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Review
Electrical properties of high-temperature oxides, borides, carbides, and nitrides

C. C. WANG, S. A. AKBAR, W. CHEN, V. D. PATTON
Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210, USA

High-temperature materials including oxides, borides, carbides, and nitrides encompass all types of conductors: metallic, semiconducting, and ionic. Their electrical conductivities are generally very sensitive to impurities regardless of the type of conductor. For large band-gap materials, which includes most of the oxides, the conductivities at low temperatures are frequently dominated by impurities or dopants, and intrinsic conduction only becomes significant above a temperature which depends largely on the level of dopant, the band gap, and the defect structure of the base material. The borides, carbides, and nitrides of transition metals are metallic conductors with conductivities and temperature coefficients of resistivity comparable to that of their parent metals.

1. Introduction

This review focuses on material systems which have been and are being investigated for their potential use as thermistors (thermally sensitive resistors) at high temperatures. The meaning of "high temperature" and the value assigned to it varies among industries and disciplines; however, in this paper the term refers to temperatures in excess of 1700 °C, the upper limit of platinum-based thermocouples. Because a high melting point is the most important criterion in the selection of materials for high-temperature thermistor applications, the refractory compounds of oxides, borides, carbides, and nitrides are included in this review; silicides are not included due mainly to (i) their relatively lower melting points, and (ii) the loss of oxidation protective coating (SiO_2) at temperatures above 1700 °C. Because the emphasis is on high-temperature applications, low-temperature thermistors will not be included; Fagan and Amarakoon [1, 2] have recently reviewed this area.

It is well known that refractory compounds based on the oxides, nitrides, carbides, and borides exhibit an unusual combination of physical and chemical properties and are of great interest in technology and science. However, this review will focus only on the electrical conductivity. Electrical conduction, being a kinetic phenomenon, will be discussed with regard to its temperature dependence. For thermistor applications, the temperature dependence represents the materials' sensitivity to temperature change. Because thermistor materials require insensitivity to the probing environment, the influence of atmosphere on the electrical conductivities of the materials will also be discussed.

In general, electrical conduction in high-temperature materials is a function of temperature and composition (non-stoichiometry and impurities), irrespective of the type of conduction, i.e. metallic, semiconducting or ionic. Also, electrical conduction in most solids is not so much sensitive to the structure of the material itself as to defects or impurities in the structure. Many of these compounds are characterized with wide composition range and can have a highly variable defect concentration on the metal and/or non-metal sublattices (i.e. significant deviation from stoichiometric composition). A number of compounds, especially carbides and nitrides, cannot be obtained under normal conditions with a strictly stoichiometric composition [3–5]. Deviation from stoichiometry may also come from incongruent vaporization of the constituent components, which may result in the decomposition of the compound at elevated temperatures. This obviously will have a dramatic effect upon the chemical and physical properties of the materials. Therefore, the stability of high-melting point materials will also be included, if possible, in the discussion of electrical properties. The high-temperature materials discussed here encompass all types of electrical conduction. Therefore, we will briefly summarize the characteristics of each type of conduction. Then, problems associated with the measurements of electrical properties of high-temperature materials, which greatly affect the interpretation of the conduction mechanism, will be summarized.

The present review is not intended to be, in any sense, an extensive survey of the electrical properties of high-temperature materials. There are handbooks and monographs available for the various materials discussed (for example, [3–14]). For convenience, owing to the similarity of the latter types of compounds in their physical and chemical properties, the material systems are grouped into two: (1) oxides, and (2) borides, nitrides, and carbides. We have adopted different strategies in the review of these two groups of materials simply because it may make the review too unwieldy if done otherwise. For the oxides, we have focused on a few of the better known compounds in the hope of giving a more complete account of their properties. For the borides, nitrides, and carbides, only a general account of the characteristics of the electrical and related properties is given. Because the literature on the electrical properties of these high-temperature materials is far too large to be included in this paper, the references cited are mainly to make specific points. And, because much information can be found in some monographs and handbooks, when appropriate, we shall refer to these sources rather than to the original publications. Note also that although in some cases grain-boundaries can significantly influence electrical properties, no distinction with respect to the aggregate state (mono- or poly-crystalline) of the reviewed materials will be made. This is due primarily to the lack of systematic study of the effect of grain-boundaries in the literature.

2. Temperature dependence of electrical conduction

The electrical conduction in solids is generally determined by two parameters: carrier concentration, n (the number of carriers of charge q per unit volume), and carrier mobility, μ. In terms of n and μ, the electrical conductivity, σ, can be expressed as

$$\sigma = nq\mu \tag{1a}$$

For solids with more than one type of charge carrier, the electrical conductivity is the sum of the partial conductivities, σ_i, of all the charge carriers: electrons, holes, cations, and anions, and can be expressed as

$$\begin{aligned} \sigma &= \sum \sigma_i \\ &= \sum n_i q_i \mu_i \end{aligned} \tag{1b}$$

The overall conductivity can be either electronic, ionic or a mixture of the two, depending on the relative magnitude of the product of n_i and μ_i of all carriers. In predominantly ionic compounds such as oxides, charge transport is, in principle, characterized by both ionic and electronic conduction. Often one type of charge carrier dominates the charge transport, but transition to the other types of conduction may occur at certain temperatures and/or atmospheres as a result of a change in composition or stoichiometry of the solids [15, 16].

In Equation 1, both the carrier concentration and mobility can contribute to the temperature dependence of electrical conduction. For materials with a band gap, both processes may be thermally activated and therefore the temperature dependence of electrical conduction can generally be described by an Arrhenius-type equation

$$\sigma = \sigma_0 \exp\left(-\frac{Q}{kT}\right) \tag{2}$$

where Q is the activation energy of electrical conduction, and σ_0 is the pre-exponential factor. It is important to note that σ_0 may be a function of temperature and, therefore, Equation 2 may be written as

$$\sigma = CT^{\eta} \exp\left(-\frac{Q}{kT}\right) \tag{3}$$

where C is a constant, and the value of η depends on the type or mechanism of conduction. For example, η is zero for a pure non-polar semiconductor (i.e. an ideal covalent semiconductor), $+1$ for a highly ionic solid where the large polaron mechanism operates, and -1 or $-\frac{3}{2}$ for a polar ionic solid where the small polaron mechanism (hopping conduction) operates.

For a metallic solid, only electrons contribute to the electrical conduction, and the temperature dependence comes solely from the mobility term. At temperatures above the Debye temperature, the mobility decreases with temperature, owing to scattering of the conducting electrons by lattice phonons [17]. In other words, the electronic mobility is inversely proportional to the temperature. Consequently, the temperature dependence of electrical conduction, when described in terms of resistivity, ρ, takes the form

$$\rho(T) = \rho^* + \Phi T \tag{4}$$

where Φ is the temperature coefficient or the slope in the plot of ρ versus T, and ρ^* is the intercept of ρ in the limit of $T = 0$.

In general, the temperature dependence of electrical conduction comes mainly from the temperature dependence of carrier mobility and/or concentration and depends on the nature and mechanism of electrical conduction. The overall temperature dependence may give rise to either a positive or negative temperature coefficient of resistivity, α_T, defined as

$$\alpha_T = \left(\frac{1}{\rho}\right)\left(\frac{\partial \rho}{\partial T}\right) \tag{5}$$

which represents the sensitivity of the materials in response to temperature variation. Table I summarizes the α_T of the major types or mechanisms of electrical conduction in solids.

