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Electrical conductivity, thermopower, and Hall effect of Ti_3AlC_2, Ti_4AlN_3, and Ti_3SiC_2

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In this paper we report on the thermopower and electrical conductivities of $Ti_4AlN_{2.9}$ and $Ti_3Al_{1.1}C_{1.8}$ in the 300–850 K temperature range. We also measured the room temperature Hall effect in Ti_3SiC_2, $Ti_4AlN_{2.9}$, and $Ti_3Al_{1.1}C_{1.8}$. Based on these results we conclude that holes are the majority carriers at room temperature in $Ti_3Al_{1.1}C_{1.8}$ and $Ti_4AlN_{2.9}$. At higher temperatures free electrons contribute to the transport properties. Ti_3SiC_2 is a mixed conductor wherein the concentrations and mobilities of the free electrons are, respectively, equal to those of the holes over an extended temperature range. The high conductivity of Ti_3SiC_2 is due to the presence of a large concentration of charge carriers. The lower conductivity of $Ti_3Al_{1.1}C_{1.8}$ is due to a dearth of charge carriers. The even lower conductivity of $Ti_4AlN_{2.9}$ is attributed to a reduced mobility, most probably due to vacancy scattering of the charge carriers.

I. INTRODUCTION

The phases with the general formula $M_{N+1}AX_N$, where $N=1-3$, M an early transition metal, A an A-group element (mostly IIIA and IVA), and X, either C and or N, are structurally related.[1–9] In these compounds, hexagonal nets of pure A-group element layers are interleaved with $Ti_{N+1}X_N$ layers. And whereas, over 50 phases with $N=1$, are known to exist,[1] to date, only three phases with $N=2$ have been identified: Ti_3SiC_2,[4] Ti_3GeC_2,[5] and Ti_3AlC_2.[6,7] More recently, we reported on a phase,[8,9] $Ti_4AlN_{2.9}$, with $N=3$, that is also structurally related in that pure Al layers are interleaved with four layers of near-close packed Ti.

Over the past few years, we have shown that these ternary carbides and nitrides represent a class of solids that possess an unusual combination of properties.[10–23] They are anomalously soft (Vickers hardness values from 2 to 4 GPa) for transition-metal carbides and nitrides, and are all readily machinable with regular high-speed tool steels with no lubrication or cooling required. They are all good thermal and electrical conductors.

More specifically, Ti_3SiC_2, $Ti_4AlN_{2.9}$, and $Ti_3Al_{1.1}C_{1.8}$ are elastically stiff[18] (Young's moduli$>$300 GPa), damage and thermal shock tolerant, and behave quasiplastically in compression.[14–17] Above ≈1000°C, they are quite plastic.[10–12,14,15] The electrical resistivities ρ of these phases were measured in the 100–300-K range and found to decrease linearly with decreasing temperature.[10,12,14,15] These results are summarized in Table I, together with the results of Li, Sato, and Watanabe[24] for Ti_3SiC_2. Of the three, $Ti_4AlN_{2.9}$ is the least conductive and Ti_3SiC_2 the most. Also included in Table I are the results for pure Ti.[25–28]

The Debye temperatures of Ti_3SiC_2, $Ti_4AlN_{2.9}$, and $Ti_3Al_{1.1}C_{1.8}$ are comparable and relatively high[20] (>700 K). The density of states $N(E_F)$ near the Fermi level E_F are comparable, substantial, and, on a per Ti-atom basis, are 0.83, 0.86, 0.63 $(\mathrm{eV\,Ti\,atom})^{-1}$ for Ti_3SiC_2, $Ti_4AlN_{2.9}$, and $Ti_3Al_{1.1}C_{1.8}$, respectively.[20] These values are roughly half those of pure metallic Ti $(1.44\ \mathrm{eV\,Ti\,atom})^{-1}$.

Thermally Ti_3SiC_2 and $Ti_4AlN_{2.9}$ are quite comparable to stoichiometric TiC.[13,19] Rietveld analysis of neutron diffraction data indicate that the Si and Al atoms in Ti_3SiC_2 and $Ti_4AlN_{2.9}$ vibrate with significantly higher amplitudes than the other atoms in the structure. Furthermore, the vibrations of the Si atoms, especially at higher temperatures in Ti_3SiC_2 are significantly higher than those of Al in $Ti_4AlN_{2.9}$.

