Thermal Conductivity of Refractory Materials

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RAPID TECHNOLOGICAL GROWTH imposes an increased demand for materials that will withstand high temperatures, high heat fluxes, and thermal shock. New materials and composites of all types appear constantly. As a result, there is a critical lack of reliable data on thermal properties which are required to evaluate and compare the high temperature performance of materials.

One obvious answer to the lack of thermal property data is an accelerated measurement program. Another approach is a fundamental study of theoretical and empirical mechanisms which may be used to predict thermal properties. The fundamental study could help to close the gap between the required property data and our present measurement capacity. The semitheoretical treatment of heat transfer in polycrystalline dielectric ceramics, presented in this article, is one facet of the fundamental study which could be made for various thermal properties.

EXPERIMENTAL

Thermal conductivity–temperature curves have been determined for 23 high-temperature materials: beryllia, six beryllia-beryllium cermets, a beryllia-beryllium-molybdenum cermet, silicon carbide, three silicon carbide–graphite mixtures, boron nitride, a boron nitride–graphite mixture, four grades of beryllium, and the beryllides of molybdenum, zirconium, titanium, and niobium. Except for beryllium, measurements were made up to 950° or 1000° C.

Thermal conductivities of the refractory materials were measured by two methods—an absolute method requiring a precise measurement of heat input, and a comparative method using a material of known conductivity to measure the heat flow. An absolute uniaxial system has been used for a number of years at this laboratory for liquid metals (*4, 5*). This system was modified for the precise, simultaneous measurement of one to six solid samples from 300° to 950° C. Samples 1A through 9A and 16A through 19A were measured in this system. To permit the remaining samples to be measured during the same time, two uniaxial systems were built. All systems employed cylindrical samples (1-⅝ inches in diameter and 1 inch long).

Absolute Measurement System. The modified apparatus (Figure 1) and integral control systems were similar to those described in detail in preceding articles (*4, 5*), and only a brief description will be included here to clarify the presentation of data. The actual conductivity measurements were made on a central bar with the unknown samples stacked for series heat flow under spring compression. The bar was compensated for radial heat exchange by the surrounding, thick metal guard ring (7 inches o.d. 5.5 inches i.d.). Thermal gradients within the bar and compensating gradients in the guard ring were established and controlled by direct current heaters at the top (*A* and *K*) in combination with uniform air cooling at the base (*G* and *H*). To permit radial equilization of temperatures in the vicinity of the unknown samples, auxiliary heating and cooling points were provided on the guard ring at *I* opposite the samples. The entire guard ring assembly was maintained at measurement temperature by an electric furnace, *M*, with 11 uniformly wound elements which provided a secondary guarding action.

Temperatures were measured with 30 calibrated platinum/platinum–10%-rhodium thermocouples suitably positioned at known levels on the bar and guard ring. To accommodate the thermocouples, small holes were drilled perpendicular to the axis of each sample piece. All thermocouples were individually stabilized and intercalibrated against primary standard couples from the National Bureau of Standards at 100° intervals up to 1000° C. For both calibration and measurement, Rubicon, 6-dial, microvolt potentiometers were employed with completely shielded thermocouple systems to give the required degree of accuracy for the measurement of couple potentials.