It is important to note that α_T is not a constant for a material but is a function of temperature (as indicated by the subscript T). For a metallic solid, the temperature coefficient of resistivity, α_T, can be obtained from Equations 4 and 5 as

$$\alpha_T = \Phi/\rho \tag{6a}$$

which gives rise to a positive temperature coefficient of resistivity (i.e. $\alpha_T > 0$). It can be seen that α_T for a metallic solid is inversely proportional to temperature; it becomes smaller as temperature increases. In comparison, α_T for a semiconducting solid is negative according to Equations 2 and 5

$$\alpha_T = \frac{B}{T^2} \tag{6b}$$

where $B = Q/k$. It can be seen that the magnitude of α_T is proportional to the activation energy of conduction; the larger the activation energy the greater the

TABLE I Temperature dependence of electrical conduction in solids [1, 2, 18]

α_T[a]	Conduction characteristics	Materials
Positive	Metallic	Pt, TiB_2, $MoSi_2$
	Impurity-exhausted semiconducting	Si
	Grain-boundary controlled	$BaTiO_3$ (doped, polycrystalline)
Negative	Ionic	Stabilized ZrO_2
	Predominantly p-conductor in air	Y_2O_3
	Valency-controlled semiconducting	$(NiMn)_3O_4$

[a] Temperature coefficient of resistivity.

material's sensitivity to a temperature change. Equation 6b also shows that α_T has a strong non-linear temperature dependence; it decreases with a factor of T^{-2} as temperature increases. For example, the magnitude of α_T for materials with $Q = 1$ eV is about 0.009 at 850 °C but decreases to 0.003 at 1700 °C. These characteristics suggest that a potential thermistor material must have sufficiently large activation energy so that the sensitivity, α_T, would be high enough for it to be useful at high temperatures.

However, as shown in Table I, α_T may become positive over a temperature range for semiconducting or insulating materials [1, 2, 18]. This can be found in (i) ionic polycrystalline oxides such as doped $BaTiO_3$ where the resistivity increases several orders of magnitude near the tetragonal-to-cubic phase transformation, a characteristic usually attributed to grain-boundary controlled behaviour [18], and (ii) a non-polar impurity semiconductor (e.g. doped Si) where all donors or impurities (impurity exhaustion) are ionized and, as a result, the temperature dependence comes mainly from the scattering of conduction electrons or holes.

For an ionic conductor, where the movement of ions takes place by the transport of lattice defects, the electrical conduction can also be described by Equation 3. In other words, the temperature dependence is determined by the combined effect of the concentration (intrinsic or extrinsic) and mobility of the ionic charge carriers. In general, $\eta = -1$ in Equation 3 with Q representing the activation energy of ionic conduction. It should be noted, however, that in the case of intrinsic ionic conduction, Q is the sum of the formation energy of defect (carriers) and the migration energy (mobility). For ionic conduction via defects created extrinsically, Q accounts for the migration energy and, possibly, the dissociation energy of impurities and defects at lower temperatures or high dopant concentrations.

The overall transport property of a compound may depend on the type and concentration of defects contributing to the electrical conduction, both of which, however, can vary with temperature and atmosphere. Therefore, a more general form of Equation 2 may include a factor representing the influence of atmosphere on the dominant types and concentrations of defects [6, 15, 16]. In the case of semiconducting oxides, a general form can be written as

$$\sigma = CT^{\eta}P_{O_2}^{\lambda}\exp\left(-\frac{Q}{kT}\right) \qquad (7)$$

The value of λ can be positive or negative, depending on the type of charge carrier (electrons or holes), and may remain constant over several decades of oxygen pressure. At a given temperature, resistance is a function of P_{O_2} alone, and this is the basis of semiconducting-type gas sensors [19].

3. Problems associated with electrical measurement

Unfortunately, the electrical measurement of high-temperature materials are generally plagued with many difficulties and uncertainties. As a consequence, data reported for a single material may show significant scatter and even cover several orders of magnitude. This can be clearly seen from Figs 1 and 2, which summarize the results of electrical measurements reported in the literature for insulating α-Al_2O_3 [20] and metallic TiB_2 [21], respectively. The problems associated with electrical measurements in insulating materials have been addressed in a number of studies on α-Al_2O_3 [22–26]. For metallic conducting compounds of nitrides, borides and carbides, the problems have been summarized by Toth [3] and can be clearly seen in some systematic studies on TiB_2 [21] and TaC [27].

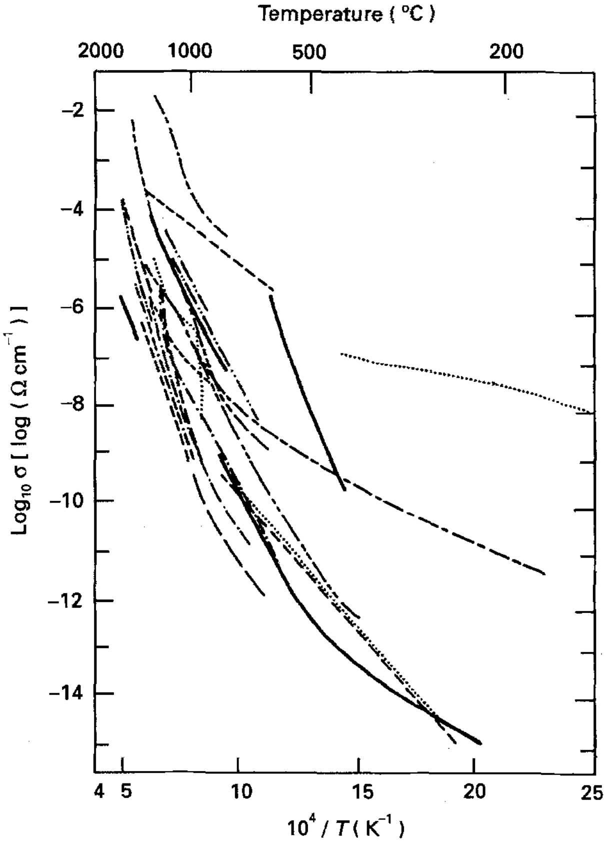

Figure 1 Reported literature data for the electrical conductivity of α-Al_2O_3 [20].

