

# Materials Selection Guidelines for Low Thermal Conductivity Thermal Barrier Coatings

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## Abstract

Materials selection guidelines are desirable in identifying and developing alternative materials for higher-temperature capability thermal barrier coatings. Some relate to identifying candidate materials that exhibit particularly low values of thermal conductivity at high temperatures and others relate to thermodynamic stability in contact with the thermally grown oxides formed on bond-coat alloys and superalloys. By using existing theories of the minimum thermal conductivity, a materials parameter is developed that can be used to identify candidate alternatives to yttria-stabilized zirconia for high-temperature applications.

## Introduction

As engine temperatures are expected to continue to increase as higher efficiency engines having higher power-to-weight ratios are being designed, alternatives to yttria-stabilized zirconia (YSZ) for thermal barrier coatings are being sought. In part this is because the YSZ currently used comprises t-prime (t') zirconia that, being metastable, becomes increasingly unstable at higher temperatures, decomposing to a mixture of tetragonal and cubic zirconia. On cooling the tetragonal phase transforms to monoclinic zirconia, a disruptive transformation. In part, also, the recent demonstration that certain rare-earth zirconates, such as  $Gd_2Zr_2O_7$  and  $Sm_2Zr_2O_7$ , have lower thermal conductivity than 8 w/o YSZ (8YSZ) has also spurred a fresh examination of the prospects for discovering alternative thermal barrier coating materials. Nevertheless, YSZ has several important characteristics that will make it difficult to displace. It is, thermodynamically, stable in contact with alumina, the oxide formed at high-temperatures on all present bond-coat alloys. It can also be deposited by electron beam evaporation since the vapor pressures of ZrO and YO are comparable. The 8YSZ composition also appears, for reasons that as yet remain unclear, to have unusually good erosion resistance compared with other ceramics.

There are three major difficulties in searching for candidate thermal barrier coatings. The first is to select oxide materials that have the potential for having low thermal conductivity. This is a major undertaking since there are thousands of three-component oxides and countless others with more than three components. The second difficulty, perhaps even more intractable, is to assess the thermodynamic stability with alumina without laborious experimentation. The third difficulty is to create and then stabilize internal porosity since the decrease in heat transport cross-section provided by the presence of pores leads to a substantial reduction in thermal conductivity from that intrinsic to the material itself. In this short contribution, we focus on the first task, the selection of oxides that may have low thermal conductivity. In the absence of rigorous theories for high-temperature thermal conductivity, we make use of existing models to estimate the minimum thermal conductivity of insulating materials. We start by briefly describing the temperature dependence of thermal conductivity, review the data on several oxides and then existing models of thermal conductivity to place the work in context.

## Temperature Dependence of Thermal Conductivity

Figure 1 represents the general features of the thermal conductivity against temperature for a crystalline solid, in this case illustrating data on single crystal germanium [1]. (The data is represented on a logarithmic plot to capture the large variation in thermal conductivity with temperature). Four regions can be identified. At very low temperatures typically less than 20 K, the thermal conductivity is determined by the physical size of the material, grain size and dislocation spacing. The thermal conductivity in this region increases rapidly ( $\sim T^3$ ) with temperature. It peaks and then decreases. At temperatures above the peak, in region III, the thermal conductivity (corrected for the thermal expansion) decreases as  $1/T$  largely due to anharmonic phonon scattering, the Umklapp phonon-phonon process. In region III, the actual values of thermal conductivity depend sensitively on the concentration of defects so the values in region II, which is determined by the intersection of the behavior in regions I and III, is particularly sensitive to the presence of defects. Then, at very high temperatures, the thermal conductivity plateaus out and becomes independent of temperature. (If not blocked, radiative heat transport through a material during thermal conductivity measurement can lead to an apparent increase in thermal conductivity at high temperatures). In selecting candidate materials, the materials designer needs to know what material properties determine this plateau value and at what temperature the transition from the  $1/T$  dependence to plateau behavior occurs.

To gain some insight into the factors that influence thermal conductivity, it is instructive to compare the thermal conductivity of a range of electrically insulating materials. An example of such a comparison is shown in figure 2 for a number of ceramic materials with data drawn from the work of Kingery and colleagues [2]. Although obtained several decades ago, this data probably still represents the most comprehensive for oxides. The low temperature data in regions I and II is not shown but the  $1/T$  dependence and the transition to a constant, temperature independent region is evident in most of the oxides. Some of the data, for instance for MgO, shows an upturn at very high temperatures that is attributed to radiative heat transport.

