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REFRACTORY MATERIALS FOR HIGH-TEMPERATURE THERMOELECTRIC ENERGY CONVERSION

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INTRODUCTION

The maximum efficiency (η) for the conversion of heat to electrical energy using a thermoelectric couple with a hot junction at temperature T_1 and a cold junction at temperature T_0 is given by [1]

$$\eta = \frac{\text{electrical energy delivered to external circuit}}{\text{energy consumed from heat source}}$$

$$= \left(\frac{T_1 - T_0}{T_1} \right) \left(\frac{M-1}{M+T_0/T_1} \right) \quad (1)$$

where $M = [1 + Z_c (T_1 + T_0) / 2]^{1/2}$ (2)

Z_c is a materials parameter called the figure of merit of the thermocouple. It is a function of the Seebeck coefficients, α_1, α_2 , the electrical resistivities, ρ_1, ρ_2 , and the total thermal conductivities, κ_1, κ_2 , of the two respective legs of the thermocouple:

$$Z_c = \frac{(\alpha_1 - \alpha_2)^2}{[(\rho_1 \kappa_1)^{1/2} + (\rho_2 \kappa_2)^{1/2}]^2} \quad (3)$$

The thermodynamic efficiency of an ideal reversible engine, the first factor of Eq. (1), is reduced by the irreversible losses of heat conduction and Joule heating in the thermocouple, accounted for in the second factor. Obviously, increasing the hot junction temperature, T_1 , and the figure of merit, Z_c , both increase the conversion efficiency. For the purpose of comparing individual materials, it is convenient to define a figure of merit for a single material:

$$Z = \frac{\alpha^2}{\rho \kappa} = \frac{\alpha^2 \sigma}{\kappa}, \quad (4)$$

where σ is the electrical conductivity. The dimensions of Z are deg^{-1} . Thermoelectrics are generally characterized by the value of the dimensionless parameter ZT , since the efficiency is a function of $(T_1 + T_0)Z$.

Semiconductors, as distinct from metals or insulators, have the highest Z values. Therefore they are used for thermoelectric energy conversion. As illustrated in Fig. 1, metals are excellent conductors but their Seebeck coefficients are too low. Insulators can have high Seebeck coefficients but are too electrically resistive. A good compromise can be made by choosing highly-doped semiconductors with α and σ values intermediate between the properties of insulators and metals.

In the search for refractory semiconductors for high-temperature thermoelectric devices, materials with both itinerant and hopping-type charge transport are under study. With itinerant motion the charge carriers are generally viewed as quasi-free particles which undergo occasional

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scattering events. These carriers are associated with mobilities greater than or comparable to $1 \text{ cm}^2/\text{V}\cdot\text{sec}$. In the hopping-type semiconductors, the charge carriers are localized at atomic sites [2]. The equilibrium positions of the surrounding atoms are displaced to positions that are consistent with the presence of the localized carrier. That is, the carriers form small-polarons. Small-polarons move between sites via multi-phonon assisted hopping. The resulting mobilities tend to rise with temperature to a maximum which is typically comparable to $1 \text{ cm}^2/\text{V}\cdot\text{sec}$. Both classes of semiconductor have yielded promising candidates for high-temperature thermoelectric devices. We shall review the distinguishing features of promising materials of both classes: Itinerant motion in rare-earth chalcogenides and small-polaron hopping in boron-rich borides.