Apart from these preliminary conductivity results, very little information exists concerning their electrical properties. Very recently we showed that the absolute thermopower Θ of Ti_3SiC_2 is essentially zero over at least the 300–850 K temperature range.[21] This unique and unusual response prompted us to measure Θ for $Ti_3Al_{1.1}C_{1.8}$ and $Ti_4AlN_{2.9}$. The stoichiometries of the compounds tested are the ones that yielded predominantly single phase samples.[14,15] In this work, we report on Θ and ρ of these two phases in the 300–850 K temperature range. Additionally, we report on the room temperature Hall effect of these phases and Ti_3SiC_2.

II. EXPERIMENTAL PROCEDURE

Single phase samples of Ti_3SiC_2, $Ti_3Al_{1.1}C_{1.8}$, and $Ti_4AlN_{2.9}$ were cut, using a low-speed saw with water as a lubricant, into the parallelepiped specimens measuring $\approx 2\times 2\times 20\ \mathrm{mm}^3$. The fabrication details and microstructural details can be found elsewhere.[10,14,15] The starting powders for the Ti_3SiC_2 samples were titanium hydride (−325 mesh, 99.5%, Timet, Henderson, AZ), silicon carbide (−325 mesh, 99.5%, Atlantic Engineering Equipment, Bergenfield, NJ), and graphite ($d_m=1\ \mu$m, 99%, Aldrich Chemicals, Milwaukee, WI). The electrical conductivity σ and Θ of each composition was measured on the same sample, using a dc four-probe technique and a heat pulse technique,[29] respectively. All the electrical connections were made with 0.2-mm-thick Pt wires and Pt paste. Further details can be found in Ref. 29.

All measurements were carried out in an Ar atmosphere (the oxygen partial pressure of which was $\approx 10^{-5}$ atm). The applied currents for the conductivity measurements were

TABLE I. Summary of electrical properties of $Ti_4AlN_{2.9}$, Ti_3SiC_2, and $Ti_3Al_{1.1}C_{1.8}$. Also included are the results for Ti.

Compound	ρ_0 ($\mu\Omega$ m)	$d\rho/dT$ ($\mu\Omega$ m K^{-1})	α (K^{-1})	Temp. range (K)	Ref.
$Ti_3Al_{1.1}C_{1.8}$	0.3871 ± 0.0068	0.000 95	$0.002\,45\pm0.000\,26$	300–850	This work
	0.345	0.001 07	0.0031	120–300	14
$Ti_4AlN_{2.9}$	2.64 ± 0.017	0.000 9	0.000 34(0.000 01)	300–620	This work
	2.0	0.001 5	0.000 75	120–300	15
Ti_3SiC_2	0.2273 ± 0.0035	0.000 75	0.003 28(0.000 01)	300–850	This work
	0.222	0.000 89	0.004	120–300	12
	0.21	0.000 9	0.004 3	298–1073	24
Ti	0.465	0.002 1	0.004 5	77–300	25
	0.492	0.002	0.004 1	4–300	26
	0.400	0.001 7	0.004 25	300–1100	27
	0.478	0.001 7	0.003 9	196–1000	28

in the 10–100 mA range (through a cross-sectional area of $\sim 2\times2\ mm^2$). All the specimens displayed very stable and reproducible signals of voltage drop and thermovoltage up to 775–825 K depending on composition. Above these temperatures, the signals became unstable for reasons that are not immediately clear. One possibility could be the incipient oxidation of the specimen surfaces. The oxygen partial pressure of the Ar gas used is significantly higher than the equilibrium oxygen partial pressure at which these compounds oxidize.

The Hall coefficients R were measured at room temperature in low electric and magnetic ($H=8$ kG) fields. The samples tested were in the form of rectangular parallelepipeds. Ohmic contacts were made by vapor chemical deposition of pure Cu.

The uncertainty associated with conductivity measurement was on the order of 1%, which mostly stems from the error of the geometric factor of the specimens. The thermopower was determined typically within ±0.3 μV/K. The as-measured thermopower of each specimen was later corrected against the absolute thermopower of Pt (Ref. 30) to obtain the absolute thermopower of the specimen itself. The estimated errors in R are $\approx$10%.