## Models for Thermal Conductivity

The thermal conductivity of a material describes the diffusivity of heat flow by phonon transport in a temperature gradient. In the first successful model for thermal conductivity, Debye used an analogy of the kinetic theory of gases to derive an expression of the thermal conductivity [3]:

$$\mathbf{k} = C_V v_m \Lambda / 3 \quad (1)$$

where  $C_V$  is the specific heat,  $v_m$  is the speed of sound and  $\Lambda$  is the phonon mean-free path. In the subsequent developments, a temperature that is characteristic of the material and now known as the Debye temperature,  $\Theta_D$ , plays a central role in phonon theories of thermal conductivity of solids. At the Debye temperature, the wavelength of the shortest wavelength phonon corresponds to the size of the unit cell. The formal relation is given by:

$$\Theta = \frac{2\hbar v_m}{a_o k_B} \quad (2)$$

where  $a_o$  is the unit cell parameter and  $\hbar$  and  $k_B$  are Planck's and Boltzmann's constant, respectively.

Broadly speaking, the higher the temperature the less precise and predictive the models for calculating thermal conductivity of electrically insulating materials. Although the  $1/T$  dependence in region III is exhibited by almost all crystalline materials, the actual values cannot presently be predicted *a-priori* since the thermal conductivity depends on the concentration and type of defects in the material as well as the crystal structure and the atoms in the structure.

Nevertheless, a number of guidelines have been presented that serve to be of value. By appealing to the idea that lattice heat conductivity is related to the anharmonicity of a crystal and using dimensional arguments, Dugdale and McDonald [4] proposed that the phonon mean free path must be of the form:

$$\Lambda = \frac{a}{\alpha \gamma T} \quad (3)$$

where  $a$  is an inter-atomic distance,  $\alpha$  is the thermal expansion coefficient, and  $\gamma$  is the Gruneisen parameter. This was subsequently incorporated by Lawson [5] to express the thermal conductivity in region III as:

$$\mathbf{k} = \frac{aK^{3/2}}{3g^2 \rho^{1/2} T} \quad (4)$$

by assuming that the average phonon velocity in equation 1 is taken to be the same as the dilatational wave velocity.  $K$  is the bulk modulus and  $\rho$  is the density of the crystal structure. The thermal conductivity has also been expressed in a slightly different form by Berman [6] in terms of the Debye temperature as:

$$\mathbf{k} \propto \frac{\overline{M} a \Theta_D^3}{g^2 T} \quad (5)$$

where  $\overline{M}$  is the average atomic weight which is the atomic weight of the molecule,  $M$ , divided by the number of atoms in the molecule,  $m$ . In extending this type of analysis, Slack [7] has shown that if the thermal conductivity of one compound is known at its' Debye temperature, then the thermal conductivity of other compounds having the same crystal structure at their Debye temperatures can be calculated directly using a simple scaling relation. He then demonstrated substantial agreement between the predictions of his scaling relation and measured thermal conductivity (at the Debye temperature) for a range of rare-gases and crystals with the adamantine structure. Slack's work was a major step forward in advancing understanding the effects of crystal structure and atomic weight on thermal conductivity. The difficulty encountered in extending his analysis is that many materials are not perfect and the effect of point defects, dislocations and alloying is to decrease the thermal conductivity within regime III. Unfortunately, to compute their effects on phonon scattering and hence on thermal conductivity is enormously complex. Consequently, there are few reliable models except for the simplest cases of inter-mixing of one element with another, such as mixing Si with Ge [8] or GaAs with InAs [9]. To calculate the effect of defects, one approach [10] is by analogy with Rayleigh scattering of light; the material is considered to contain isolated defects that scatter phonons, much as particles scatter light, under the assumption that the phonon wavelength is large compared to the defect size and its strain field. One difficulty with this approach is that as the temperature increases, the average wavelength of the phonons decreases until it is no longer greater than the defect size and the mathematical basis for the analogy breaks down. This, unfortunately, begins to occur at temperatures generally below the Debye temperature. Consequently, one has to conclude that despite the success of Slack's approach the thermal conductivity in region III remains a region of limited predictive capabilities.

Fortunately, for many high temperature applications, the temperatures of interest are above the Debye temperature and so the thermal conductivity of interest is such that the plateau behavior, region IV, pertains. A number of models have been proposed to describe the value of the minimum thermal conductivity in this region. Slack's approach [11], which is an extension of his earlier work, is to enumerate the different phonon modes that a particular crystal structure can possess and account for the contributions to the thermal conductivity of every phonon in the structure. Cahill and Pohl [12], who began with an interest in computing the temperature