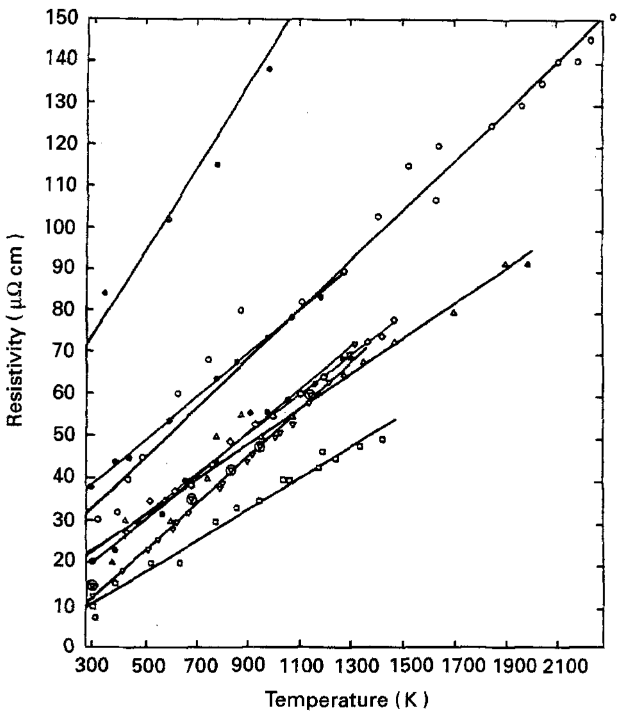

Figure 2 Reported literature values for the electrical resistivity of polycrystalline TiB_2 [21].

For large band-gap materials, such as α-Al_2O_3, MgO and BeO, conductivity measurements become more difficult because the conduction of bulk material can be over-ridden by the conduction via surface (at low temperatures) and gas phase (at high temperatures) [28–33]. Also, the measurements are more sensitive to impurities, and are frequently dominated by impurities acting as donors or acceptors. Other variables, which can cause significant scattering in the results are uncertainty in composition (non-stoichiometry, type and level of impurities), and difference in measurement method and heat-treatment history. The latter variable may become significant when factors such as grain-boundary effects and defect association or ordering are involved.

For nitrides, borides, and carbides, variability in the results of electrical measurements, and other physicochemical properties (melting point, vaporization, and chemical reactivity), arises mainly from uncertainty of composition, including non-stoichiometry and impurities. Owing to the large mutual solubility of these compounds, impurities of non-metal elements can be easily incorporated into the system during sample preparation or testing at high temperatures. For example, the Hf–C system is very difficult to make oxygen free [10, 34], and the carbides of the transition metals may go through a change in the conduction behaviour from metallic to semiconducting when the carbon content varies [35–38]. Other variability in the results for these compounds is caused by differences in residual porosity and empirical formulas for correcting the effect of this porosity [3].

In summary, difficulties associated with materials and experiments give rise to scatter and discrepancies in data found in the literature and make the analysis of data, and, thus, interpretation of the electrical conduction behaviour a formidable task. The discrepancies come mainly from compositional uncertainties, particularly impurities and non-stoichiometry, for both good and poor conductors, as demonstrated in Figs 1 and 2. In view of this, the data presented in this paper are provisional and serve mainly for the purpose of qualitative discussions. And, to avoid unnecessary controversy, the discussions on semiconducting materials will be based on the activation, Q, or band-gap energy, E_g, of electrical conduction.

4. Oxides

Oxides, which are predominantly ionic compounds, are the most exploited high-temperature materials. In general, the overall transport properties of oxides are determined by the defects formed in response to both impurities and deviations from stoichiometry, and are influenced by both the temperature and oxygen pressure [15, 16]. As a result, an oxide may be predominantly an electronic conductor under one circumstance, while becoming an ionic conductor under another, and, under some circumstances, may have electronic and ionic carriers contributing simultaneously to the overall electrical conductivity, resulting in mixed conduction [15, 16]. However, most oxides usually have only one type of carrier dominating the charge transport, and therefore, can be conveniently categorized either as electronic or ionic conductors. Listed in Table II are 13 well-known high-temperature oxides; properties shown are melting points, band gap (room temperature), or activation energies; stabilities of some of the refractory oxides at high temperatures are given in Table III. In the following sections these oxides are conveniently categorized into three groups: (1) fluorite, (2) perovskite and (3) other refractory oxides.

4.1. Fluorite-type oxides

Among the oxides, ZrO_2, ThO_2, CeO_2, and HfO_2 are characterized by their high melting points (> 2600 °C). Phase relations and electrical conductivities of these oxides have been reviewed by Etsell and Flengas [39]; their mixed conduction behaviour has been reviewed by Heyne [15] and Tuller [16]. Among them, pure ZrO_2 and HfO_2 are of monoclinic structure at low temperatures, and undergo monoclinic to tetragonal phase transformation upon heating. When doped with appropriate amounts of lower valence cations, such as calcium, magnesium, yttrium and rare-earth elements, a cubic phase of the fluorite structure can be stabilized to room temperature. The predominant intrinsic defects in fluorite oxides are known to be oxygen vacancies and oxygen interstitials. The band gaps of these systems are reported to be about 5 eV [40] and, as a consequence, have few intrinsic electrons and holes even at elevated temperatures. The density of electronic carriers of ThO_2, for example, is calculated to be only of the order of $10^{12}\,cm^{-3}$ at 1500 °C [15]. In contrast, a large concentration of oxygen vacancies can form when doped with lower valence cations at levels of 10–15 mol %

TABLE II Selected properties of some refractory oxides

Materials	Melting point (°C) [6, 11]	Q or E_g (eV)	Remarks on Q or E_g	Ref.
α-Al_2O_3	2015	~ 10	Band gap	[140, 141]
BeO	2550	> 10	Band gap	[142]
MgO	2800	~ 7.7	Band gap	[143]
CaO	2614	~ 7.7	Band gap	[144]
Y_2O_3	2410	> 4	Band gap	[145, 146]
Cr_2O_3	2266	⩾ 3.6	Band gap	[102, 147]
$LaCrO_3$[a]	~ 2500	0.1–0.3	Activation energy of p-type	[77]
$SrZrO_3$	2750	2.6[b]	Activation energy of p-type	[88]
ZrO_2[c]	> 2000	0.65–1.4	Activation energy of O^{2-}	[39, 44]
ThO_2[a]	3300	~ 1	Activation energy of O^{2-}	[39, 54]
HfO_2[c]	> 2700	~ 1	Activation energy of O^{2-}	[39, 73]
$CaZrO_3$[d]	2370	~ 2.0	Activation energy of O^{2-}	[89, 91–95]
CeO_2[a]	2400	< 1	Activation energy of O^{2-}	[39]

[a] Doped.

[b] Activation energy for conduction measured between 800 and 1200 °C [88].

[c] Stabilized.

[d] $CaZrO_3$ with excess of CaO or ZrO_2 [93, 94].

TABLE III Stability of some refractory oxides at elevated temperatures [9, 14, 15]

	Vapour pressure at 1927 °C (atm)	Temperature for appreciable volatilization (°C)		Principal limitation
		Vacuum	Air	
BeO	10^{-7}	2100	2400	Volatile in $H_2O_{(g)}$
MgO	10^{-2}	1600	1900	Reacts with water to form $Mg(OH)_2$
α-Al_2O_3	10^{-1}	–	1750	–
CaO	10^{-2}	1700		Reacts with water to form $Ca(OH)_2$
ZrO_2	10^{-6}	> 2300	–	–
CeO_2	–		1875	Multivalent of cerium ions
ThO_2	10^{-8}	> 2300		Radioactivity

(e.g. $\sim 5 \times 10^{21}$ cm^{-3} for CaO-doped ZrO_2 [41]). Coupled with relatively high ionic mobilities, this gives rise to predominantly ionic conduction at intermediate temperatures. A detailed analysis of the influence of the type and concentration of dopants on the ionic conductivity is given by Kilner and Steele [42].