III. RESULTS AND DISCUSSION

The temperature dependencies of ρ and Θ of $Ti_3Al_{1.1}C_{1.8}$ and $Ti_4AlN_{2.9}$ are plotted in Figs. 1(a) and 2, respectively. Also included in Fig. 1(a), for comparison purposes, are the corresponding values for Ti_3SiC_2 (Ref. 21) and Ti metal.[28] Like Ti_3SiC_2, the conductivities of $Ti_4AlN_{2.9}$ and $Ti_3Al_{1.1}C_{1.8}$ are metalliclike and can be represented by an equation of the type

$$\rho=\rho_0[1+\alpha(T-300)], \tag{1}$$

where ρ_0 is the resistivity at 300 K, and α is the temperature coefficient of resistivity. A least squares fit of the data yields the α and $d\rho/dT$ values listed in Table I. The agreement between our previous results[15] and this work is good for $Ti_3Al_{1.1}C_{1.8}$ [Fig. 1(a)].

For reasons that are not clear, the agreement is not as good for $Ti_4AlN_{2.9}$. Furthermore, in contrast to $Ti_3Al_{1.1}C_{1.8}$,

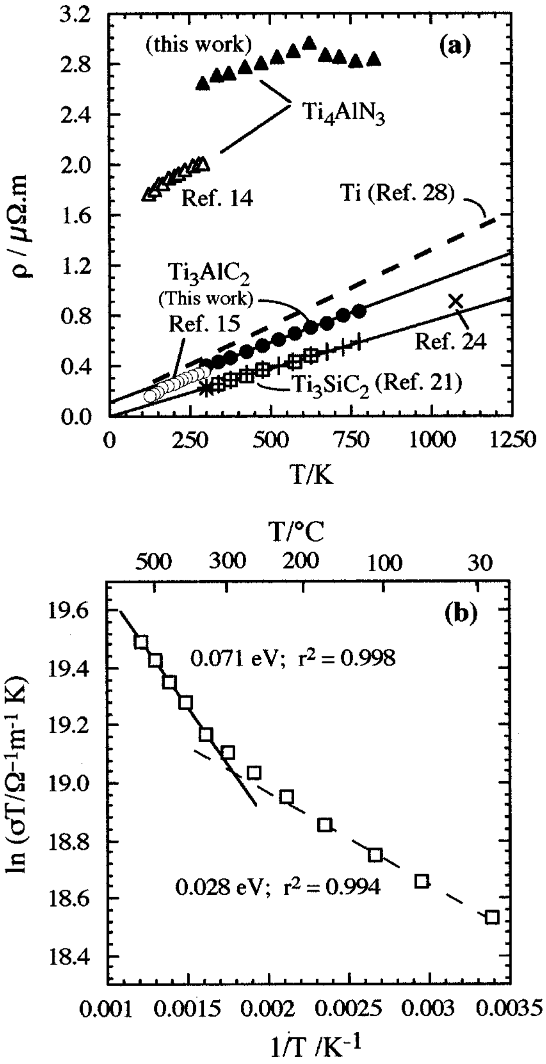

FIG. 1. (a) Temperature dependencies of the resistivities of $Ti_3Al_{1.1}C_{1.8}$ and $Ti_4AlN_{2.9}$ measured in this work and those previously determined. Also included are data for Ti_3SiC_2 and Ti. (b) Arrhenian plot of conductivity data for $Ti_4AlN_{2.9}$. The activation energy changes from 0.028 to 0.71 eV at $\approx$ 300 °C. The r^2 value from the least squares fit of the data is also shown.

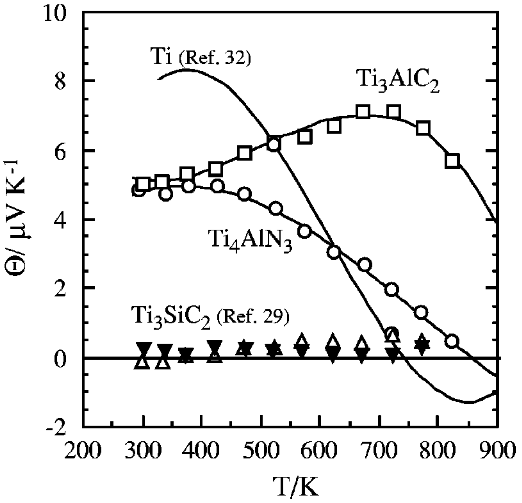

FIG. 2. Temperature dependence of absolute thermoelectric power Θ of $Ti_3Al_{1.1}C_{1.8}$ and $Ti_4AlN_{2.9}$. Also included are values for Ti_3SiC_2 (Ref. 21) and polycrystalline Ti (Ref. 31).