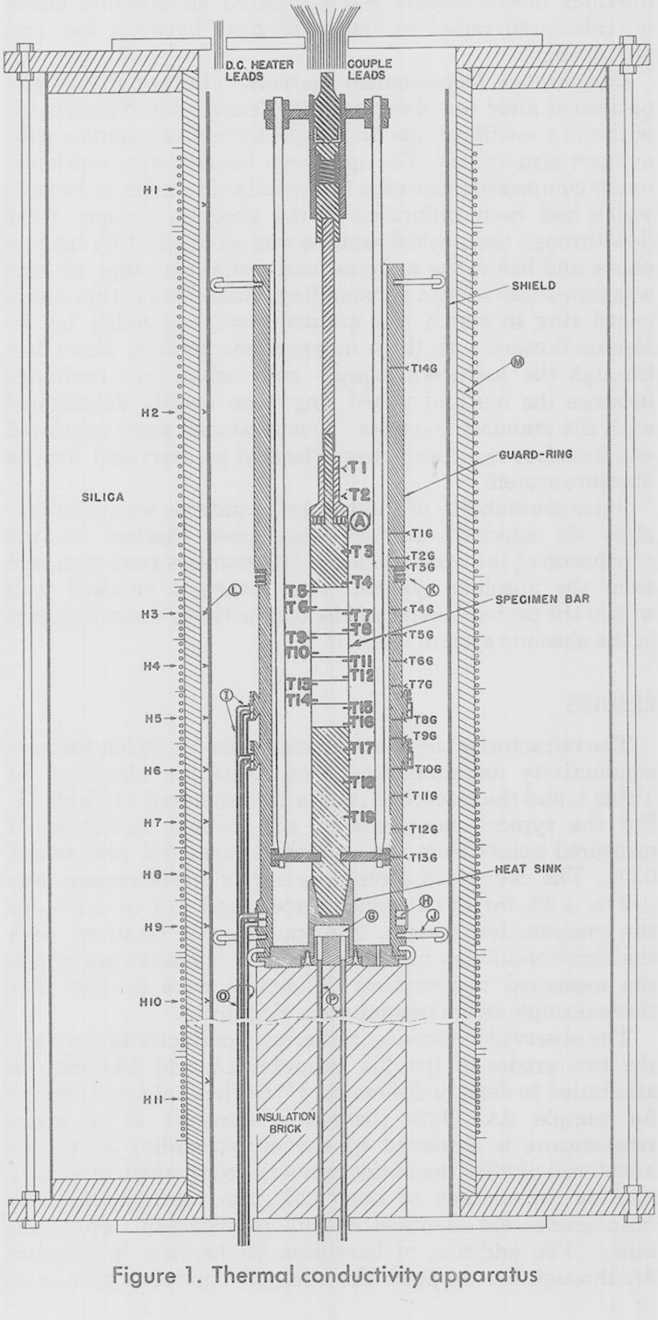

Figure 1. Thermal conductivity apparatus

A typical measurement of conductivity required the establishment of a steady heat-flow state in which temperatures at corresponding levels on the bar, guard ring, and furnace were matched within predetermined limits. The equilibrium heat flow through the sample bar was obtained by an absolute measurement of power input to the sample heater (*A*). Thermal conductivities were calculated from equilibrium measurements of heat flow and thermal gradients using the standard conduction equation (*4, 5*) with due corrections for thermal expansion and heat exchanges.

Interface resistance, a common source of error when heat flows through samples in series, was reduced by the use of very smooth surfaces, platinum foil at interfaces, and high contact pressures. An extrapolation of measured temperatures in the samples to corresponding interfaces permitted the detection of any interface resistance of sufficient magnitude to disrupt the uniform distribution of heat in the bar.

Simultaneous thermal conductivities were measured for standardized Inconel or Type 310 stainless steel at positions directly above and below the ceramic samples. This provided a continuous cross check of results against previous measurements and permitted an absolute check on calculated radial exchange of heat between bar and guard ring.

Comparative Measurement Systems. The apparatus was patterned after one described by Francl and Kingery (*8*) with some modifications for the protection of samples with an inert atmosphere. The unknown sample was positioned under compression between two standard samples of Inconel which had been calibrated in the absolute system. Heat flow through the stacked samples was established by heaters above and below the samples, and radial exchange of heat was compensated by a surrounding, close-fitting, thin metal guard ring in which the gradient was controlled by an electric furnace with three independent heaters. Heat flow through the unknown sample and radial heat exchange between the bar and guard ring were readily determined with the standard samples. Temperatures were measured and interface resistances were checked as described for the absolute system.

Since the stability of the Inconel standards was questionable, all standard samples were cross checked at the conclusion of the work against a 310 stainless steel standard from the absolute system. The materials checked well within the probable error of the conductivity measurements in the absolute system (±2%).

RESULTS

The refractories and metallic materials for which thermal conductivity measurements were made are identified in Table I, and the smoothed results are tabulated in Table II. For the typical measurement, the average deviation of measured points from the smoothed curve did not exceed 0.5%. The calculated probable error of measurement was ±2 to ±4% for the absolute system and ±4 to ±6% for the comparative system. Maximum error occurred with the high-conducting materials at lower temperatures where the measured temperature differences were so low that thermocouple errors became more significant.

The observed difference in thermal conductivity between the two grades of beryllia (samples 1A and 2A) can be attributed to density difference. If the thermal conductivity for sample 2A (94% theoretical density) at a given temperature is corrected to the corresponding value for a material of 98% theoretical density (equivalent to sample 1A) by the method of Loeb (*15*), the conductivities for both grades are identical within experimental reproducibility. The addition of beryllium to beryllia in samples 3A through 6A dropped the thermal conductivity curves for the cermets below that for pure beryllia. This is normal, since the addition of a small metal content, a discontinuous phase, would reduce the mean-free path for phonon transfer. Cermet samples 7A through 9A were furnished by a different manufacturer and are not comparable to the preceding samples.