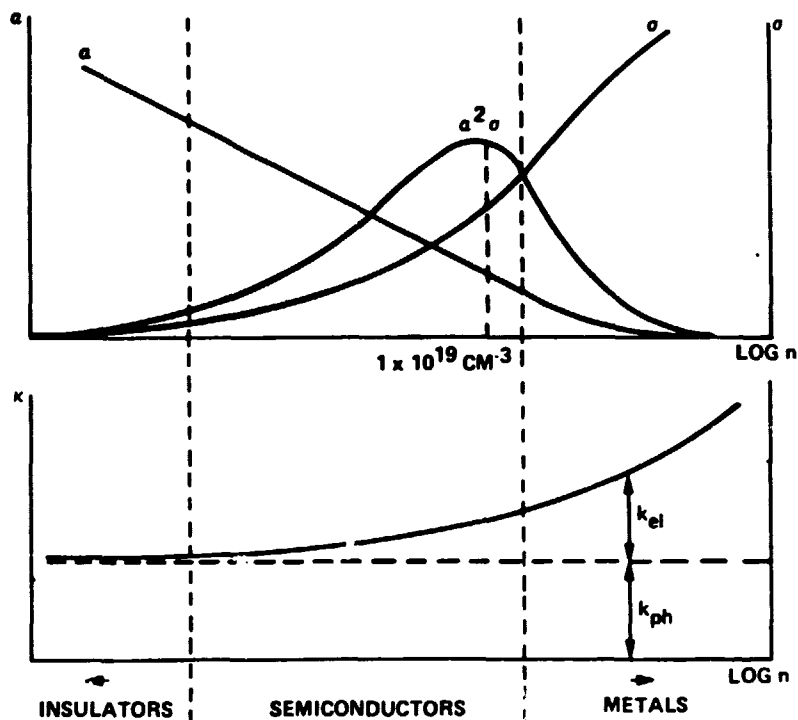


Fig. 1. Typical Variation of Thermoelectric Properties with Charge-Carrier Concentration.

Rare Earth Chalcogenides: Structure

One class of refractory materials receiving considerable attention for high temperature thermoelectric energy conversion is the rare-earth chalcogenides. Rare-earth chalcogenides generally form the following binary compounds: RX , $R_3X_4 - R_2X_3$, RX_2 , where R represents the rare-earth and X the chalcogenide atoms S , Se , or Te . The RX compounds crystallize in a fcc NaCl structure, the $R_3X_4 - R_2X_3$ form solid solutions in a bcc (Th_3P_4) tetragonal or orthorhombic structure, and the RX_2 compounds usually are found in either cubic or tetragonal structure [3].

Only compounds in the homogenous range $R_3X_4 - R_2X_3$ have been extensively investigated for high-temperature thermoelectric applications. There are often two and sometimes three polymorphic modifications of the solid solutions $R_3X_4 - R_2X_3$: (i) a low-temperature ($< 900 - 1000^\circ\text{C}$) orthorhombic α -phase; (ii) an intermediate temperature (900 to 1300°C) tetragonal β -phase; and (iii) a high temperature ($> 1300^\circ\text{C}$) cubic (Th_3P_4) metastable γ -phase. It is not clear whether these polymorphic forms occur over the whole compositional range from R_2X_3 to R_3X_4 . Furthermore, with the exception of La_2S_3 it is not yet resolved whether β -phase R_2X_3 is truly a polymorph or is representative of a ternary compound involving oxygen [4].

In the cubic Th_3P_4 structure it is convenient to designate the unit cell as $4(\text{R}_{3-x}\text{V}_x\text{X}_4)$ where V is a rare-earth vacancy. For R_2X_3 compounds 1/3 of the 12 rare-earth sites are vacant, i.e., $x = 1/3$. For the R_3X_4 compounds there are no vacant sites, i.e., $x = 0$. Each $\text{R}_{3-x}\text{V}_x\text{X}_4$ unit provides $(1-3x)$ electrons for conduction. Hence R_2X_3 ($x = 1/3$) is an insulator and R_3X_4 ($x = 0$) is a metal.

Degenerate semiconductors for thermoelectric applications are produced from hot-pressed powders or single crystals of R_{3-x}X_4 compounds with varying degrees of excess rare-earth atoms. These stoichiometries have been found to yield degenerate wide band-gap semiconductors, with electrical conductivities of $\sim 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$, carrier concentrations greater than $\sim 10^{20} \text{ cm}^{-3}$ and charge carrier mobilities of ~ 1 to $10 \text{ cm}^2/\text{volt sec}$.

Thermal Conductivity

Lattice thermal conductivities (κ_{ph}) of the R_{3-x}X_4 compounds are generally low, in the range 0.005 to 0.01 watt/cm-deg. [5] This results from three factors. First, the Debye temperatures, θ_{D} , are anomalously low fractions of the melting temperatures, $\theta_{\text{D}} \sim 200\text{-}400 \text{ K}$, with $\kappa_{\text{ph}} \propto \theta_{\text{D}}^3$. Secondly, these are complicated crystal structures with a fairly large number of atoms (28) per unit cell. Since there are 3 acoustic modes per unit cell the number of optic modes, is $N = 3(28) - 3$. Examination of the dispersion curves, ω versus k , shows that these optic modes of vibration have very low propagation velocities. Therefore, the majority of phonons are optical and have low velocities. Thirdly, the rare-earth ion vacancies produce disorder which inhibits thermal transport.