where ρ increases monotonically with temperature, ρ of $Ti_4AlN_{2.9}$ appears to reach a maximum around 620 K above which it drops slightly. This behavior, together with the fact that the value of its conductivity is marginal between metallic and semiconducting, led us to suspect the presence of a small gap. To test this hypothesis the conductivity data were replotted as an Arrhenian plot of $\ln \sigma T$ vs $1/T$, which resulted in two straight-line segments with a knee in between [Fig. 1(b)]. The activation energies of the low and high temperature segments are 0.028 and 0.071 eV, respectively. Based on these results, it is reasonable to conclude that the decrease in resistivity at the higher temperatures is due to an increased contribution of free electrons; a conclusion supported by the variations in Θ with temperature discussed below.

From Fig. 1(a), it is clear that the residual resistivity, or resistance at 0 K, of $Ti_4AlN_{2.9}$ is substantially higher than either Ti_3SiC_2 or $Ti_3Al_{1.1}C_{1.8}$. Given the fact that the three compounds have very comparable structures, Debye temperatures, and $N(E_F)$, this difference must be ascribed to the scattering of the holes by the N vacancies present in $Ti_4AlN_{2.9}$.[9] The residual resistivities of Ti_3SiC_2 and $Ti_3Al_{1.1}C_{1.8}$ are low indicating the presence of few defects.

In contrast to the residual resistivities which are functions of impurity or defect content, and for which the scatter is large, the scatter in $d\rho/dT$ is much less (Table I, column 3). Here again this result is not too surprising, given that the Debye temperatures of the ternaries are comparable.[20] Note that $d\rho/dT$ for Ti is roughly double that of the ternaries, reflecting its lower Debye temperature.

At room temperature, the Θ values of Ti_3AlC_2 and $Ti_4AlN_{2.9}$ are positive and increase, initially slightly, with increasing temperature, after which they decrease toward zero. This behavior, while comparable to that of metallic Ti,[31] is in stark contrast to Ti_3SiC_2, for which Θ is essentially zero over the entire temperature range examined.[21] Based on these results there is little doubt that $Ti_3Al_{1.1}C_{1.8}$ and $Ti_4AlN_{2.9}$ are *p*-type conductors at room temperature. With increasing temperatures, however, the contributions of free electrons become more important.

This conclusion is consistent with the fact that the *R* values for Ti_3AlC_2 and $Ti_4AlN_{2.9}$ are positive at room temperature (Table II). A crude interpretation of the Hall data can be made if a single band and a spherical Fermi surface are assumed. The hole concentration *p* can be estimated from the formula $p = 1/R_e$, where it was further assumed that the anisotropy and scattering factors are both equal to unity. Based on the *R* values, the hole concentration in $Ti_4AlN_{2.9}$ is roughly twice that in $Ti_3Al_{1.1}C_{1.8}$ (Table II). This result is in reasonable agreement with the ratio (3.4) of the cube of the density of states, $N(E_F)$, expressed in $J^{-1}\,m^{-3}$, determined from low-temperature heat capacity measurements of the two compounds.[20]

Knowing *p*, the mobility of the holes μ_p can be calculated from the conductivity expression assuming that the holes are

TABLE II. Summary of electrical transport parameters as calculated from room temperature conductivity and Hall measurements determined in this work. Also included are the results for TiC_x and Ti for comparison purposes.

