THE THERMAL CONDUCTIVITY OF POLYCRYSTALLINE CORUNDUM IN THE RANGE FROM 90 to 1100°K

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We describe a method for the measurement of the thermal conductivity of a dielectric ceramic at low temperatures. We present the results from the measurements carried out on polycrystalline Al_2O_3 in the range from 90 to 1100°K, and we discuss the nature of the temperature relationship to thermal conductivity.

The measurement of the thermal conductivity of dielectrics and semiconductors at low temperature is of interest for purposes of comparing the theoretical and experimental temperature relationships $\varkappa = f(T)$, as well as to determine the influence of structural defects on the phonon scattering processes. The latter is all the more important, the lower the temperature, since the contribution of anharmonic processes to the thermal resistance of the crystal lattice is markedly reduced in this case.

To carry out the investigations in the range from 80 to 300°K, we developed a comparatively simple test installation to determine the thermal conductivity and we carried out these measurements on polycrystalline Al_2O_3. Above 300° K, we used the method of [1] to determine the thermal conductivity.

We based our design for the low-temperature instrument on the method of two specimens in a steady-state thermal regime, used for measurements at high temperatures. A diagram of the installation is shown in Fig. 1.

Between two specimens 1 in the form of square plates 15×15 mm² and a thickness of 12 mm we position a flat nichrome spiral ~0.5 mm in length heater 2, which is imbedded with mica insulation into copper foil.

The specimens are held in place by means of guide strips and a socket in support 3. The support is attached to a massive copper rod 4, which is sealed into the liquid-nitrogen vessel 5. The specimens with the heaters are pressed up against the support by means of screw 6. Copper springs 7, attached to the support plate of the screw and to screen 8, serve to even out the temperature along the specimen axes.

Reduction of the heat losses due to radiation from the side surfaces of the specimens is achieved by the chrome platting of screen 9 covering the specimens with a clearance of ~1.5 mm. The side surfaces of the specimens are blackened with carbon black or graphite.

The specified measurement temperature is attained by means of cylindrical heater 10. To reduce the nitrogen flow rate, the measurements from 150 to 300°K are carried out with the use of a laminated Bakelite spacer 11 whose thickness is chosen so as to alter the magnitude of the transition thermal resistance, thus to regulate the extent to which the specimens are cooled.

The quantity of heat passing through the specimens is determined from the electrical power consumed in the flat heater. The measurement of the temperature gradients is accomplished by means of copper-constantan differential thermocouples 12, with 0.08-mm-thi thick thermal electrodes which are mounted in orifices filled with Wood's alloy. To reduce the removal of heat from the thermal electrodes, current-conducting and potentiometric wires are wound onto coil 13.

The installation is evacuated to a pressure of $\sim 5 \cdot 10^{-3}$ N · m^{-2}.

We find the thermal conductivity from the formulas

$$\varkappa = \frac{W - Q}{\frac{s_1}{l_1}\Delta T_1 + \frac{s_2}{l_2}\Delta T_2}, \qquad (1)$$

$$Q = \sigma_0 (T^4_{\text{spec}} - T^4_{\text{sc}})\, s_{\text{side}}. \qquad (2)$$

It is obvious that Q increases with a rise in temperature. For Al_2O_3 specimens, when T ~ 270°K, the radiation correction does not exceed 5% of the main heat flow. This quantity is in agreement with the calculation of the heat balance in an analogous system [2].

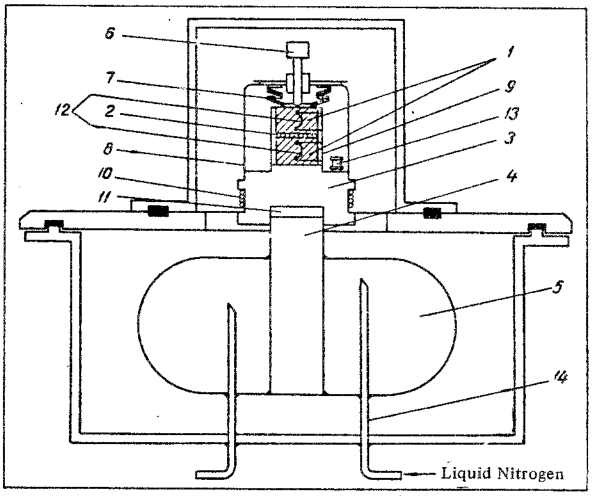

Fig. 1. Instrument for measuring thermal conductivity substitution impurity from 80 to 300⁰ K: 1) specimens; 2) plane heater; 3) support; 4) copper rod; 5) vessel for liquid nitrogen; 6) regulating screw; 7) springs; 8) outer screen; 9) inner screen; 10) cylindrical heater; 11) spacer; 12) differential thermocouples; 13) coil; 14) tube for nitrogen supply.