Table I. Nominal Analyses and Densities of Specimens

Sample No.	Observed Bulk Density, G./Cc.	Theoretical Density, %	Nominal Analysis, Wt. %
1A	2.950	98	BeO grade (I)
2A	2.823	94	BeO grade (II)
3A	2.945	99+	97BeO(I)-3Be
4A	2.905	99+	94BeO(I)-6Be
5A	2.834	99+	91BeO(I)-9Be
6A	2.787	99+	88BeO(I)-12Be
7A	2.842	98+	93BeO(III)-7Be
8A	2.917	100	93BeO(I)-7Be
9A	2.975	98	86BeO(III)-7Be-7Mo
10A	3.01	95	96.5SiC-2.5Si-0.4C-0.4Al-0.2Fe
11A	2.722	92	78SiC-20C-2Si
12A	1.974	74	50SiC-46C-4Si
13A	1.602	66	23SiC-77C
14A	2.102	94	97BN-2.4B_2O_3-0.2Al and Si
15A	1.621	72	80BN-20C
16A	1.845	99+	99.0Be-0.85BeO-0.11Fe-0.02Al
17A	1.835	99	99.0Be-0.83BeO-0.16Fe-0.10Al
18A	1.851	99+	98.6Be-1.43BeO-0.17Fe-0.04Al
19A	1.851	99+	98.9Be-1.20BeO-0.13Fe-0.05Al
20A	2.916	99+	$MoBe_{12}$
21A	2.750		$ZrBe_{13}$
22A	2.180		$TiBe_{12}$
23A	2.711		$NbBe_{12}$

Silicon carbide, boron nitride, and graphite are known to exhibit anisotropy, and the results measured for samples 10A through 15A represent conductivities parallel to the direction of the pressing pressure. The expected increase in thermal conductivity at lower temperatures with the addition of graphite, a high phonon conductor, to silicon carbide occurs only with the sample containing 77% graphite. For lower additions of graphite the reduced mean-free path for phonon transfer by scattering overrides the higher conductivity of graphite.

The conductivity-temperature curves for the four beryllium samples (16A through 19A) are substantially different, but are in line with the impurity analyses presented in Table I. The conductivity for a high purity beryllium metal should be substantially higher than that reported for the purest material measured, sample 16A.

The refractory metal beryllides (samples 20A through 23A) are electronic conductors and exhibit a variety of conductivity-temperature curves. The zirconium beryllide sample developed a few fine cracks during measurement. The cracks, which appeared to be localized and on the surface, should not have influenced the results.

POLYCRYSTALLINE DIELECTRIC MATERIALS

Before the introduction of a new and somewhat radical treatment of heat transfer in ceramics, a brief survey of prevalent theories is appropriate. Four modes of heat transfer are considered significant for refractory materials: molecular or momentum transfer, transfer by phonons or thermoelectric lattice vibrations, transfer by electrons, and transfer by photons or electromagnetic waves. In addition to these modes, an exciton transfer (*10*) by electron-hole pairs has been proposed to explain anomalies in conductivity-temperature curves for some materials at very high temperatures. However, this mode of transfer is, at best,

Table II. Measured Thermal Conductivities of Refractory Materials[a]