	R $(10^{11}\ m^3/C)$	σ_{300} $[(M\Omega\, m)^{-1}]$	μ_ρ $[10^5 m^2 (V\, s)^{-1}]$	μ_n $[10^5 m^2 (V\, s)^{-1}]$	p $(10^{28} m^{-3})$	n $(10^{28} m^{-3})$	Refs.
Ti_3SiC_2	± 0	4.5	$\approx 6^a$	$\approx 6^a$	24	24	This work
			10^b	10^b	14	14	
$Ti_3Al_{1.1}C_{1.8}$	7 ± 1	2.75 ± 0.2	$\approx 19 \pm 0.3$		9 ± 1		This work
$Ti_4AlN_{2.9}$	3.5 ± 1	0.23 ± 0.5	0.8 ± 0.3		18 ± 5		This work
Ti	-0.05 to -4.5	2.0 to 2.05		4.3 to 9		15 ± 1	26
	$+2.8 \pm 0.9$						27
	-2.0						32
	-1.06 to $+1.02$						33
	-2.4	2.5		5		31	34
$TiC_{0.928}$	-155	0.57		89.6		0.4	36
$TiC_{0.939}$	-150	0.613		92		0.416	36
$TiC_{0.969}$	-166	0.735		122		0.38	36
$TiC_{>0.969}$	-150	1.05		158		0.4	36
$TiC_{0.95}$	-261	0.645		168		0.24	35
$TiC_{0.92}$	-167	0.58		97		0.37	35

[a] Calculated from Eq. (5) using data for $Ti_3Al_{1.1}C_{1.8}$.

[b] Calculated from Eq. (5) using data for $Ti_4AlN_{2.9}$.

the dominant charge carriers. The mobilities of $Ti_4AlN_{2.9}$ and $Ti_3Al_{1.1}C_{1.8}$ are, respectively, 0.8×10^{-5} and 19×10^{-5} m^2/V s. Note that the ratio of the calculated mobilities, 22.5, is in good agreement with the ratio of conductivities extrapolated to 50 K, viz., 27.

The situation for Ti_3SiC_2 is slightly more complicated because it most probably conducts by both electrons and holes.[21] The simplest interpretation of the negligible values of Θ over the extended temperature range measured is that $n\approx p$ and $\mu_p\approx\mu_e$, the electron mobility. Since R for a mixed conductor (two-band model) is given by

$$R=\frac{p-nb^2}{e\,(p+nb)^2}, \tag{2}$$

where b is the ratio of the mobilities, μ_e/μ_p. It follows that if indeed, $n\approx p$ and $\mu_p\approx\mu_e$, for Ti_3SiC_2, its R should fluctuate around 0. Four samples of Ti_3SiC_2 were tested, three gave negative R values and one a positive R value, in agreement with the assumptions made. In another set of experiments the Hall coefficient was below the detectability of the equipment. It is important to note here that similar fluctuations in the absolute value of R are well documented for metallic Ti (see Table II). These fluctuations have been assumed to result from the balancing effect of both holes and electrons in the overlapping $4s$, $4p$, and $3d$ bands of Ti. The scatter and variations in the R values for Ti are much greater than the variations in its resistivity values because the former depends on the difference, $p\,\mu_p^2-n\,\mu_n^2$, while the latter on the sum, $p\mu_p+n\mu_e$.

When the R values are sensitive to small variations in defect structure and/or small deviations in chemistry, i.e., when the system is in a mixed n/p regime, they cannot be used to estimate the number of carriers. To solve for the latter, the following assumptions are made. In the free electron model the number of electrons is proportional to cube of $N(E_F)$, when it is expressed on a per unit volume. It follows that the room temperature conductivity of Ti_3SiC_2 is given by (assuming $n=p$ and $\mu_e=\mu_p$)

$$\sigma_{\mathrm{Si}}\approx e\,n\,\mu_e+e\,p\,\mu_p\approx 2\,e\,\mu_p^{\mathrm{Si}}\xi N^3(E_F)_{\mathrm{Si}}, \tag{3}$$

where ξ is a constant. Similarly, for $Ti_3Al_{1.1}C_{1.8}$,

$$\sigma_{\mathrm{Al}}\approx e\,\mu_p^{\mathrm{Al}}\,\xi\,N^3(E_F)_{\mathrm{Al}}. \tag{4}$$

Given the structural and chemical similarities, it is reasonable to assume that the constants ξ are equal, in which case

$$\frac{\sigma_{\mathrm{Si}}}{\sigma_{\mathrm{Al}}}=\frac{2\mu_p^{\mathrm{Si}}N^3\,(E_F)_{\mathrm{Si}}}{\mu_p^{\mathrm{Al}}N^3(E_F)_{\mathrm{Al}}}=\frac{2\mu_p^{\mathrm{Si}}}{19\times10^{-5}}\left(\frac{3.5}{2.53}\right)^3=\frac{4.5}{2.75}. \tag{5}$$