dependence of the thermal conductivity of non-crystalline solids, developed a model for the minimum thermal conductivity by adopting the assumption used in the Einstein model for thermal conductivity, namely that the individual oscillators vibrated independently of one another. The phonon scattering length then corresponds to the size of the oscillating unit in the structure. Both Kittel (in 1949) [13] and Kingery (in 1954) [14] suggested that the minimum value of the thermal conductivity was that given by equation 1 with the phonon mean free path being equal to the inter-atomic spacing. Although all these approaches are quite distinct, the predictions are quite similar for two principal reasons. Firstly, at temperatures in excess of the Debye temperature,  $T > \Theta_D$ , the specific heat is close to its asymptotic, temperature independent value of  $C_V \rightarrow 3k_B$  per atom predicted by the Dulong-Petit equation [3]. Secondly, it is assumed in all the treatments that the major contribution to the thermal conductivity in the plateau regime is due to phonons whose mean free path is the inter-atomic spacing. This is sometimes expressed in terms of the concept of the “dominant phonon” but once the phonon wavelength becomes as small as the inter-atomic spacing it has reached its lowest possible value. The only other variable is then the phonon group velocity that is fixed for a particular material. Cahill and Pohl have suggested that the value computed from their expression for the minimum thermal conductivity differs only by  $\sim 20\%$  from the limit of equation 1 where the phonon mean free path is equal to the lattice parameter. A particularly important feature of the minimum thermal conductivity is that it is independent of the presence of defects, such as dislocations, individual vacancies and long-range strain fields associated with inclusions and dislocations. This is largely because these defects affect phonon transport over length scales much larger than the inter-atomic spacing.

### Minimum High-Temperature Thermal Conductivity

For the present purposes of developing a materials selection approach for identifying candidate compounds, we will use the Debye equation (equation 1 above) as a basis for calculation. At high temperatures, the thermal conductivity approaches a minimum value given by:

$$\mathbf{k} \rightarrow k_B v_m \Lambda \rightarrow k_B v_m \Lambda_{\min} \quad (6)$$

where  $\Lambda_{\min}$  is the minimum phonon mean free path. To use this equation we need expressions for the minimum phonon mean free path and the mean phonon velocity. There are two complications. The first is how to account for the fact that materials of interest contain more than one type of atom per unit cell or per formula unit. The other is how to express the phonon mean free path and mean phonon velocity in terms of more readily obtainable or tabulated materials parameters. To address the first complication we assume we can replace the different atoms in a molecule with an equivalent atom having a mean atomic mass given by  $M/m$  where  $M$  is the molecular mass and  $m$  is the number of atoms per molecule. This effective mass approximation has been used before in calculating the thermal conductivity of mixtures of atoms [15] and is commonly used in several problems in geophysics [16]. One drawback, whose consequences are not fully known, is that the equivalent material does not have any optical phonon modes and hence leads to an underestimate of the thermal conductivity. To address the second complication, we assume that the minimum phonon mean free path is the cube root of the volume of a molecule and that the mean phonon velocity can be written in terms of the Young’s modulus of the material and its density. Strictly speaking, the mean phonon velocity is given in terms of the longitudinal and transverse wave velocities [3] as:

$$v_m = 3^{1/3} \left( \frac{1}{v_p^3} + \frac{2}{v_s^3} \right)^{-1/3} \quad (7)$$

Over a wide range of Poisson ratios, however, the mean acoustic velocity can be approximated by

$$v_m = A \sqrt{\frac{E}{\mathbf{r}}} \quad (8)$$

where A has a value of  $0.87 \pm 0.02$ . Since the values of Young's modulus are rarely known with any precision and seldom better than  $\pm 20\%$ , we can use  $A = 0.87$  with little loss in accuracy. Combining these terms, the minimum thermal conductivity can be expressed as:

$$\mathbf{k}_{\min} \rightarrow 0.87 k_B N_A^{2/3} \frac{m^{2/3} \mathbf{r}^{1/6} E^{1/2}}{M^{2/3}} \quad (9)$$

Using the same approximations, the Debye temperature can be expressed as:

$$\Theta_D = 3.39 \frac{\hbar}{k_B} N_A^{1/3} \frac{m^{1/3} E^{1/2}}{M^{1/3} \mathbf{r}^{1/6}} \quad (10)$$

Using these expressions, the minimum thermal conductivity for a range of oxides can be readily computed from available data in the literature on their elastic constants and densities. The results are presented in table I.