Sample No.	Material, Wt. %	Thermal Conductivity, Watt/Cm., ° C., at Specified Temp., ° C.							
		300	400	500	600	700	800	900	1000
1A	BeO I	(0.961)	0.777	0.631	0.526	0.449	0.390	0.338	(0.300)
2A	BeO II	(0.891)	0.726	0.595	0.498	0.427	0.370	0.321	(0.289)
3A	97BeO I-Be	(0.931)	0.756	0.627	0.524	0.448	0.388	0.340	(0.309)
4A	94BeO I-6Be	(0.786)	0.646	0.538	0.457	0.397	0.354	0.317	(0.293)
5A	91BeO I-9Be	(0.893)	0.734	0.603	0.503	0.430	0.379	0.337	(0.305)
6A	88BeO I-12Be	(0.914)	0.735	0.577	0.482	0.413	0.357	0.303	(0.265)
7A	93BeO III-7Be	1.132	0.911	0.740	0.605	0.498	0.414	0.356	(0.313)
8A	93BeO I-7Be	0.995	0.794	0.652	0.542	0.455	0.388	0.329	(0.291)
9A	86BeO III-7Be-7Mo	0.875	0.701	0.597	0.511	0.439	0.374	0.318	(0.295)
10A	SiC(2.5%Si)	(1.186)	0.960	0.828	0.725	0.640	0.570	0.518	0.483
11A	78SiC-20C-2Si	(0.926)	0.825	0.750	0.688	0.650	0.620	0.597	(0.584)
12A	50SiC-46C-4Si	(0.989)	0.825	0.737	0.667	0.613	0.566	0.525	0.492
13A	23SiC-77C	(2.041)	1.740	1.345	1.155	1.015	0.910	0.816	0.748
14A	BN(2.4B_2O_3)	(0.187)	0.171	0.167	0.164	0.161	0.159	0.158	0.157
15A	80BN-20C	(0.190)	0.173	0.170	0.167	0.166	0.164	0.163	(0.162)
16A	Be	1.55	1.44	1.38	1.22				
17A	Be	1.48	1.32	1.19	1.10				
18A	Be	1.25	1.15	1.06	0.96				
19A	Be	1.26	1.13	1.06	1.03				
20A	$MoBe_{12}$	0.432	0.415	0.339	0.387	0.380	0.380	0.392	0.420
21A	$ZrBe_{13}$	0.397	0.386	0.380	0.383	0.397	0.412	0.426	0.442
22A	$TiBe_{12}$	(0.239)	0.239	0.242	0.254	0.279	0.316	0.360	0.409
23A	$NbBe_{12}$	(0.184)	0.194	0.206	0.220	0.236	0.258	0.293	0.337

[a] Results reported for samples as measured and not corrected to zero porosity.

questionable and can be considered insignificant for temperatures up to 2000° C.

It is virtually impossible to correlate and study materials where all four mechanisms are contributing to total conduction. Therefore, the materials for consideration have been limited to the large subclass of ceramics, the polycrystalline dielectrics, in which there are only two or three modes of transfer. The designation "dielectric" limits the materials in this subclass to those having electrical resistivities higher than 0.1 ohm-cm. at 1800° C. The Wiedemann-Franz relationship,

$$k_e = \frac{LT}{\rho} \tag{1}$$

where

k_e = equivalent conduction by electrons
L = Lorentz number
T = absolute temperature
ρ = electrical resistivity

is known to predict the electronic transfer of heat for metals and semiconductors. The value of Lorentz' number is predicted in the electronic theory of Riecke (*18*) and Drude (*3*). With accepted values for the constants involved in the theoretical derivations of the Lorentz number, a value of 2.45×10^{-8} watt-ohm/(° C., ° K.) is obtained, and this value predicts the electronic contribution at 1800° C. to be significant only for materials with electrical resistivities lower than 0.1 ohm-cm. No material considered in this section is known to have an electrical resistivity lower than 0.1 ohm-cm. at 1800° C.

The mathematical treatment of radiant transfer within a material is complex and can be solved only for the simplest cases (*1, 11*). Two mechanisms of radiant transfer have been identified (*11*). The first is by transmission directly through the material and follows the normal absorption laws for light. The second is by transmission, absorption, and reradiation within the body of the material. Transparent and translucent materials such as fused silica, sapphire, and other single-crystalline materials in very short sections should exhibit radiant transfer predominantly by the first mechanism, and for longer sections by both mechanisms. Transparent materials of this type have not been considered in this article. The polycrystalline materials with high absorption coefficients would be expected to exhibit any photon transfer by reradiation below 2000° C.

The mathematics of the reradiation process has been fully documented by Monroe (*17*). An approximate mathematical expression generally derived for the equivalent conduction by reradiation is

$$k_r = \frac{16\, n^2 \sigma T^3}{3\alpha} \tag{2}$$

where

k_r = equivalent conduction by reradiation
α = total absorption coefficient for total emission from a black body source at T
n = refractive index of the sample
σ = Stefan-Boltzman constant
T = mean absolute temperature of the sample

The principal mode of transfer in dielectric ceramics at lower temperatures is by phonons or elastic waves. A common equation used to express this type of transfer is

$$k = \tfrac{1}{3}\, Cul \tag{3}$$

Above the Debye temperature the velocity of the transfer, u, and the specific heat, C, are known to vary only slightly for a given material. Thus, the variation of conduction with temperature by this mode results from changes in the mean-free path, l, by thermal scattering processes. Accepted theory (2) predicts that the mean-free path and, therefore, the phonon transfer should be proportional to $1/T$.