Fluorite-type oxides become mixed conductors only when significant intrinsic electronic conduction appears at high temperatures or non-stoichiometry occurs under extremely high or low oxygen pressures. In other words, the range or span of temperatures at which the conduction is predominantly ionic depends on the type and concentration of dopant as well as oxygen pressure. Fig. 3 shows a schematic representation of the domain boundaries of stabilized zirconia as a function of oxygen pressure and temperature [15]. The domain boundary is defined as the temperature or oxygen pressure at which $\sigma_{\text{ionic}} = \sigma_{\text{electronic}}$. Near and beyond the domain boundaries, electronic conduction becomes significant and the oxides exhibit mixed conduction. In Fig. 4, the dependence of the domain boundaries on three independent variables μ^* (oxygen chemical potential), $1/T$, and dopant concentration $[A^-]$ is schematically shown to emphasize the effect of dopant concentration on the domain size [15]. The interior of the tent-like structure corresponds to predominantly ionic conductivity region. This three-dimensional representation demonstrates that the ionic conduction domain can be extended (i.e. increase in the range of P_{O_2} and the maximum temperatures within which the conductivity of oxides remain predominantly ionic) with an increase in dopant concentration. It is worth noting that although this type of three-dimensional representation is, in principle, possible for all oxides, a distinct ionic conduction domain is likely to be found only in oxides with predominantly atomic or ionic defects (e.g. fluorite-type oxides).

Pure ZrO_2 is an insulator with a band gap of about 5 eV at room temperature [43]. When doped with lower valence cations, the electrical conductivity exhibits a maximum at or near the lowest dopant concentration required to stabilize the cubic phase, and decreases with increasing dopant concentration [39, 44]. This trend is accompanied by an increase in the activation energy for ionic conduction. For example, the activation energies of oxygen ionic conduction for CaO-doped ZrO_2 vary between 1 and 1.4 eV [45–47], increasing with the dopant concentration. For Y_2O_3-doped ZrO_2, the activation energies lie between 0.7 and 1.2 eV [39]. Similar results have been observed in ceria [48, 49] and in thoria-based oxides [50, 51]. For a given composition, the ionic conductivity of ZrO_2 doped with oxides of trivalent cations (M_2O_3) decreases as the radius of the cation

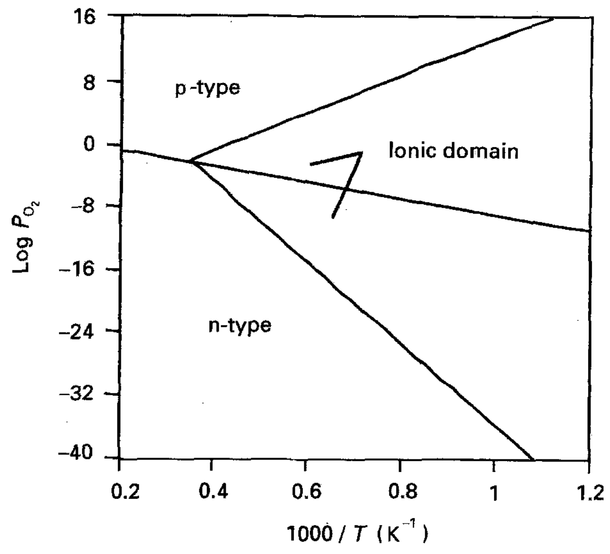

Figure 3 Schematic representation of the electrical conduction domain boundaries of stabilized zirconia as a function of oxygen partial pressure and temperature [15].

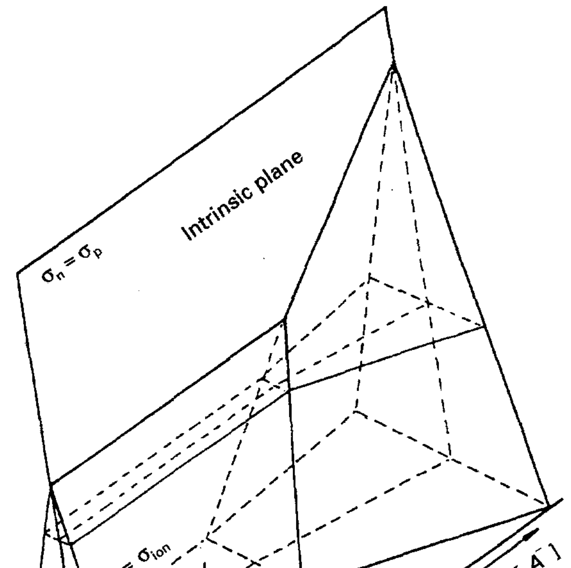

Figure 4 Dependence of the electrical conduction domain boundaries on three independent variables, μ^*, $1/T$, and dopant concentration [A^-]. The interior of the tent-like structure corresponds to predominantly ionic conductivity region [15].

increases [39]. Among the dopants for ZrO_2, CaO and Y_2O_3 are commonly utilized. One of the main uses of CaO- and Y_2O_3-doped ZrO_2 is for solid electrolytes in various devices. They are characterized by relatively high ionic conductivity at both high and low oxygen pressures. However, their usefulness has been limited by electronic conduction at elevated temperatures and reducing atmospheres. p-type electronic conduction in calcia-doped zirconia, for example, becomes significant above 1700 °C in air [52].

Pure ThO_2 has the cubic fluorite structure, but is an insulator with a band gap of 5.75 eV [53]. The ionic conductivity of pure thoria at 1000 °C is 2×10^{-6}–$4\times10^{-5}\,\Omega^{-1}\text{cm}^{-1}$ [50, 54, 55]. Doped ThO_2 systems have an activation energy of ionic conduction similar to that of ZrO_2-based oxides, but are more stable under reducing conditions [52, 56]. This makes thoria-based oxides more attractive for use in extreme reducing atmospheres and elevated temperatures. The transport properties of thoria and thoria-based solid solutions have also been reviewed by Etsell [57] and Tuller [16]. It appears that the electrolytic transition temperature, i.e. the temperature at which electronic conduction becomes significant, may be lower than that of ZrO_2-based oxides [52, 57–60]. ThO_2 doped with 7 mol % Y_2O_3, for example, loses the predominance of ionic conduction in air at temperatures above 1300 °C [57] as compared to 1700 °C for ZrO_2-based oxides (Table IV). The domain boundaries for calcia-doped ThO_2 are found to be lower in P_{O_2} (at which p-type conductivity equals that of ionic conductivity) than that of yttria-doped materials.

Analogous to ThO_2, pure CeO_2 has the cubic fluorite structure. Because cerium is a multivalent cation (+ 4, + 3), pure CeO_2 deviates greatly from stoichiometry at elevated temperatures and low oxygen pressures, and becomes an oxygen-deficient n-type conductor. Ce^{4+} ions, however, can be stabilized by lower valence cations such as Ca^{2+} and Y^{3+}. As an oxygen ion conductor, the activation energies of CeO_2-based systems have been reported to be smaller than that of stabilized ZrO_2 [61–65]. However, ionic conduction loses its predominance at temperatures much lower than that of stabilized ZrO_2 due to the reduction of CeO_2 [66–68].