Electronic Transport

Rare-earth chalcogenides behave as highly-degenerate n-type semiconductors over most of the composition range R_3X_4 to R_2X_3 . However, the large values of effective mass and the small values of the mobility suggest that the conduction band is somewhat narrow.

For itinerant motion a material's figure of merit is essentially determined by a simple combination of its transport parameters. Namely, $Z \propto m^{*3/2} \mu / \kappa$, where m^* and μ are, respectively, the carrier's effective mass and mobility and κ is the material's thermal conductivity [6]. Since the thermal conductivities of the R_{3-x}X_4 materials are close to one another it is only the numerator of this expression for Z which varies much between materials. The values of m^* and μ for various R_3X_4 compounds have been tabulated [7]. In Table I these values and the $m^{*3/2} \mu$ -product are listed.

TABLE I. Properties of Rare Earth Chalcogenides (R_3X_4) at Room-Temperature

Compound	Mobility, μ ($\text{cm}^2/\text{v-s}$)	Effective Mass, m^*	$m^{*3/2} \mu$
La_3S_4	3.5	3.6	23.9
Ce_3S_4	3.1	2.8	14.5
Nd_3S_4	3.2	2.7	14.2
Pr_3Se_4	2.6	2.6	10.9
La_3Te_4	11.5	1.8	27.8
Ce_3Te_4	4.2	2.1	12.8
Pr_3Te_4	6.2	1.6	12.5
Nd_3Te_4	5.0	2.0	14.1

It is seen that $\text{La}_{3-x}\text{Te}_4$ has the greatest potential for high Z values.

This is supported by the work of Golikova and Rudnik [8] who claim that La_3Te_4 has the highest Z of the $R_{2-x}X_4$ compounds: $0.91 \times 10^{-3} \text{deg}^{-1}$ at 1150 K. Zhuze et al. [7], quote a Z of 0.53×10^{-3} at 1400 K. From Lugev and Smirnov's data [10] on higher conductivity La_3Te_4 ($\sim 3000 \text{ ohm}^{-1}\text{cm}^{-1}$ at 300 K) it appears that $Z \sim 2.5 \times 10^{-4} \text{deg}^{-1}$ at ~ 700 K. This and other thermoelectric data on rare-earth chalcogenides [7]-[13] is illustrated by the plot of ZT versus T in Fig. 2.

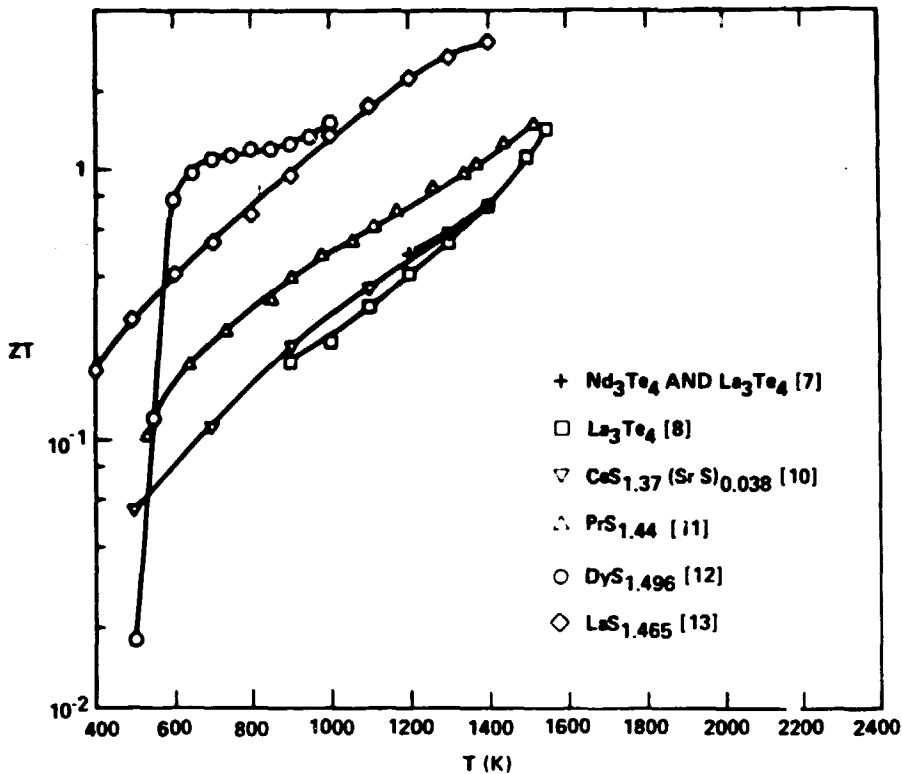


FIG. 2. ZT Values for Rare-Earth Chalcogenides.