Table 1

Concentration of Impurities in Al_2O_3 Specimens (mole %)

SiO_2	TiO_2	Fe_2O_3	CaO	MgO	Al_2O_3 (various)
$5.96 \cdot 10^{-2}$	$7.6 \cdot 10^{-3}$	$1,28 \cdot 10^{-2}$	$5.4 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$	99.91

The instrumental measurement error is determined primarily by the accuracy with which the temperature gradients are measured, and these are functions of the thermal conductivity of the material. For $\varkappa \simeq 500$ W∘m^{-1}∘deg^{-1} we have $\Delta\varkappa/\varkappa \simeq 14\%$, while for $\varkappa \simeq 1$–50 W∘m^{-1}∘deg^{-1} we have $\Delta\varkappa/\varkappa \simeq 4$–6%.

The calibration of the installation in the region of small values for $\varkappa$ was carried out on specimens of molten quartz, which is regarded as a material typical of poor heat conductors [3]. The measurement results showed excellent agreement with the standard calibration curve for quartz containing impurities of ~1.4 wt.%. The data for purer quartz (a content of $SiO_2 > 99.5$ wt.%) are found to be approximately 40% higher. The scattering of the points from the smoothed values does not exceed the instrument error.

We measured the thermal conductivities of polycrystalline corundum specimens on the installation described here; the Al_2O_3 specimens exhibited a purity of 99.9% and were sintered to zero porosity.

Table 1 shows the chemical composition of the Al_2O_3 test specimens on the basis of spectral analysis.

The data on the temperature relationship to the thermal conductivity $\varkappa$ and the thermal resistance R are shown in Fig. 2.

Comparison with the thermal conductivity of a high-purity Al_2O_3 monocrystal [4] shows that at 100°K the value of $\varkappa$ is greater by 15% than the value of $\varkappa$; this difference is gradually reduced with increasing temperature and, starting at 150°K, has virtually disappeared. Such a result is naturally explained by the greater effect of the impurities at the low temperatures. The boundary scattering at T ⩾ 100°K can be neglected, since the mean free path of the phonons is 10^{-6} cm, which is considerably smaller than the dimensions of the crystallites.

The low-temperature measurements, together with the results from the interval between 300 to 100°K are presented in Fig. 3 and make up a single smooth curve. The function $\varkappa = f(T)$ in the high-temperature region is in good agreement with that given in [5].

In the 140–300°K interval the function $R = f(T)$ is a straight line whose equation is given by $R = (1.316 \cdot 10^{-4} T - 0.0128$ W^{-1}∙ m ∘ deg, which is virtually coincident with the line extrapolated from the low-temperature region (Fig 4).

Thus, the temperature as a function of the thermal resistance of Al_2O_3 from 140 to 1100°K is described by a linear function of the form

$$R = aT - b. \tag{3}$$

An analogous relationship was observed for several high-melting oxides between 300 and 2100°K [6] and for alkali-halide crystals from 80 to 400°K [7].

In accordance with the Leibfried and Schlömann theory [8], the thermal resistance of a dielectric crystal, determined exclusively by the processes of three-phonon interaction, must be described by the straight line passing through the point T = 0:

$$R = R_\theta \frac{T}{\theta}, \tag{4}$$

$R_\theta = L(h/2\pi k)^3 \gamma^2/\bar{M}\delta\theta^2$ is the thermal resistance at the Debye temperature. Assuming $\gamma \simeq 2$ and $\theta \simeq 1010$°K [4], we have $\varkappa_\theta \simeq 60$ W∙ m^{-1}∙ deg^{-1} against an experimental value of 8.3 W ∘m^{-1}∘ deg^{-1}. Consequently, we are not in a position to describe the properly the derived experimental data by means of (4).

Qualitatively speaking, the experimental results are in better agreement with the concepts of Ioffe [9], who assumed that the mean free path for the phonons is inversely proportional to the total thermal energy of the crystal,

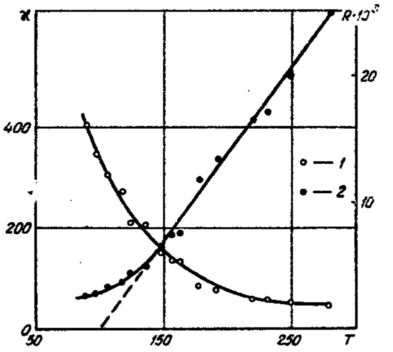

Fig. 2. Temperature dependence of thermal conductivity (W ∘ m^{-1}∘deg^{-1}) and thermal resistance Al_2O_3 (W^{-1}∘m ∙ deg): 1) thermal conductivity; 2) thermal resistance.

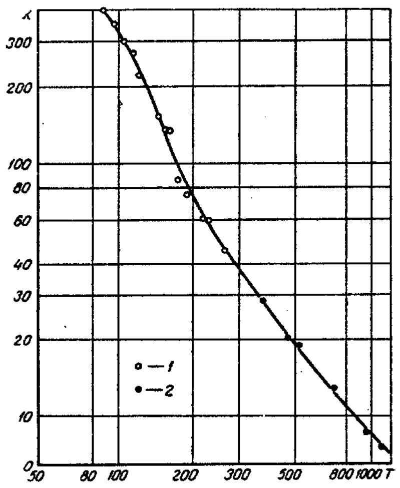

Fig. 3. Thermal conductivity Al_2O_3 (W ∙ m^{-1} ∙ ∘ deg^{-1}) 80 to 1100°K: 1) low-temperature measurements; 2) high-temperature measurements.