It became clear in correlating the polycrystalline dielectrics that phonon transfer does not vary as $1/T$, but varies exponentially with temperature. Reradiation is significant only at higher temperature, but another definable transfer was present at lower temperatures and was considered to represent that portion of conduction contributed by a momentum transfer. The equivalent total conductivity for any polycrystalline dielectric can be represented effectively by

$$k = k_m + k_p + k_r \tag{4}$$

or

$$k_s = A\,\frac{c_p\mathrm{d}^2}{M} + B\,e^{-0.002625T} + \frac{4\,n^2}{3\alpha}\,(4\sigma\,T^3) \tag{5}$$

where

k_s = total equivalent conductivity for a sample of zero porosity
c_p = specific heat per unit weight
d = theoretical density
M = average atomic weight of compound or mixture
T = absolute temperature
A and B = constants for a particular sample

Equation 5 totals contributions from three sources: simple momentum transfer, k_m; phonon transfer, k_p; and photon transfer, k_r. The first two terms were derived empirically and the assigned mechanisms are based on the relationship between the terms.

Thermal conductivity-temperature curves for ceramic materials, even where no reradiation is present, exhibit minima. The minimum in a given conductivity curve could represent either a constancy of the mean-free path for phonon transfer or a pure momentum transfer independent of lattice structure. The present work would indicate the latter supposition to be true, since a definable transfer, which cannot be correlated with lattice structure, exists in all ceramics tested. The term $A(c_p\mathrm{d}^2/M)$ in Equation 5 is presumed to represent a transfer of momentum by van der Waal bonds as distinguished from phonon transfer by ionic and covalent lattice bonds. Relationships which combine specific heat and conduction have appeared regularly in the literature. The ratio, $k/c_p\mathrm{d}$ (where c_p is specific heat per unit weight and d is density), has been shown by Weber (*21*) and Graetz (*9*) to vary only slightly for many fluids. A modified term with $c_p\mathrm{d}^2/M$ has been used effectively to correlate momentum transfer for metals (*6*). The introduction of either $c_p\mathrm{d}$ or $c_p\mathrm{d}^2/M$ in Equation 5 is equally effective in correlating the ceramics, but the latter term gives more constant values for the coefficient A.

Phonon transfer in a given material varies exponentially with temperature and can be represented by $B\ e^{-0.002625T}$, where B is a constant for a given material. The constant in the exponent which can be obtained from graphical plots of data at lower temperatures, where radiation and momentum contributions are small, varied surprisingly little for all ceramic materials studied.

Absorption coefficients for samples of a particular polycrystalline material have been shown by Lee and Kingery (*14*) to be markedly influenced by impurity content, grain size, and porosity. Therefore, absorption coefficients, to be applicable in Equation 5, would have to be measured on a material identical to that used for the measurement of thermal conductivity. However, only a few absorption coefficients for polycrystalline materials at higher temperatures have been determined. To circumvent this lack of applicable data and to permit a correlation of thermal conductivity with Equation 5, all transmission terms for reradiation have been reduced to a pseudoradiation coefficient, C_t. The equation then reduces to

$$k_s = A\,\frac{C_p\mathrm{d}^2}{M} + B\,e^{-0.002625T} + C_t\,(4\sigma\,T^3) \tag{6}$$

For transmission between two infinite plates separated by a nonabsorbing medium, the approximate equivalent conductivity for radiation can be represented by

$$k_r' = F\,\Delta x\,\sigma\,[(T_c + 1)^4 - T_c^4] \tag{7}$$

where

k_r' = equivalent conductivity for radiation
F = emissivity factor for the radiating surfaces
Δx = distance between the two plates
T_c = absolute temperature of the cooler plate

Since $(4\ \sigma\ T^3)$ in Equation 6 is numerically equivalent to $\sigma[(T_c + 1)^4 - T_c^4]$, the coefficient C_t for reradiation, which is equal to $4n^2/3\alpha$, must have a value well below unity, since a value of unity or higher for $(F\Delta x)$ in Equation 7 would imply a mechanism of pure transmission directly through the material.