## Normalized Thermal Conductivity

To compare the computed minimum thermal conductivities of different materials, we have taken the measured values of the thermal conductivity shown in figure 2, divided them by the respective values of their  $\mathbf{k}_{\min}$  presented in table I and plotted the normalized thermal conductivity obtained this way in figure 3 against the temperature divided by the Debye temperature. If there were no other contributions to the thermal conductivity apart from the acoustic phonons, then at high temperatures all the normalized data would converge to a value of unity. Where the data has been obtained at temperatures well in excess of the Debye temperature, the data all tends to a constant but the values are consistently greater than unity. There is a definite trend in that the smaller the mean molecular weight, the larger the constant suggesting that replacing all the atoms in the molecule with an equivalent atom having the average molecular weight ignores an important molecular weight effect. Better convergence is obtained by using a mean square average molecular weight but the validity of using such a weighting is not evident. A second explanation for the fact that the normalized thermal conductivity is greater than unity is that the equations developed above are based on the contributions of the acoustic phonons and have ignored the contributions from the optical modes of vibration. These optical modes correspond to out-of-phase and local vibrations of neighboring planes of atoms and consequently have small wave-vectors. Although they are not usually considered to transport much energy since their group velocities are much less than acoustic phonons, their contributions at high temperatures may nevertheless be significant compared to the acoustic modes especially when there are many such optical modes. If there are  $p$ -atoms per primitive unit cell, then for each value of the wave-vector,  $\mathbf{k}$ , there are  $3p$  frequencies, each corresponding to one normal mode. Of these, 3 are acoustic modes (one longitudinal mode and two transverse modes). The other  $3p-3$  modes are optical modes, so their number increases rapidly with the number of atoms per primitive unit cell.

The analysis presented in the preceding section provides some guidance in selecting candidate oxides. Since there is only a weak dependence on both the density and elastic modulus, the strongest influence on the minimum thermal conductivity is the ratio of the atomic weight to the number of atoms per molecule. As the phonon scattering length approaches the inter-atomic spacing in the high-temperature limit, the effect of mixing different atoms within the unit cell has

little effect unless it leads to a reduction in the mean atomic weight. Thus, whilst there is very little change in the mean atomic weight as yttrium is added to zirconia since the atomic weights of Y and Zr are almost identical, there is a considerable increase in going from zirconia, which has a mean atomic weight of 41 amu/atom to  $Gd_2Zr_2O_7$  which has a mean atomic weight of 55 amu/atom. This increase is consistent with the lower thermal conductivity reported for  $Gd_2Zr_2O_7$  at very high temperatures. There is a precedence for this effect of inter-mixing in the literature on SiGe alloys: At temperatures well below the Debye temperature, there is a strong effect of adding Ge to Si and at a 50:50 random mixture the thermal conductivity is reduced by a factor of  $\sim 20$ . Although no data has been published above the Debye temperature, as the temperature is raised and approaches the Debye temperature, the difference between the thermal conductivity of the alloy and the mean value of that of pure Si and pure Ge decreases.

The graph of normalized thermal conductivity data in figure 3 illustrates the importance of comparing thermal conductivity data of different materials at temperatures well above the Debye temperature where the data is independent of temperature. If data is compared at lower temperatures, then the differing temperature dependence complicates the comparison since the comparison is being made in region III. Whilst it is legitimate to compare which of two materials has the lower thermal conductivity at a particular temperature for engineering design purposes, it is not a valid comparison of the intrinsic thermal conductivities of materials at the highest temperatures. Indeed, as shown in figure 2, a material that has a lower thermal conductivity at an intermediate temperature than another can have a higher value at higher temperatures. Part of the rationale of this contrary behavior is that crystal defects can have a greater effect in decreasing thermal conductivity in some solids than in others in region III and that it is only well into region IV that the thermal conductivity is independent of the presence and concentration of crystal defects. The comparison is particularly difficult to make at temperatures near the transition to region IV behavior. At temperatures well above the transition, the majority of the phonons have a wavelength corresponding to the inter-atomic spacing. However, at somewhat lower temperatures, a proportion of the phonon spectrum has a wavelength somewhat greater than the inter-atomic spacing. Assuming a continuous distribution of phonons, the spectral contribution of phonons of different wavelengths to the specific heat is just the derivative of the Debye equation:

$$\frac{dC_v}{d\omega} = 9N_A \frac{\hbar}{T} \left( \frac{T}{\Theta_D} \right)^3 \left( \frac{\hbar\omega}{k_B T} \right)^4 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \quad (11)$$

From this the wavelength of the dominant phonon,  $\lambda_{dom}$ , (in meters), which is the wavelength at which the phonon distribution is a peak, is given by the relationship:

$$\lambda_{dom} = \frac{12.566 v_m}{T} \times 10^{-12} \approx \frac{1}{T} \sqrt{\frac{E}{\rho}} \times 10^{-11} \quad (12)$$

Although the wavelength of the phonons below the peak in the phonon distribution is much too short to consider their scattering by individual defects by classic Rayleigh scattering, they can nevertheless be scattered, for instance by point-defect clusters and by unusual phonon modes such as librations, and add to the overall thermal conductivity.