BORON-RICH BORIDES: SMALL-POLARON HOPPING

In the discussion so far we have considered materials which conduct by the itinerant motion of charge carriers. However, in other materials, electronic conduction is by the phonon assisted hopping of charge carriers from site to site, i.e., small-polaron hopping.

The mobility associated with the (adiabatic) hopping of a small polaron between equivalent sites at temperatures above (or comparable to) the phonon temperature is [14]

$$\mu = \frac{e\upsilon}{kT} a^2 \exp \left[- \frac{E_A}{kT} \right] \quad (5)$$

Here υ is the characteristic vibrational frequency, a is the intersite separation, and E_A is the hopping activation energy. The Seebeck coefficient associated with the hopping of a small-polaron is [15][16]

$$\alpha = \frac{k}{e} \left\{ \ln \left[\frac{2(1-c)}{c} \right] + AT \right\} \quad (6)$$

where c is the fraction of sites which are occupied by a carrier; A is a constant.

The first term is just the entropy per charge associated with the carrier concentration c . The second term arises from the heat transported with a carrier as it hops between inequivalent sites [11] [12]. For hopping between equivalent sites it vanishes. With a temperature independent carrier concentration, as in mixed valence semiconductors, the Seebeck coefficient and the electrical conductivity can both increase with temperature for hopping between inequivalent sites. Consequently, Z can increase significantly with temperature. In fact, Z is often considerably larger than the upper limit set by Heikes and Ure [17] from considerations of hopping solely between equivalent sites.

The boron-rich borides are materials in which the charge carriers form small polarons [12]. We will consider below the performance of some boron-rich borides as high temperature thermoelectric materials.

Boron and Borides Structures

Boron forms refractory compounds with a large number of elements. Several of these compounds have been investigated for high-temperature thermoelectric conversion. Elemental boron is also highly refractory (m.p. $\sim 2500^\circ\text{C}$). Boron is generally accepted to have at least three and possibly four allotropic forms [18]: α -rhombohedral ($R\bar{3}m$, $a = 5.075 \text{ \AA}$, $\alpha = 58^\circ 06'$); β -rhombohedral ($R\bar{3}m$, $a = 10.145 \text{ \AA}$, $\alpha = 65^\circ 17'$); α - or I - tetragonal ($P4\bar{2}m$, $a = 8.75 \text{ \AA}$, $c = 5.06 \text{ \AA}$) which may not correspond to an allotropic form of pure boron and β - or II- or III- tetragonal ($P4_122$, $a = 10.12 \text{ \AA}$, $c = 14.14 \text{ \AA}$). Boron also occurs in the amorphous form. Many boron-rich borides are structural analogs of one of these four boron crystalline modifications. These structures are characterized by arrangements of boron icosahedra bound either to one another or to isolated atoms by directed bonds.

Four borides have been the object of intense investigation for thermoelectric applications, i.e., β -boron (105 atoms/unit cell), $B_{14}Si$ (isostructural with β -boron and with 105 atoms/unit cell), B_xC (an analog of α -boron with 15 atoms/unit cell) and α - AB_{12} (same space group as β or II tetragonal boron with from 187 to 208 atoms/unit cell). ZT -data [19]-[23] for these materials is shown in Fig. 3.