Equation 5 and 6 are strictly valid only for a material of zero porosity. Since most measurements of thermal conductivity are made on samples with measurable porosities and radiant transmission in the equations must relate to the measured sample, Equation 6 will be consistent only when all terms apply to a sample of given porosity. Loeb (*15*) has shown that the thermal conductivity k_s of a material with zero porosity can be related to the conductivity k_t of the same material with porosity p by

$$k_s = \frac{k_t}{(1 - p)} \tag{8}$$

Therefore, Equation 6 can be reduced to the more general equation,

$$k_t = A\,(1 - p)\,\frac{C_p\mathrm{d}^2}{M} + B\,(1 - p)\,e^{-0.002625T} + C_t(4\,\sigma\,T^3) \tag{9}$$

since k_t can be substituted for k_s when the terms for momentum transfer and phonon transfer are compensated by Loeb's correction for porosity.

The form of the general conduction equation can be verified by the fit obtained to measured conductivities for polycrystalline materials. For the bulk of these materials, which do not exhibit reradiation transfer in the temperature range of interest, the coefficients A and B can be readily obtained by a linear plot of

$$\frac{k_t}{(1 - p)\,c_p\mathrm{d}^2/M}$$

against

$$\frac{e^{-0.002625T}}{c_p\mathrm{d}^2/M}$$

with B as slope and A as intercept. Only a few of the pure white materials of low molecular weight exhibit significant reradiation up to 1800° C. For these materials the coefficients A, B, and C_t can be determined by successive graphical plots. With an assumed constant value for C_t, a plot of $[k_t - C_t\ (4\ \sigma\ T^3)]/[(1 - p)\ c_p\mathrm{d}^2/M]$ will give a preliminary value of A as intercept and B as slope. Using these preliminary values for A and B, another linear plot of

$$\frac{k_t - B(1 - p)\,e^{-0.002625T}}{(1 - p)\,c_p\mathrm{d}^2/M}$$

against

$$\frac{4\,\sigma\,T^3}{(1 - p)\,c_p\mathrm{d}^2/M}$$

will give a more accurate value of C_t as slope. The graphical procedure is repeated until both plots are linear with the same intercept. The rough constancy of C_t, which implies a constancy of n^2/α, was verified by the experimental data.

In this manner, coefficients for the general equation were determined for the 15 polycrystalline materials measured at (Naval Research Laboratory). The materials gave no evidence of radiant transfer and the coefficient C_t is assumed to be zero within the temperature range of measurement. However, the materials have high conductivities, and a small reradiation at 1000° C. would be effectively masked. The coefficients *A* and *B* for each material are presented in the upper part of Table III, together with the temperature range covered by each set of measured results, and the average per cent deviation of the observed conductivities from those calculated using the derived coefficients. The accurate fit of the general equation is demonstrated by the fact that the average deviation for all 15 materials is less than ±1.0%.

The general equation was further verified by its application to available literature measurements for other dielectric materials (lower part of Table III). The materials measured at NRL represented the best conductors of heat in the ceramic field while the literature materials represent conductors in the moderate and low ranges. For each material the temperature range of the data and the coefficients in the general equation are again presented. Where the temperature range was too abbreviated, the reradiation coefficient is omitted and is assumed to be zero in this analysis. The last column again presents the average deviation of the observed conductivities from those calculated using the derived coefficients. The general fit of the equation is approximately ±2.0% over wide temperature ranges—in many cases from 100° to 1400° or 1600° C. Kingery (*13*) reported values for beryllia from 100° to 1600° C. which are not consistent with this analysis. However, the smoothed values reported represent a composite of three measurements for three samples covering three temperature ranges, and the coefficient *B* would not be expected to be identical for all samples.