### Effect of Porosity

Other than the choice of material, the presence of porosity has the greatest effect in decreasing the thermal conductivity of a solid. Pores primarily decrease the net-section area through which heat can be transported by phonons and so the reduction in thermal conductivity

depends on not only the volume fraction,  $p$ , of pores but also their aspect ratio and their spatial distribution. As a result, despite the large number of papers, both theoretical and experimental, discussing the effect of porosity on thermal conductivity there is no single expression for the relationship between the volume fraction of pores and thermal conductivity. The effect of pore shape can be large as has been known for almost a century and is utilized in many plasma-sprayed coatings. A particularly dramatic illustration of the effect of pore shape and orientation is shown in recent computations by Lu et al. [17]. Ideally, flat-pancake shaped pores perpendicular to the temperature gradient, as are formed at splat-boundaries in some plasma-sprayed coatings, lead to the greatest decrease in thermal conductivity. In the absence of a detailed knowledge of pore shape and distribution, the effective thermal conductivity,  $\mathbf{k}_{eff}$ , can be expressed as a power law expansion of volume fraction:

$$\mathbf{k}_{eff} = \mathbf{k}(1 - cp - dp^2 \dots) \quad (13)$$

where constants  $c$  and  $d$  are dependent on the way in which the pores are formed and on their spatial distribution. On prolonged high-temperature exposure, however, all pores will tend to spheroidize (or form faceted spheres) in order to minimize their excess surface energy. Consequently, one can consider, in the limit, that all the pores are spherical. Over a range of volume fraction, the constant  $c$  then has a value of  $\sim 2.5$  so the effective thermal conductivity can be approximated by:

$$\mathbf{k}_{eff} = \mathbf{k}(1 - 2.5p) = \mathbf{k}\left[1 - 2.5\frac{(\mathbf{r} - \mathbf{r}_{measured})}{\mathbf{r}}\right] \quad (14)$$

There are believed to be secondary affects of porosity on thermal conductivity but, at the present time, they are not well understood and cannot be quantified. One secondary effect is when the pores are of a size commensurate with the dominant phonon wavelength. Such pores are known to form in many materials under high-rate deposition conditions. Another secondary effect is interface scattering from the surface of the pores themselves. This effect, originally investigated by Kapitza, has not been studied in the context of porosity but can be important in materials with interfaces [18].

### Additional Materials Selection Criteria

At the present time, the majority of thermal barrier coatings are used in conjunction with alumina-forming alloys. This imposes the additional constraint on the selection of prospective coatings that, as mentioned in the Introduction, they must be thermodynamically stable with aluminum oxide. If they are not, then it will be necessary to utilize an intermediate layer that is thermodynamically stable with both alumina and the selected compound. An additional materials selection criterion is that the compounds do not exhibit appreciable mass loss at high temperatures. This, unfortunately, appears to rule out many of the silicates, which although exhibiting low thermal conductivity are liable to SiO vaporization, especially in the presence of water vapor.

One of the factors affecting the design of thermal coatings, especially for aerospace applications, is their weight. As the weight of a coating increases linearly with both its thickness and density, one selection criterion is the specific thermal conductivity, namely the product of the thermal conductivity and the physical density,  $\mathbf{rk}$ . Using equation 9 derived above, the minimum specific thermal conductivity can be expressed as:

$$\mathbf{rk}_{min} \rightarrow 0.87k_B N_A^{2/3} \frac{m^{2/3} \mathbf{r}^{7/6} E^{1/2}}{M^{2/3}} \quad (15)$$

for a dense body. For a porous coating, the specific thermal conductivity becomes:

$$\mathbf{r}_{meas} \mathbf{k}_{eff} \rightarrow 0.87 k_B N_A^{2/3} \frac{m^{2/3} \mathbf{r}^{1/6} E^{1/2}}{M^{2/3}} \mathbf{r}_{meas} (1 - 2.5p) \quad (15)$$

## Modifying the Thermal Conductivity of Partially Stabilized Zirconia

Although the principal objective of this contribution is to identify materials selection criteria for future thermal barrier applications where the temperatures are significantly higher than those today, it is worthwhile to place in context the approaches presently being taken to modify the thermal conductivity of partially stabilized zirconia by doping. Whilst they are unlikely to lead to large decreases in thermal conductivity, even decreases of 25% can be significant, especially if the doped materials also resist densification during use.

The thermal conductivity of yttria-stabilized zirconia is low and almost independent of temperature above room temperature. In part this is because it has a low elastic modulus and large mean molecular weight combined with a relatively low Debye temperature ( $\sim 475$  K). In part it is because of the high concentration of structural vacancies required to compensate for the additional valence charge associated with the substitution of yttrium for zirconium. The spacing of these vacancies is of the order of the unit cell and hence commensurate with the dominant phonon wavelength at temperatures as low as  $\sim 300^\circ\text{C}$ . Although the concentration of these structural vacancies increases linearly with yttrium concentration, very little improvement in the thermal conductivity results above 8 m/o  $\text{Y}_2\text{O}_3$  can be expected since vacancy clustering begins to become appreciable occurs at this concentration. Indeed, recent measurements by Bisson et al. [19] have shown almost no variation in thermal conductivity above about 8 m/o  $\text{Y}_2\text{O}_3$ .