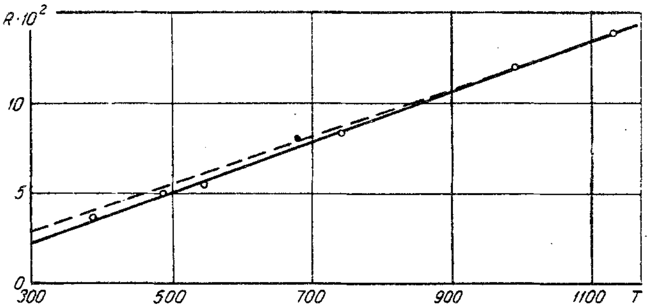

Fig. 4. Thermal resistance Al_2O_3 ($W^{-1}\cdot m\cdot deg^{-1}$) from 300 to 1100°K. Dashed line) extrapolation of low-temperature data from equation $R = (1.316\cdot 10^{-4}\ T - 0.0128)\ W^{-1}\cdot m\cdot deg$.

$$l^{-1} \sim \int_0^T c\,dT, \tag{5}$$

$$R \sim \left(T - \frac{\theta}{3}\right). \tag{6}$$

However, extrapolation of the experimental straight lines to $R = 0$ leads to values of $\theta/10$ rather than to $\theta/3$. This is not a suprising divergence, if we bear in mind that (5) is an extremely coarse approximation. Let us note that at low temperature, instead of a pronounced exponential increase, Eq. (5) again yields $\varkappa \sim T^{-1}$.

An attempt was made to compare the experimental results with the calculation based on the Calloway high-temperature model [10], which incorporates both overshoot processes with the relaxation time $\tau^{-1} = BT\omega^2$, and phonon scattering at point defects with a relaxation time $\tau^{-1} = A\omega^4$.

For $T \sim \theta$ the thermal conductivity can be written as

$$\varkappa = \frac{k}{2\pi^2 v\sqrt{ABT}} \operatorname{arctg} \frac{2\pi k\theta}{h} \sqrt{\frac{A}{BT}}. \tag{7}$$

According to [11],

$$A = \frac{V\sum\limits_j x_j\left(\frac{\bar{m} - m_j}{\bar{m}}\right)^2}{48\pi v^3}. \tag{8}$$

When $v \simeq 66\cdot 10^3\ m\cdot sec^{-1}$ [4], we obtain a value of $1\cdot 3\cdot 10^{-50}$ hr · deg^{-1} for A.

Table 2

Experimental and Theoretical Data on the Thermal Conductivity of Al_2O_3 ($W\cdot m^{-1}\cdot deg^{-1}$)

T, °K	$\varkappa_{exp}$	$\varkappa_{theor}$	$\frac{\Delta\varkappa}{\varkappa_{exp}}$, %
100	330	101	70
150	150	66	56
200	75	63	16
250	50	43	14
300	38,1	34	11
400	25,2	25	1
500	18,6	20	13
600	15,2	17	12
700	12,6	15	19
800	11	13	18
1000	8,3	10	20

On calculating B we use the expression for the thermal conductivity of the pure crystal at $T = \theta$

$$\varkappa_\theta = \frac{k^2}{\pi h v B}. \tag{9}$$

Assuming the influence of the impurities at these temperatures to be inconsequential, and further assuming that $\varkappa \simeq 8\ W\cdot m^{-1}\cdot deg^{-1}$, we have $B = 14\cdot 10^{-20}\ m\cdot deg^{-1}$.

Table 2 shows the experimental values and those calculated from (7) for the thermal conductivity at various temperatures.

As we can see from the table, we find rather good agreement between $\varkappa_{exp}$ and $\varkappa_{theor}$ starting with $T \sim 200$°K; below this temperature, the theoretical values are substantially lower than the experimental. Apparently, this is the limit of applicability for (7) in the calculation of the thermal conductivity of corundum.

NOTATION

$\varkappa$ is the thermal conductivity; R is the resistance; W_0 is the power of the plane heater; Q is the flux between the lateral surface of the specimen and the inner screen; s_1 and s_2 are the cross-sectional areas of the specimens; ΔT_1 and ΔT_2 are the temperature differences in the specimens at distances l_1 and l_2; σ_0 is the Stefan constant; k is the Boltzmann constant; $h/2\pi$ is the Planck constant; M is the mean atomic weight; δ is the distance between atoms; γ is the Grüneisen constant; θ is the Debye temperature; L is the dimensionless factor; c is the heat capacity; ω is the frequency; v is the speed of sound; V is the volume of the elementary cell; A and B are the proportionality factors; x_j and m_j are the concentration and mass of type j; m is the mean mass per one cell.

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