Table III. Correlation of Polycrystalline Dielectric Materials

Material and Reference	Temp. Range, ° C.	A^a	B^a	C_t	Deviation %
	(NRL Measurements)				
BeO I	400– 900	0.50	3.79		±0.5
BeO II	400– 900	0.52	3.62		±0.7
97BeOI-3Be	400– 900	0.52	3.58		±0.5
94BeOI-6Be	400– 900	0.53	2.90		±0.3
91BeOI-9Be	400– 900	0.54	3.36		±0.4
88BeOI-12Be	400– 900	0.48	3.33		±1.6
93BeOIII-7Be	300–1000	0.43	4.74		±0.6
93BeOI-7Be	300– 900	0.44	3.95		±0.8
86BeOIII-7Be-7Mo	300– 900	0.56	3.43		±2.1
SiC (2.5Si)	400–1000	2.33	4.38		±1.0
78SiC-20C-2Si	400– 900	3.09	2.61		±0.1
50SiC-46C-4Si	400–1000	2.77	4.20		±1.4
23SiC-77C	400–1000	3.23	11.73		±1.6
BN(2.4 B_2O_3)	400–1000	0.75	0.445		±1.5
80BN-20C	400– 900	1.01	0.551		±1.2
			Mean deviation		±1.0
	(Literature Measurements)				
Al_2O_3(*7*)	100–1600	0.20	0.313	0.06	±1.0
$3Al_2O_3$-$2SiO_2$(*13*)	100–1400	0.26	0.085	0	±1.5
CaO(*13*)	200–1000	0.84	0.145		±1.9
2MgO-SiO_2(*13*)	200–1400	0.12	0.087	0	±0.8
ZrO_2-SiO_2(*13*)	200–1400	0.38	0.092	0	±1.3
TiO_2(*13*)	200–1200	0.21	0.066		±3.1
ZrO_2(*13*)	100–1400	0.32	0.000	0	±2.5
ThO_2(*13*)	100–1400	0.28	0.232	0	±1.9
MgO-Al_2O_3(*13*)	200–1200	0.23	0.322	0	±1.9
ZnO(*13*)	200– 800	0.16	0.542		±3.5
NiO(*13*)	100–1000	0.12	0.262		±1.0
UO_2(*13*)	200–1000	0.28	0.191	0	±1.6
Al_2O_3(*13*)	200–1600	0.16	0.586	0.13	±2.9
MgO(*13*)	100–1600	0.13	0.795	0.18	±3.6
			Mean deviation		±2.0

[a] Coefficients expressed to give conductivities in watt/cm. ° C.

Several interesting facts are apparent when the empirical coefficients for the materials in Table III are compared. The coefficient *B* for phonon transfer is strongly depressed by an increase in the molecular weight of the material or by the addition of a second phase. The low phonon coefficient observed for the pure boron nitride of low molecular weight would appear to be inconsistent, but this anomaly may be attributed to the existence of two or more crystalline phases which contribute to increased thermal scattering. There is no obvious interrelationship between the two coefficients. For example, the mixed oxides have momentum coefficients which are comparable to those for the pure oxides; whereas corresponding phonon coefficients are markedly depressed by the increased thermal scattering in mixtures.

At least two investigators (*16, 12*) have observed minima in thermal conductivity–temperature curves at elevated temperatures for polycrystalline ceramics and have theorized that the deviation from predicted behavior was due to the transmission of radiant energy. The present study verifies the existence and predicts the magnitude of reradiation in several polycrystalline materials. For the two samples of alumina (Table III), the empirical analyses with Equation 9 predict transmission coefficients of 0.06 and 0.13, which are roughly constant with temperature. These predicted transmission coefficients, which should be equal to $4n^2/3\alpha$ are of the same order of magnitude as those calculated from the theoretical term with measured absorption coefficients. Monroe (*17*) obtained a total absorption coefficient for a polycrystalline alumina at 1790° C. by an extrapolation method. He calculated the equivalent conductivity of reradiation at this temperature (by Equation 2) to be 0.0275 watt per cm. ° C., which is equivalent to a transmission coefficient of 0.14. Lee (*14*) also measured absorption coefficients for two samples of alumina and calculated reradiation quantities at 1200° to 1600° C., which are equivalent to transmission coefficients of 0.03 and 0.09.

Organic and inorganic liquids at lower temperatures, where radiant transmission is normally insignificant, conduct heat predominantly by the mechanism of momentum transfer. Therefore, the momentum-contribution term, $A\,(c_p d^2/M)$, in Equation 5 for dielectric ceramics could be expected to apply for simple liquids. For solid ceramics, in which ordered arrays of individual atoms are joined by lattice forces, the average atomic weight was used in the momentum term. However, for liquid dielectrics, where ionic and covalent molecules are held together by van der Waals' forces, the molecular weight of the compound is required.

The momentum term is tested with several simple organic and inorganic liquids in Table IV. Liquids which are known to exhibit association between molecules are not included. The last column in the table presents the values of the coefficient *A* in the momentum term as calculated for each liquid from observed values of thermal conductivity, specific heat, and density. The coefficients for the liquids do show agreement in magnitude and are generally within ±8% of the average value, 0.32. Closer agreement could not be expected where inaccuracies do exist in the measured properties and where some association between molecules could exist. Flinak, as identified in the preceding article in this issue, is a mixture of fluoride salts and the formation of a double salt could explain the low coefficient observed for this material. It is of interest to compare momentum coefficients for liquids

(Table IV) with those obtained empirically for dielectric ceramics (Table III). The coefficients for ceramics which form ionic crystals show a rough agreement in magnitude with those calculated for liquids. On the other hand, coefficients for valence crystals, such as silicon carbide, graphite, and boron nitride, are several orders of magnitude higher.