It is pertinent to point out that since the atomic weight of yttrium (88.9 amu) is almost identical to that of zirconium (91.22 amu), the mean atomic weight of the cations does not change as the yttrium concentration increases. To alter the mean atomic mass of the cations, dopant ions with much higher atomic mass than yttrium must be employed and the zirconium ion has to be partially replaced with a much heavier ion. The latter can be accomplished straightforwardly by replacing Zr with Hf that has an atomic weight of 178.49 amu. Apart from its considerably higher density, hafnia has an almost identical chemistry to zirconia but it does require a higher yttria content to stabilize the t-prime phase. Using equation 9, the minimum thermal conductivity would be expected to be  $\sim 85\%$  of its yttria-stabilized zirconia counterpart. The most successful and comprehensive study of the effect of stabilizer dopants on thermal conductivity has been the work of Zhu and Miller at NASA Glenn Research Center [20]. Since their work is on plasma-sprayed and electron-beam-deposited coatings it is not possible to separate the effects of porosity from those of the changing the mean mass by using different dopants. However, if one compares the effect of adding 4.5 mol %  $\text{Yb}_2\text{O}_3$  to 4.5 mol%  $\text{Y}_2\text{O}_3$  with that of 9 mol%  $\text{Y}_2\text{O}_3$ , there is no change in the oxygen vacancy concentration but one would expect an increase in the mean cation atomic weight of only 5%. Since the atomic weight of all the middle rare-earth oxides is rather similar, no significant increases in the mean cation atomic weight can be expected by mixing rare-earth oxide dopants in stabilizing zirconia. One is therefore led to conclude that the observed decreases in thermal conductivity are probably primarily due to lower densities caused by higher incorporation of porosity during deposition. In the absence of studies on fully dense materials of the same compositions, there also remains the possibility that the Debye temperatures have been increased so that they are not all in region IV.

## Summary

A rationale for searching for compounds that can be expected to exhibit low thermal conductivity at high temperatures is presented. On the basis of existing models for the minimum thermal conductivity, it is argued that compounds having a small value of the parameter



$r^{1/6} E^{1/2} / (M / m)^{2/3}$  will tend to exhibit the lowest thermal conductivity. This formalizes the expectation that a material will have a low thermal conductivity at high temperatures if it satisfies four principal conditions: A large molecular weight, a complex crystal structure, non-directional bonding, and a large number of different atoms per molecule. The parameter also suggests that various traditional strategies to decrease the thermal conductivity, for instance, inter-mixing ions of different atomic mass will only decrease the minimum thermal conductivity if it leads to an increase in the mean atomic mass.

The selection process used to derive the minimum thermal conductivity parameter does not include the contributions to thermal conductivity from the non-acoustic (optical) modes whose numbers increases as the number of atoms per unit cell increase. At the present state of the field, the contribution to the overall thermal conductivity of the optical modes is poorly understood. This can be expected to become proportionally more important as the thermal conductivity is decreased. Both Slack's calculations and the more recent atomistic simulations for zirconia indicate that the contribution from optical phonons can approach that of the acoustic phonons.

Other important materials selection criteria include the thermodynamic stability of the coating with the thermally grown aluminum oxide at high-temperatures, the specific thermal conductivity, erosion resistance and the propensity towards volatilization losses in the presence of water containing atmospheres.

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## FIGURE CAPTIONS

Figure 1. The temperature dependence of the thermal conductivity of single crystal germanium from 3 K up to its melting temperature. The data illustrates the four principal regions characteristic of crystalline materials. Data extracted from reference 1.

Figure 2. The temperature dependence of the thermal conductivity of a variety of polycrystalline oxides. Redrawn from data presented by Kingery and co-workers in reference 2.

Figure 3. The data reproduced in figure 2 normalized by the computed values of the minimum thermal conductivity. At normalized temperatures in excess of  $\sim 1.5 \Theta_D$  all the data becomes constant with the exception of the  $\text{ThO}_2$ . This is probably because the reported value of the Debye temperature for  $\text{ThO}_2$  is in error.

**Table I.**  
**Calculated Minimum Thermal Conductivity**

Compound	$k_{\min}$	Compound	$k_{\min}$	Compound	$k_{\min}$
BeO	3.78	MgAl <sub>2</sub> O <sub>4</sub>	2.34	NiO	1.48
SiC	3.00	TiO <sub>2</sub>	2.07	LaMgAl <sub>11</sub> O <sub>19</sub>	1.48
Al <sub>2</sub> O <sub>3</sub>	2.89	Mg <sub>2</sub> SiO <sub>4</sub>	2.00	Gd <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	1.14
MgO	2.56	Mullite	1.68	Monazite	1.13
AlN	2.45	ZrO <sub>2</sub> (YSZ)	1.49	ThO <sub>2</sub>	0.98