Pure HfO_2 has a melting point of ~2900 °C [69]. Of the oxides, only ThO_2 has a substantially higher melting point than HfO_2. Analogous to ZrO_2, pure HfO_2 undergoes a monoclinic to tetragonal phase transformation upon heating. For HfO_2-based oxides, lower ionic conductivities have been observed but with activation energies comparable to ZrO_2-based oxides. For example, the activation energy of HfO_2 doped with 12 mol % CaO, is 1.43 eV from 800–2000 °C but the conductivity is $4\times10^{-3}\,\Omega^{-1}\text{cm}^{-1}$ at 1000 °C [70] (see Table IV). Similar to that of ZrO_2, the activation energy of ionic conduction for Y_2O_3-stabilized HfO_2 increases with dopant concentration [71–73].

In summary, for the fluorite-type oxides, CeO_2-based oxides can achieve the highest ionic conductivity via doping, while the ThO_2-based oxides can attain the lowest. Although the activation energies of ionic conduction vary with the type and concentration of dopant, they generally are about 1 eV. It appears that at high dopant concentrations the activation energy of ionic conduction increases with doping concentration for the fluorite-type oxides, which is probably due to the association or ordering of defects [42, 56].

4.2. Perovskite-type oxides

Like fluorites, perovskite-type oxides can often accommodate substantial concentrations of lower valence impurities and result in the formation of oxygen

TABLE IV Electrical conductivities of fluorite oxides with predominantly ionic conduction (Etsell and Flengas [39][a])

Oxides	Max./min. activation energy (eV)	Conductivity ($10^2\ \Omega^{-1}\,cm^{-1}$) at 1000 °C	Domain boundary[b] (°C) in air
ZrO_2	1.3 (15% CaO)/0.65 (8% Sc_2O_3)	1.5–12	1700 (CaO doped) [57]
HfO_2	1.4 (12% CaO)/0.73 (8% Y_2O_3)[c]	3–4	
ThO_2	1.7 (undoped)[d]/1.0 (8.1% Y_2O_3)	0.1–2.9	1300 (Y_2O_3 doped) [60]

[a] Major reference.
[b] Temperature at which $\sigma_{ionic} = \sigma_{electronic}$.
[c] See [73].
[d] See [74].

vacancies [75]. The defect chemistry of p-type perovskite oxides was recently reviewed by Anderson [76]. Here, three perovskite-type oxides with high-melting points, $LaCrO_3$, $CaZrO_3$, and $SrZrO_3$, are reviewed.

Lanthanum chromite, pure and acceptor-doped, shows p-type conduction by a hopping mechanism which depends weakly on temperature, i.e. the activation energy of conduction is only about 0.1–0.3 eV [77–83]. When doped with donor-type impurities such as niobium, the material shows a transition from p-type to n-type conduction as the oxygen partial pressure is lowered [84]. The substitution of either lanthanum or chromium with a divalent cation results in a p-type conduction due to the formation of oxygen vacancies or Cr^{4+} [76, 85]. Pure $LaCrO_3$ shows considerable weight loss at elevated temperatures (1700–1800 °C), especially in a moist atmosphere due to the formation of volatile $CrO_2(OH)$, but this can be greatly reduced by the replacement of chromium with other cations such as aluminium [85, 86].

Calcium zirconate, $CaZrO_3$, has an orthorhombic structure at temperatures below 1600 °C, above which it transforms to a cubic perovskite structure [87]. Undoped stoichiometric $CaZrO_3$ has been observed to be a p-type semiconductor (in air) with an activation energy of 3.3 eV over the temperature range 800–1200 °C [88], probably due to impurities. Using a two-probe d.c. technique, Anthony *et al.* [89, 90] have obtained an activation energy of conduction about 2.6 eV in the temperature range 1300–1900 °C, for which no discussion regarding the mechanism of conduction was made. However, it has been found that $CaZrO_3$ is a predominantly ionic conductor with a small excess of ZrO_2 or CaO, or when doped with oxides such as Al_2O_3, Y_2O_3 and MgO [91–95]. Two temperature regimes of ionic conduction were observed for samples doped with Al_2O_3, Y_2O_3 and MgO [91], and were attributed to phase transformation from orthorhombic to perovskite structure. In comparison to ZrO_2-based oxides, $CaZrO_3$ oxides have higher activation energies for ionic conduction (~ 2 eV), but exhibit a much lower partial electronic conductivity at temperatures near 1600 °C.

Pure $SrZrO_3$ has a melting point of 2750 °C, significantly higher than that of $CaZrO_3$ (2370 °C). A number of studies on the electrical conduction of strontium zirconate can be found in the literature [88–90, 96–98]. In general, $SrZrO_3$, doped or *unintentionally* doped, has two temperature regimes of conduction [89, 90, 96]. The results of electrical measurement in argon by Pivovar and Tolstaya-Belik [96] show that it is a predominantly ionic conductor at temperatures $\leqslant 1600$ °C, but becomes a p-type semiconductor at higher temperatures. However, Pretis *et al.* [88] found it to be a predominantly p-type semiconductor in air over the temperature range 800–1200 °C (with an activation energy of 2.6 eV). Browall *et al.* [97] have studied the effect of dopants (Yb_2O_3 and MgO) and oxygen pressures on $SrZrO_3$. They found that p-type conduction is predominant at high oxygen pressures but loses its predominance to oxygen ion conduction at lower oxygen pressures. In comparison to $CaZrO_3$, $SrZrO_3$ apparently has higher conductivity at all temperatures irrespective of the mechanism of conduction.

4.3. Other refractory oxides

For oxides with relatively large band gaps (> 4 eV), such as BeO, MgO, α-Al_2O_3, Cr_2O_3, and Y_2O_3, electrical conduction at low temperatures are dominated by impurities acting as donors or acceptors. This can be easily understood in terms of the relative concentration of impurities and intrinsic carriers in these oxides. Although modern technology has been able to reduce most impurities in oxides down to the levels of a few parts per million, impurities even as low as 1 p.p.m. can contribute donors, acceptors or other point defects of concentration on the order of $10^{16}\ cm^{-3}$. In comparison, the concentrations of intrinsic carriers are about $10^9\ cm^{-3}$ at 1000 °C for an oxide with a band gap of 5 eV [16, 99]. This suggests that intrinsic electronic conduction may become significant only at sufficiently high temperatures. Therefore, at least two temperature regimes of electrical conduction can be distinguished: (1) a low-temperature region in which conductivity depends on impurities or dopants; and (2) a high-temperature region in which "intrinsic" conduction becomes significant. The demarcation between the two regions, i.e. the transition temperature, depends on the dopants or impurities and their concentrations. In the high-temperature region, the conductivity may or may not depend on the oxygen pressure, depending on the type of "intrinsic" charge carrier formed. For example, at high temperatures (> 1200–1400 °C) the conductivity of MgO is found to be P_{O_2} dependent as the magnesium ion vacancy becomes the predominant ionic charge carrier [100–103]; the high-temperature conductivity of Cr_2O_3, however, is independent of P_{O_2} and can be simply attributed to the excitation of a carrier across the band gap [104–107].