Solving for μ_p^{Si} yields $\approx5.9\times10^{-5}$ m^2/(V s), from which it follows that: $n\approx p\approx24\times10^{28}\,\mathrm{m}^{-3}$. An identical analysis using the data for $Ti_4AlN_{2.9}$ instead of $Ti_3Al_{1.1}C_{1.8}$ yields the following parameters: $\mu_p^{\mathrm{Si}}\approx10\times10^{-5}$ m^2/(V s); $n\approx p\approx14\times10^{28}\,\mathrm{m}^{-3}$. Note that the first yields 5.7 electrons per Ti atom, while the latter, yields 3.33 electrons per Ti atoms. The actual value probably lies somewhere in between.

A perusal of the results shown in Table II indicate that Ti_3SiC_2 is the most conductive because both n and p are high and both contribute to the conductivity. The slightly lower mobility of the carriers in Ti_3SiC_2 is probably due to the scattering of the Si atoms, that tend to vibrate more in that structure[13] than the Al atoms do in $Ti_4AlN_{2.9}$.[19] According to Table II, the conductivity of $Ti_3Al_{1.1}C_{1.8}$ is depressed because of a reduction in the number of charge carriers. Given that E_F in $Ti_3Al_{1.1}C_{1.8}$ falls in a local minimum in the total density of states (DOS),[39] this result is not too surprising. In contradistinction, E_F Ti_3SiC_2 occurs near a local maximum.[37–40] Last, $Ti_4AlN_{2.9}$ is the least conductive, not because of lack of carriers—its DOS at E_F is higher than either Ti_3SiC_2 or $Ti_3Al_{1.1}C_{1.8}$ (Ref. 20)—but because the mobility of those carriers is low, presumably due to scattering by vacancies. It is fairly well established that at low temperature vacancies in nonstoichiometric transition metal carbides and nitrides are potent scatterers of electrons.[35,36]

A comparison of the shape of the total DOS curves of Ti_3SiC_2, $Ti_3Al_{1.1}C_{1.8}$, or $Ti_4AlN_{2.9}$ with those of Ti indicate many similarities. It is thus instructive to compare the results listed in Table II, to the corresponding parameters for Ti.[26,27,32–34] For example, based on Berlincourt's results[26] the average room temperature mobility of the electrons in Ti ($\approx7\pm2\times10^{-5}$ m^2/V s) is comparable to that of Ti_3SiC_2. In Ti, $n\approx15\times10^{28}\,\mathrm{m}^{-3}$, which translates to ≈2.6 electrons per Ti atom.

The low relative conductivity of near stoichiometric TiC_x results from a dearth of carriers, rather than low mobilities (Table II). Despite being thermally quite comparable,[13] the electron mobility in TiC_x is significantly higher than in Ti_3SiC_2. This is noteworthy because it probably reflects the scattering potency of the Si atoms in Ti_3SiC_2 whose amplitude of vibrations are quite high relative to the other atoms.[13] The same argument can explain the fact that the mobility of the charge carriers in Ti and Ti_3SiC_2 are comparable despite the latter having a much higher Debye temperature. It is also consistent with the fact that the mobility is higher in $Ti_3Al_{1.1}C_{1.8}$ than in Ti_3SiC_2 despite their identical structures; the Al atoms are better bound in $Ti_3Al_{1.1}C_{1.8}$ than the Si atoms in Ti_3SiC_2.

Finally, the number of carriers per Ti atom in Ti_3SiC_2 and $Ti_4AlN_{2.9}$ are ≈4; a not unreasonable result given the valence of Ti and the excellent shielding of the Ti atoms as determined from x-ray photoemission spectroscopy.[22,23] This result notwithstanding, it is hereby acknowledged that the calculations carried out herein are somewhat crude and do not take into account many factors that are known to influence the electrical transport, such as anisotropy of the Fermi surface and that of scattering that the theoretical calculations predict.[32,35,39,40] These caveats notwithstanding, these calculations do serve a useful purpose in shedding light on the conductivity mechanisms operative in these novel ternary carbides and nitrides, and should be useful in tailoring their electrical and thermal properties.

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