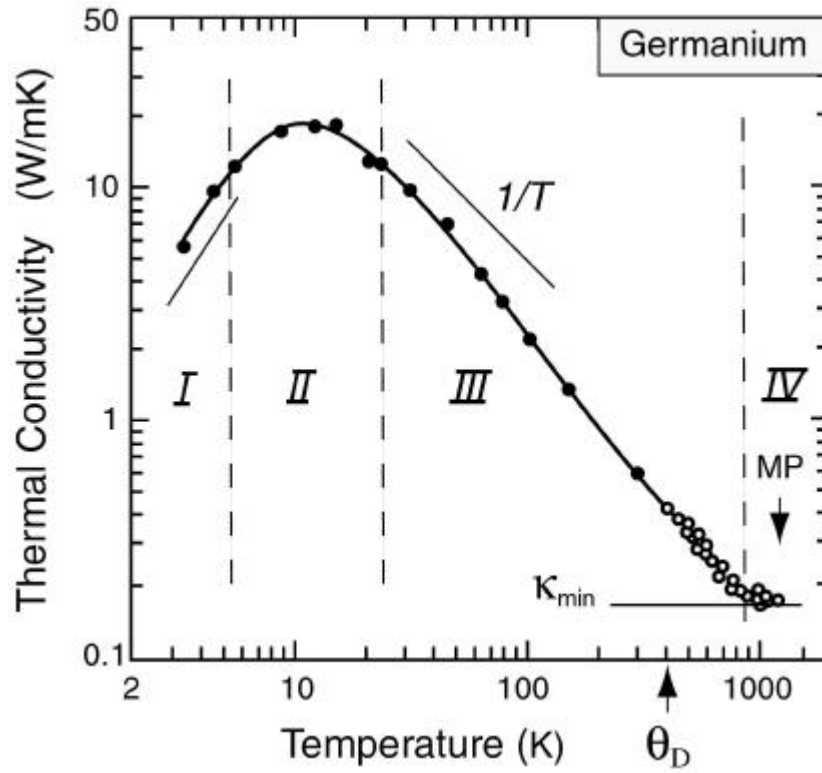


Figure 1. The temperature dependence of the thermal conductivity of single crystal germanium from 3 K up to its melting temperature. The data illustrates the four principal regions characteristic of crystalline materials. Data extracted from reference 1.

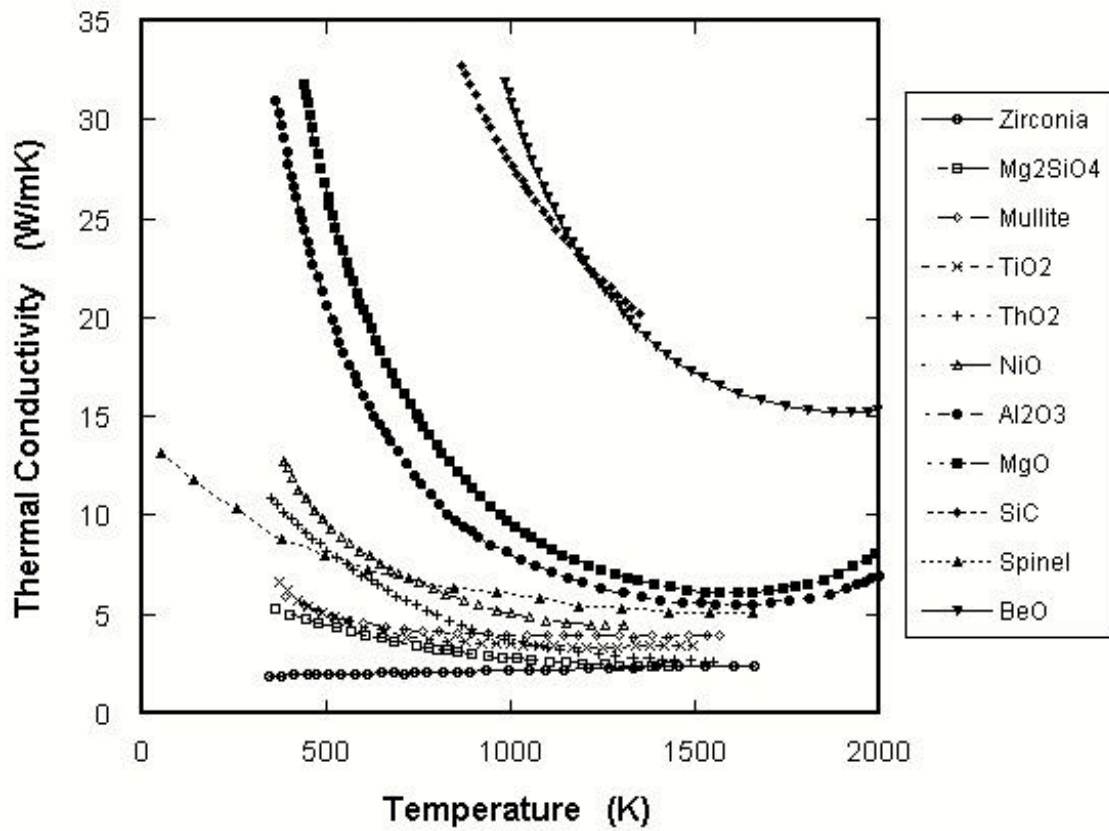


Figure 2. The temperature dependence of the thermal conductivity of a variety of polycrystalline oxides. Redrawn from data presented by Kingery and co-workers in reference 2.