Because α-Al_2O_3, is of great technological importance, its transport properties and defect structure have been extensively investigated. The transport properties of the oxide have been reviewed by Kröger [108] and by Dörre and Hübner [109]. The effect of dopants on the electrical properties of α-Al_2O_3 has been systematically studied by Kröger and co-workers [110–117]. Mixed conduction (ionic and electronic) is generally found in all studies, with the ratio between ionic and electronic conduction depending on oxygen pressure and type and concentration of dopants. Owing to the large band gap (~ 10 eV) and high energies of formation of various defects (> 5 eV) [118, 119], at temperatures up to 1600 °C, the electrical properties of α-Al_3O_3 are always determined by the presence of impurities [120]. Differences in the type and concentration of impurities in α-Al_2O_3 samples along with the difference in measurement methods are the major causes of scatter in reported literature data as shown in Fig. 1.

A combination of high-melting point (2550 °C), relatively low vapour pressure (10^{-6}–10^{-5} atm near 2000 °C) and electrical resistivity greater than that of alumina or magnesia makes BeO an attractive high-temperature oxide (Table III) [9]. However, it has been reported that BeO becomes volatile at high temperatures in the presence of water vapour [121]. Because of the large band gap (> 10 eV), the conductivity is very sensitive to impurities. The conductivity is generally of mixed character with the ionic contribution increasing with temperature [122–124].

MgO has a melting point higher than that of BeO (2800 °C), but is very volatile in comparison; it has a vapour pressure of 0.01 atm at 2000 °C [9]. With a large band gap of about 8 eV, at low temperatures the conductivity is dominated by impurities, and the material becomes a mixed conductor at high temperatures with a significant fraction of ionic conduction (> 1200–1400 °C) [100–103]. The results of conductivity and diffusion measurements in MgO tend to suggest a mechanism for ionic conduction involving a magnesium ion or impurity cation motion via a magnesium vacancy (see the discussions in [101, 103, 122], for example). The importance of aliovalent impurities on the electrical conductivity of MgO has been systematically studied by Sempolinky *et al.* in the temperature range 1200–1600 °C [102, 103]. They found that MgO with controlled impurity levels (320–1500 p.p.m.) of aluminium, scandium and iron is a mixed conductor with its ionic contribution increasing with the impurity concentration.

Y_2O_3 is a C-type rare-earth sesquioxide with a melting point of 2410 °C. The C-type cubic structure is almost identical to the fluorite structure but a quarter of the oxygen ions are missing on the oxygen ion sublattice, providing relatively open pathways for diffusion. Recently, the conductivity characteristics and the defect structure of Y_2O_3 have been studied and reviewed by Norby and Kofstad [125–127]. While some earlier studies on the electrical conductivity suggested cation vacancies as the dominant ionic defects in pure Y_2O_3 [128, 129], their studies showed that oxygen vacancies and interstitials were predominant. The specific conductivities and activation energies of undoped and doped Y_2O_3 reported in the literature differ greatly [98, 125–139], and this may be due to the influence of impurities and the interstitial protons introduced from the water vapour in the ambient gas, as suggested by Norby and Kofstad [125–127].

In summarizing the electrical properties of the oxides reviewed in this section, the activation energies or Q values of electrical conduction are mostly larger than 1 eV. This warrants them to have relatively high temperature coefficients of resistivity, α_T, at high temperatures. For example, at 1700 °C the sensitivity of B-type platinum-based thermocouple (defined in a similar form to that of Equation 5, with Seebeck e.m.f. replacing ρ) is about 5×10^{-6}, while the value of α_T for a thermistor material with $Q = 1$ eV is about three orders of magnitude larger.

It is important to note that although a high Q value is essential in the selection or design of oxide materials for thermistor applications, there are at least two other factors which need to be considered: atmosphere sensitivity and temperature range of operation of the device. For the oxides just reviewed, it becomes obvious that materials of high Q value may exhibit the following characteristics: (i) a high resistivity at low temperatures, which sets the lower limit of operating temperature, (ii) two temperature regimes of electrical conduction, generally observed for large band-gap materials, and (iii) a time-dependent electrical signal (voltage or current) during electrical measurement, due to polarization, slow diffusion, and non-equilibrium distribution of defects and impurity ions at low temperatures, which often results in non-reproducible operation of the device. It is, therefore, important to select or engineer (e.g. by doping) a material of reasonable Q value so that the device is operational in the desired temperature range of application. Furthermore, it is desirable that the thermistor material is insensitive to atmospheric variation such as the change of oxygen partial pressure and humidity. Y_2O_3, for example, may not be suitable for thermistor applications because the electrical conduction is found to be sensitive to humidity [125–127]. Also, according to Equation 7, the electrical conduction in oxides can be a function of oxygen partial pressure. This clearly imposes further limitations in the selection of materials for high-temperature thermistor applications.

5. Borides, carbides, nitrides

The compounds of boron, carbon, and nitrogen have attracted interest during the past decades because they provide a wide range of physical and chemical properties for various applications [3, 8, 148]. Their large affinities to and solubilities of oxygen, however,

TABLE V Melting points and band gaps for selected carbides, nitrides, and borides

Materials	Melting point (°C) [6, 9, 144]	E_g(eV)	Ref. for E_g
Al_4C_3	2800	3	[156]
$B_{4+x}C$	~ 2450	0.15–0.18[a]	[157]
β-SiC	2100[b]	2.3	[7]
α-SiC	2700	2.86	[7]
BN[c]	2730	3.8–6	[7, 176, 179]
AlN	Subl. 2400	6	[7, 167]
Si_3N_4	Subl. 1900	5	[18]
CaB_6	> 2100	0.2–0.4	[13, 148]
SrB_6	> 2100	0.38	[13, 148]
BaB_6	> 2100	0.12–0.15	[13, 148]

[a] Hopping activation energy.
[b] Transition to α-SiC.
[c] Hexagonal.

suggest that the "doping" with oxygen to form compounds such as oxynitrides and oxycarbides may make them more reliable materials for use in oxidizing environments. Similar to oxides, their electrical properties encompass all types of conductors: metal, superconductor, semiconductor and insulator. However, unlike oxides, most of these compounds of transition metals exhibit metallic conduction. Hägg [149, 150] has observed that if the size ratio of non-metal to metal atom is less than 0.59, many transition metal carbides, nitrides, and borides can form simple structures and exhibit metallic properties.

The borides, nitrides, and carbides with semiconducting characteristics are generally formed with the elements in groups IA and IIA of the Periodic Table, and with other elements in groups IIIB to VB. Table V lists the melting points and band gap energies reported for some of the semiconducting or insulating compounds.

The borides, carbides, and nitrides of transition metals, including actinide and rare-earth elements are characterized by high-melting points, hardness, and good thermal and electrical conductivities which make them very attractive for high-temperature applications. Like metals, they have a positive temperature coefficient of resistivity (PTCR) and often show a linear increase of resistivity up to very high temperatures. Table VI tabulates the melting points, room-temperature resistivities, and the temperature coefficients, Φ, as defined in Equation 4, of some of the refractory metals and the borides, carbides, and nitrides of transition metals.