CONCLUSIONS

Three independent mechanisms of heat transfer through polycrystalline dielectric materials have been identified by an empirical treatment of experimental data.

A definable transfer, which cannot be correlated with lattice structure, has been identified in both crystalline and amorphous materials and is believed to be a molecular transfer of momentum by van der Waal bonds. This mode becomes predominant for many polycrystalline dielectric materials above 1000° C. The term $c_p d^2/M$ used for momentum transfer implies that the molecular conductivity at unit gradient is directly proportional to the energy difference across a centimeter cube and directly proportional to the number of particles per centimeter cube.

The momentum term may be used to estimate the transfer by pure conduction in a simple organic or inorganic liquid which is known to be nonassociated or only slightly associated. Association factors for liquids are not well known, and a test of the term with adjusted molecular weights for associated liquids is impractical at present.

The major part of total conduction for polycrystalline dielectrics at lower temperatures varies exponentially with temperature, can be expressed by $B\,e^{-0.002625T}$, and is believed to represent phonon transfer by ionic and covalent lattice bonds. The term, $e^{-0.002625T}$, would represent the temperature dependency of the lattice bonding forces which give rise to phonon transfer, and B for a given sample would then become a coefficient related to the continuity of the lattice structure (thermal scattering) and to the magnitude of bonding forces.

Table IV. Momentum Transfer in Liquid Organics and Inorganics

Material and Reference to $k_{\text{obsd.}}$	Temp., ° C.	$k_{\text{obsd.}} \times 10^3$ Watt/Cm., ° C.	$\frac{k_{\text{obsd.}}}{c_p d^2/M}$
Carbon disulfide(*19*)	30	1.60	0.32
Carbon tetrachloride(*19*)	20	1.03	0.31
Diethyl ether(*19*)	20	1.30	0.35
Methyl acetate(*19*)	12	1.41	0.26
Ethyl acetate(*19*)	16	1.41	0.32
Diethyl sulfide(*19*)	12	1.37	0.37
Ethyl formate(*19*)	12	1.69	0.30
Ethyl bromide(*19*)	30	1.20	0.30
Ethyl iodide(*19*)	30	1.11	0.29
Cresol (*m*)(*19*)	20	1.50	0.32
Methyl ethyl ketone(*19*)	40	1.48	0.32
Dichloroethane(*19*)	20	1.35	0.28
Glycerol(*19*)	40	3.10	0.31
Trichloromethane(*19*)	20	1.21	0.29
Benzene(*19*)	20	1.46	0.36
Bromobenzene(*19*)	20	1.12	0.34
Aluminum bromide(*20*)	205	0.694	0.34
	427	0.658	0.36
Boric oxide[a]	500	5.4	0.32
	900	5.4	0.37
Flinak[a]	700	6.0	0.14
	900	6.0	0.17

[a] Observed thermal conductivities obtained from preceding article in this issue.

The polycrystalline dielectrics have high absorption coefficients and any radiant transfer of heat below 2000° C. should occur essentially by a reradiation mechanism which is well documented in the literature. Pure materials of low molecular weight at 1600° C. are shown to exhibit significant transfer by reradiation, which could become the predominant mechanism at higher temperatures. However, polycrystalline materials of high molecular weight, mixtures, and dark materials show no detectable transmission below 1400° C. and would not be expected to exhibit significant transmission until much higher temperatures are reached.

The general transfer equation for polycrystalline materials (Equation 9) can be useful in the extension and prediction of conductivity coefficients. Phonon transfer, which must be related to the coefficient B for a given material, is sensitive to many factors, including previous firing history, particle size, and anisotropy. The coefficient A, though not sensitive to these factors, can be predicted only roughly for those materials which exhibit predominant ionic bonding. Even so, where there are at least two measured results for a particular sample over a reasonable temperature range, the equation permits the extension of measured values to both lower and higher temperatures. For the few white materials of low molecular weight which may exhibit significant reradiation above 1200° C., transmission factors must be estimated or calculated from observed absorption coefficients.

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