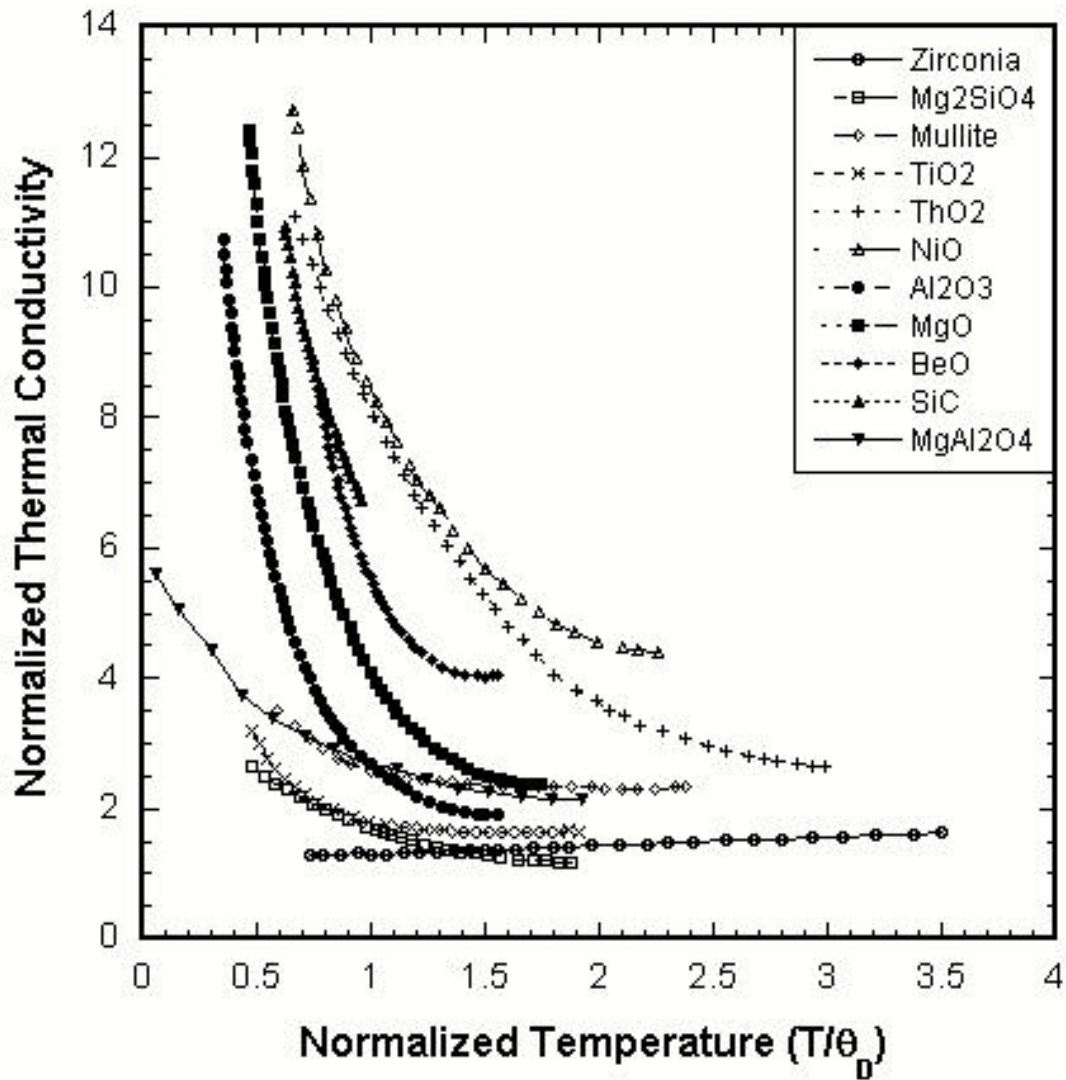


Figure 3. The data reproduced in figure 2 normalized by the computed values of the minimum thermal conductivity. At normalized temperatures in excess of  $\sim 1.5 \theta_D$  all the data becomes constant with the exception of the ThO<sub>2</sub>. This is probably because the reported value of the Debye temperature for ThO<sub>2</sub> is in error.