Carbides, nitrides and borides are characterized by having a wide range of possible compositions and a tendency to deviate appreciably from stoichiometry [5]. Apparently, the nitrides of transition metals, like oxides, can accommodate significant concentrations of defects on both the metal and non-metal sublattices. The carbide and boride systems, however, can have

TABLE VI Selected properties of some refractory metals and borides, carbides, and nitrides of transition metals which display metal-like conduction

Materials	Melting point (°C) [7, 8, 182, 183]	ρ at 300 K (μΩ cm) [3, 7, 12, 13, 154]	Φ[a] (10^{-4} μΩ cm °C^{-1}) [6, 7, 155, 184, 185]
W	3407	5.44	330
Pt	1772	10.6	400
Ta	3014	13.48	400
Rh	1964	13.32	–
TiB_2	2980	28.4	300–1000
ZrB_2	3040	9.2	250–350
HfB_2	3100	10–12	300–400
ThB_6	2150	32	–
TaB_2	3100	68	350
NbB_2	2900	32	500
MoB_2	2100	22.5–45	–
LaB_6	> 2100	15–27	400
TiC	3250	180–250	800–9000
ZrC	3540	70	670–3400
HfC	3890	109	1550
VC	3830	150	–
NbC	3500	74	640
TaC	3880	30	540–3400
ThC	2625	25	–
Mo_2C	2695	97	–
W_2C	2730	80	1560
TiN	2950	21.7	600–3000
ZrN	2980	13.6	400
HfN	3310	33	–
VN	2177	200	6000(?)
NbN	2050	44–200	–
TaN	2980	135	–

[a] Temperature coefficient defined in Equation 4; values for borides, carbides, and nitrides are provisional due to uncertainty in the compositions.

defects on the non-metal sublattice only [34]. This has a very pronounced influence on their physical and chemical properties in general.

One consequence of having wide ranges of possible compositions and a tendency to deviate appreciably from stoichiometry is the large variation in the results of electrical resistivity measurements reported in the literature [3, 6, 12, 151]. Resistivities and even the values of Φ in these transition metal compounds have strong compositional dependence. Thus, the authors have found it very difficult to bring a systematic order to the large amount of available data due to a lack of definition or characterization of the materials regarding impurities and deviation from stoichiometry. It appears that the better techniques of materials preparation developed in more recent years have improved the electrical conductivity; the room-temperature conductivity of carbides of transition metals, for example, is generally higher in the more recent literature [152]. However, this is somewhat deceiving because the earlier materials were poorly characterized. Fig. 5 shows the variation in the resistivity values of the Ta–C system over the compositional range from Ta_2C to TaC [27]. In TaC_{1-x}, for example, the room-temperature resistivity decreases from about 150 to 25 μΩ cm when the value of x changes from 0.15 to 0.01. It becomes obvious why such a large variation in resistivity values for TaC and other transition metal carbides can be found in the literature.

The tendency to deviate from stoichiometry causes difficulties in defining the melting points, notably for the nitrides. Most of the stoichiometric nitrides melt at very high and normally unattainable nitrogen pressures; the loss of nitrogen at high temperatures makes the nitrides non-stoichiometric which results in the decrease of the melting temperature. Thus, the melting points of the nitrides cannot be unambiguously defined without defining the nitrogen pressure.

The variation of properties with composition and non-stoichiometry in these compounds can be understood in the light of the variation of atomic bonding with defect structure. Evidence, in general, shows that bonding in these compounds is a complex combination of metal-to-metal and metal-to-non-metal, or a complex mixture of metallic, covalent, and, possibly, ionic bonding (especially in the nitrides) [3, 35–37, 153]. Defects formed as a result of deviation from stoichiometry can bring changes in the nature of bonding [35–37] and thus the conductivity. It is important to note that from the view point of atomic bonding, transition metal nitrides and carbides are more closely related than the borides. This can be seen in the similarities of crystal structure types, phase relationships, electric and magnetic properties of transition metal nitrides and carbides [3]. It appears that the distinct structures, phases, and properties of transition metal borides can be attributed to the tendency of the boron atoms to form strong boron–boron bonds, which results in the formation of stable borides of high boron-to-metal ratio.

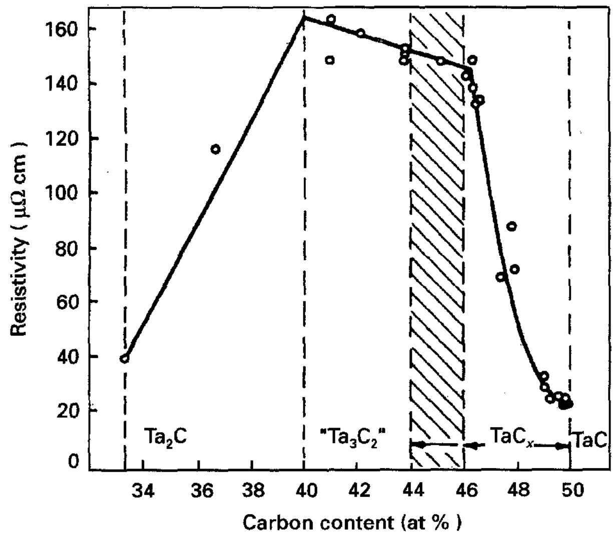

Figure 5 Room-temperature resistivity versus carbon content for TaC_x [27].

In the following sections, separate accounts of the relevant properties of borides, carbides, and nitrides are briefly given.

5.1. Borides

The engineering properties of borides have been recently reviewed by Cutler [154]. As a group, the borides are characterized by their high-melting point, extreme hardness, and high thermal conductivity. The borides of alkaline-earth metals CaB_6, SrB_6, and BaB_6 show semiconducting characteristics (see Table V). The borides of transition metals are excellent metallic conductors, and in some systems, are even better electrical conductors than are the parent metals. This can be seen from Table VII which gives a comparison of the electrical conductivities of Group IVA metals (titanium, zirconium and hafnium) and their borides, carbides, and nitrides. The differences between the metals and their borides are even greater than those between the metals and their nitrides. Electrical resistivities for a number of diborides of transition metals are given in Table VI. All of the borides of transition metals exhibit metallic conductivities.

Borides of the IVA, VA, and VIA groups in the Periodic Table and the higher borides of silicon and aluminium have unusual properties which make them very attractive for high-temperature applications [12, 148]. They have melting points ranging from 1900–3000 °C, and relatively low volatility in comparison with those of the carbides and nitrides.

TABLE VII Conductivities of group IVA borides, carbides, and nitrides at room temperature ($10^4\ \Omega^{-1}\ cm^{-1}$) [3, 7, 185, 186]

	Ti	Zr	Hf
Metals (M)	1.1–2.4	2.3	2.0–3.1
Borides (MB_2)	3.5	10.8	10
Carbides (MC)	0.4–1.8	1.4	0.9
Nitrides (MN)	4.6	7.4	3

However, they are not particularly resistant to oxidation at temperatures above 1300–1500 °C [12].

The resistivities of hexaborides of rare-earth metals were found to be similar to those of their parent metals [156]. The hexaborides of the alkaline-earth and rare-earth metals, in addition to having melting points above 2000 °C, have low work functions which render them of value as cathode materials [154].

