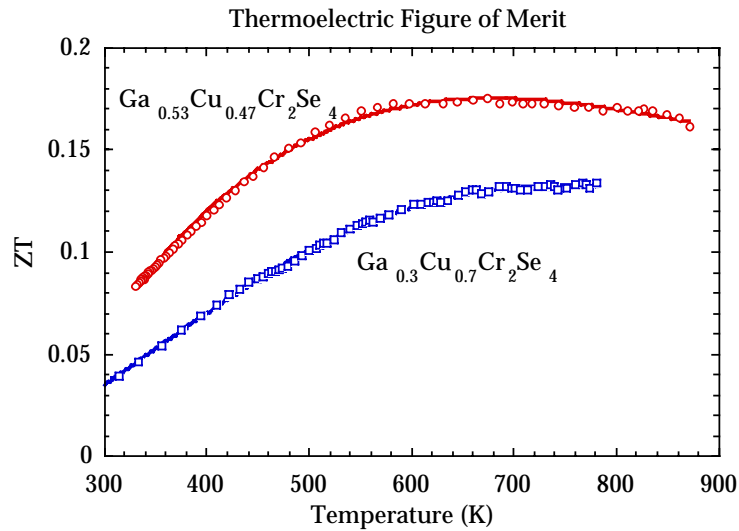


Figure 10. Thermoelectric figure of merit, ZT, for  $x = 0.3, 0.53$  in  $Ga_xCu_{1-x}Cr_2Se_4$ .

## Summary

A variety of spinel sulfides and selenides were examined for high thermoelectric figure of merit. Reported thermoelectric properties and the existence of known compounds helped guide the selection of materials to reexamine. Many showed low, glass-like thermal conductivities. Most compounds not containing chromium were eliminated due to their strongly ionic character (sulfides and rare earth selenides). Others show a variety of electronic properties from metals to small polaron semiconductors, with low carrier mobilities. A representative series of compounds  $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$  has been studied to examine the doping region of interest for thermoelectric applications. Both p- and n-type compounds have been found; the maximum figure of merit  $ZT$  is of order 0.1.

We would like to thank A. Zoltan, L. D. Zoltan, S. Chung, and A. Borshchevsky for their help on this project. This work was carried out at the Jet Propulsion Laboratory-California Institute of Technology, under contract with NASA and supported by the U. S. Defense Advanced Research Projects Agency, Grant No. E407.

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