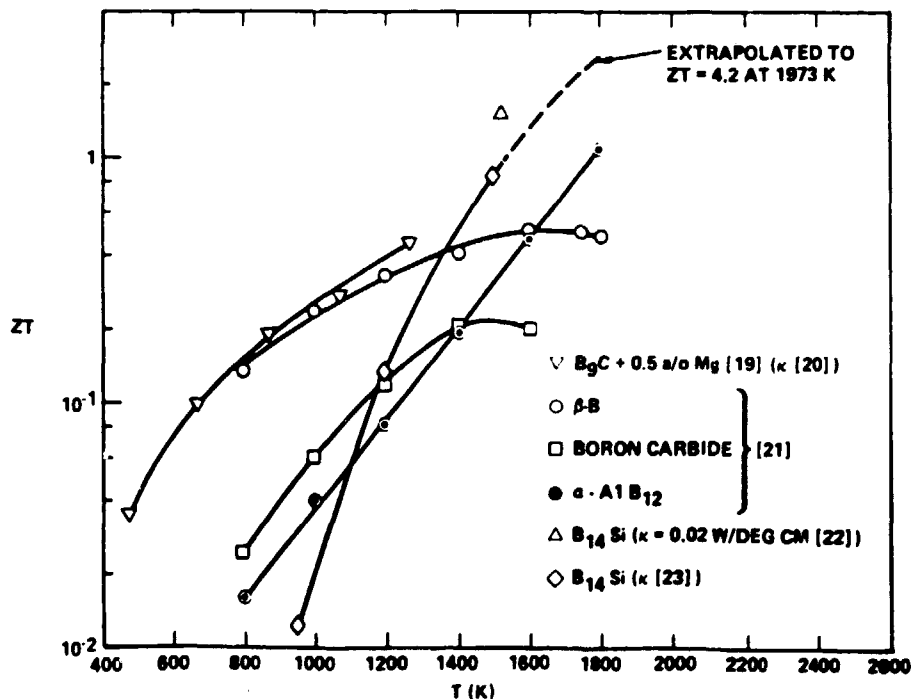


FIG. 3. ZT Values for Boron and Boron-Rich Borides

Thermal Conductivity

The low values for the high temperature thermal conductivity of boron and boron-rich borides has been attributed to the complexity of the crystal structure [24] [25]. In β -boron, for example, with 105 atoms/unit cell there are 3 acoustic branches and 312 optical branches. As the temperature is increased the relative contribution of the high frequency (optical) modes to the thermal conductivity increases and can exceed the contribution by the acoustic modes. The group velocity of optical vibration is much lower than the sound velocity so that their contribution to the thermal conductivity is low. Because of the structural complexity of boron and its analogues, groups of atoms in equivalent positions are widely separated. For an optical wave to propagate a definite phase relation must exist between these like groups of atoms. Perturbations arising from other groups of atoms in the path of propagation cause a breakdown of phase relationships i.e., independent local vibrations occur. Thus, the nature of phonon propagation in boron-rich borides closely approaches that in amorphous solids with correspondingly low values.

Electronic Transport

Boron and all of the boron-rich borides described above display a common striking and significant feature. Namely, the Seebeck coefficients and the electrical conductivities both rise with increasing temperature over a wide temperature range. This appears only to be interpretable as due to the hopping of charge carriers between inequivalent sites. This conclusion is supported by experiments showing that the Hall mobility in measured borides is low ($\lesssim 1 \text{ cm}^2/\text{V-sec}$) and increases as the temperature increases. The spin densities obtained from E.S.R. and magnetic susceptibility measurements in boron carbides [26] [27], also indicate carrier densities whose magnitudes are consistent with the low mobilities associated with hopping motion. The values of the hopping activation energies (e.g., 0.15 eV in $B_{10}C$) generally indicate that the hopping is multiphonon, i.e., that due to small polarons. The inequivalence of the sites involved in the hopping in the borides is readily understandable in terms of the structures of these borides. That is, sites in the icosahedra and those in the intericosahedral linkages have different coordinations.

CONCLUSIONS

The excellent theoretical work carried out two decades ago adequately explained the transport behavior and effectively guided the development of thermoelectric materials of high conversion efficiencies of conventional semiconductors (e.g., SiGe alloys). The more significant contributions involved the estimation of optimum doping concentrations, the reduction of thermal conductivity by solid solution doping and the development of a variety of materials with $ZT \sim 1$ in the temperature range 300 K to 1200 K. It was also shown that $ZT \sim 1$ is not a theoretical limitation although, experimentally, values in excess of one were not achieved.

In the recent years work has continued with emphasis on higher temperature energy conversion. A number of promising materials have been discovered in which it appears that $ZT > 1$ is realizable. These materials can be divided into two classes: (i) the rare-earth chalcogenides, which behave as itinerant highly-degenerate n-type semiconductors at room-temperature, and (ii) the boron-rich borides, which exhibit p-type small-polaronic hopping conductivity.

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