5.2. Carbides

The carbides generally have melting points higher than those of borides. Characteristically they have a large range of homogeneity and have the ability to dissolve other non-metals and metals to a considerable extent. Boron carbide, for example, has a phase homogeneity range $B_{10.5}C$ to B_4C [157].

The semiconducting carbides, as listed in Table V, include SiC, B_4C, and Al_4C_3. Note that among them, Al_4C_3 has the highest melting point of 2800 °C, and B_4C is a p-type semiconductor with the electrical resistivity, ρ, proportional to $T^{3/2}\exp(Q/kT)$, suggesting a small polaron hopping mechanism [157–159]. Their electrical conductivities change with the carbon content [157, 160]. For example, in $B_{4+x}C$, the hopping activation energy varies between 0.15 and 0.18 eV for x ranging between 3.5 and 0 [157].

The carbides of transition metals, when forming the cubic structure (NaCl-type), can exist over a very wide composition range by the removal of carbon atoms from the carbon sublattice. TiC_{1-x}, for example, has an extraordinarily wide composition range; x can be as large as 0.5 [10]. Variability in their carbon-to-metal ratios introduces more uncertainty in conductivity measurements. Although they generally show metallic conductivities, their conductivities may change dramatically as the ratio of metal to carbon varies. For example, stoichiometric TiC is a metallic conductor; a large deviation from stoichiometry causes TiC_{1-x} to become a semiconductor [35–38], probably due to the variation in the nature of bonding with defect structure [3, 35–37].

The stability of some of the carbides towards oxidation are tabulated in Table VIII. One problem with carbides regarding high-temperature thermistor applications is that significant oxidation in air occurs at temperatures above 1000 °C [10, 162].

5.3. Nitrides

Among the stable, high-melting point nitrides, the insulating nitrides of boron and aluminium are of particular interest for electronic and structural applications [8, 163, 164]. Their thermal-shock properties are superior to that of alumina, because they exhibit relatively high thermal conductivities and low coefficient of thermal expansion.

Aluminium nitride is an insulator with a band gap energy between 5.7 and 6.2 eV [165–167]. There is a considerable variation in the activation energies of electrical conduction reported in the literature probably due to the difference in impurities, dopants, and methods of measurement [168–172]. Two temperature regimes of electrical conduction are generally observed with a demarcation temperature around 700 °C. The use of different sintering aids as well as various sintering conditions result in a variety of grain-boundary phases and different morphologies, which, in fact, may dominate the electrical properties of the sintered samples [173, 174]. For example, AlN doped with sintering aids such as CaO, Y_2O_3 and Al_2O_3 display activation energies of electrical conduction ranging between 1.8 and 2.4 eV [173, 175]. Although the conduction mechanism in AlN is not clear, the electrical conductivity is generally found to be independent of nitrogen pressure in the temperature ranges of measurement (< 1500 °C).

Boron nitride has two crystallographic forms [176–178]: a cubic lattice (similar to zinc blende) and a hexagonal lattice (similar to graphite). Hexagonal boron nitride (HBN) is an insulator with a band gap of 5–6 eV, and sublimes at 2500 °C [179]. It is more oxidation resistant than graphite [11]. BN in the cubic form (CBN) is a very good insulator at high temperatures, being superior to CaO, α-Al_2O_3, MgO, and ThO_2 [14].

Transition elements of group IVA, VA, VIA form nitrides which show metallic conductivities. The nitrides of group IVA (titanium, zirconium, hafnium) have some unusual properties. The three nitrides have high melting points near or above 3000 °C (Table VI), and electrical conductivities slightly higher than that of the metals (Table VII). Their high-melting points, however, can be utilized only in the absence of oxygen, because they are easily converted at or even below 1000 °C into dioxides. In vacuum, a slight dissociation

TABLE VIII Chemical reactivity of some carbides [10, 12, 13]

	N_2	O_2	Other environment
TiC	Complete nitridation (1000–1300 °C at 1 atm)	> 450 °C, formation of TiO_2	> 1200 °C oxidation in CO_2 to form TiO_2
ZrC	Nitridation upon heating	> 700 °C, rapid oxidation	Protective film of ZrO_2 at ~ 2200 °C in H_2O–CO_2
VC	Gradual nitridation upon heating; structurally unstable > 2400 °C	> 800 °C, rapid oxidation in air	Noticeable evaporation > 1800 °C in vacuum
NbC	Nitridation upon heating	> 1100 °C, rapid oxidation in air	–
TaC	Nitridation > 3315 °C	> 1100 °C, rapid oxidation[a]	–
α-SiC	–	< 1500 °C, protective SiO_2 film	Enhanced oxidation in steam

[a] Non-protective oxide film.

of the nitrides occurs (liberation of nitrogen) far below their melting points. Nitrides of group VIA elements (chromium, molybdenum, and tungsten) have relatively high dissociation pressures at 1500 °C [173]. Elements of the lanthanide and actinide series also form high-melting point nitrides. However, the electrical properties of these compounds are, to a great extent, unknown.

Although the melting points of nitrides are generally high (see Tables V and VI), their high-temperature applications have been limited because the nitrides have a greater tendency to dissociate than do the corresponding oxides, carbides, and borides. This is particularly true in high-vacuum applications. With the exceptions of BN and Si_3N_4, the nitrides generally have poor resistance to oxidation. In addition to the disadvantages of higher volatility and poor oxidation resistance, the nitrides are difficult to sinter and usually require sintering aids.

In summary for this section, the electrical properties of borides, carbides and nitrides are generally very sensitive to their composition. The tendencies to deviate significantly from stoichiometry or accommodate substantial amounts of other non-metals and metals into their lattices have a very pronounced influence on their electrical properties. As a result, the reported values for the electrical conductivity are variable and sample dependent. The compounds of transition metals are metallic conductors; their conductivities and temperature coefficients of resistivity are found to be comparable to those of their parent metals and may be useful as electrical lead-wire materials for high-temperature applications. In comparison with common refractory metals such as tungsten and platinum, they generally show larger temperature dependence of resistivity and, therefore, may be of use as resistance thermometer materials. However, due to poor oxidation resistance or high tendency to dissociate, their high-temperature applications are limited to high vacuum or inert environments.

6. General conclusion

High-temperature materials including oxides, borides, carbides, and nitrides encompass all types of conductors: metallic, semiconducting, and ionic. Their electrical conductivities are generally very sensitive to impurities and are composition dependent. For large band-gap materials, the conduction at low temperatures is frequently dominated by impurities or dopants, and intrinsic conduction only becomes significant above a temperature which depends largely on the level of dopant, the band gap and the defect structure (stoichiometry) of the base materials. As a result, there are at least two temperature regimes of electrical conduction for the large band-gap materials. The choice of base materials and dopants and the level of doping is, therefore, the key to the engineering and optimization of electrical properties for sensor applications such as thermistors. The borides, carbides, and nitrides of transition metals are metallic conductors with conductivities and temperature coefficients of resistivity comparable to those of their parent metals. The general tendency of these compounds to dissolve other non-metals and metals to a considerable extent provides the possibility of adjusting carrier density and allows changes in electrical properties. However, the use of nitrides, borides, and carbides for high-temperature applications generally requires a high-vacuum or non-oxidizing environment.

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