

HEAT CONDUCTIVITY OF A BERYLLIA-BASED  
COMPOSITION AT LOW TEMPERATURES

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The thermal conductivity of beryllium oxide with additions of  $Y_2O_3$ , MgO,  $Fe_2O_3$ ,  $TiO_2$ ,  $Al_2O_3$ ,  $SiO_2$ ,  $ZrO_2$ , and glass was measured at 120–260°K. The additions were made in amounts up to 5 wt. %.

Beryllium oxide is known mainly as a high-temperature material [1]. However, its favorable combination of electrical, thermal, and mechanical properties allows it to be used in radio electronics at both room and lower temperatures [2]. Generally, substrates of beryllia made under industrial conditions contain additions of other oxides (they may be random impurities or alloying agents). These additions significantly lower the thermal conductivity of beryllia at temperatures of 300–600°K [3–6]. We know of only one work [7] in which the heat conductivity of three beryllia-based compositions at low temperatures was measured.

This article examines the effect of seven oxides and Al–Ca–Si glass on the heat conductivity of beryllium oxide. The specimens were prepared by die casting with subsequent sintering in a vacuum at 2070–2120°K. The relatively low-melting additions ( $TiO_2$ ,  $SiO_2$ , glass) were introduced in the form of finely dispersed powders, while the remaining additions were added by the salt method. The quantity added was 5 wt. %, except for  $Y_2O_3$  (0.7 wt. %, since a larger quantity would have adversely affected sintering) and glass (3 wt. %, corresponding to the commercial material Brokerit-9). The microstructure of the beryllia was changed substantially by the additions (Fig. 1): grain size was increased, the grain boundaries were widened, and density was reduced ( $Fe_2O_3$ ,  $TiO_2$ ,  $SiO_2$ ). The uniformity of the distribution of the additions throughout the volume of the specimens was confirmed by means of an electron microprobe.

The method of longitudinal thermal flux was used to measure heat conductivity. The experimental unit included a vacuum chamber cooled with nitrogen, main and compensation heaters, 20-mm-diameter specimen 50 mm high, and copper–Copel thermocouples. The measurement error was 6–8%.

TABLE 1. Heat Conductivity and the Properties of the Oxides Needed to Calculate It for 300°K [1, 3, 8, et al.]

Property	BeO	MgO	$Al_2O_3$
Debye temperature $\theta$ , °K	1150	870	1000
Bond energy $E$ , kJ/mole	1650	602	1675
Distance $d$ between ions of oxygen, Å	2,67	2,98	2,78
Heat conductivity calculated from Eq. (1), W/m·deg	255	54	78
Handbook data on heat conductivity	240–290	60–70	40–50
Heat conductivity calculated by the Leibfried–Schliemann formula	204	132	200

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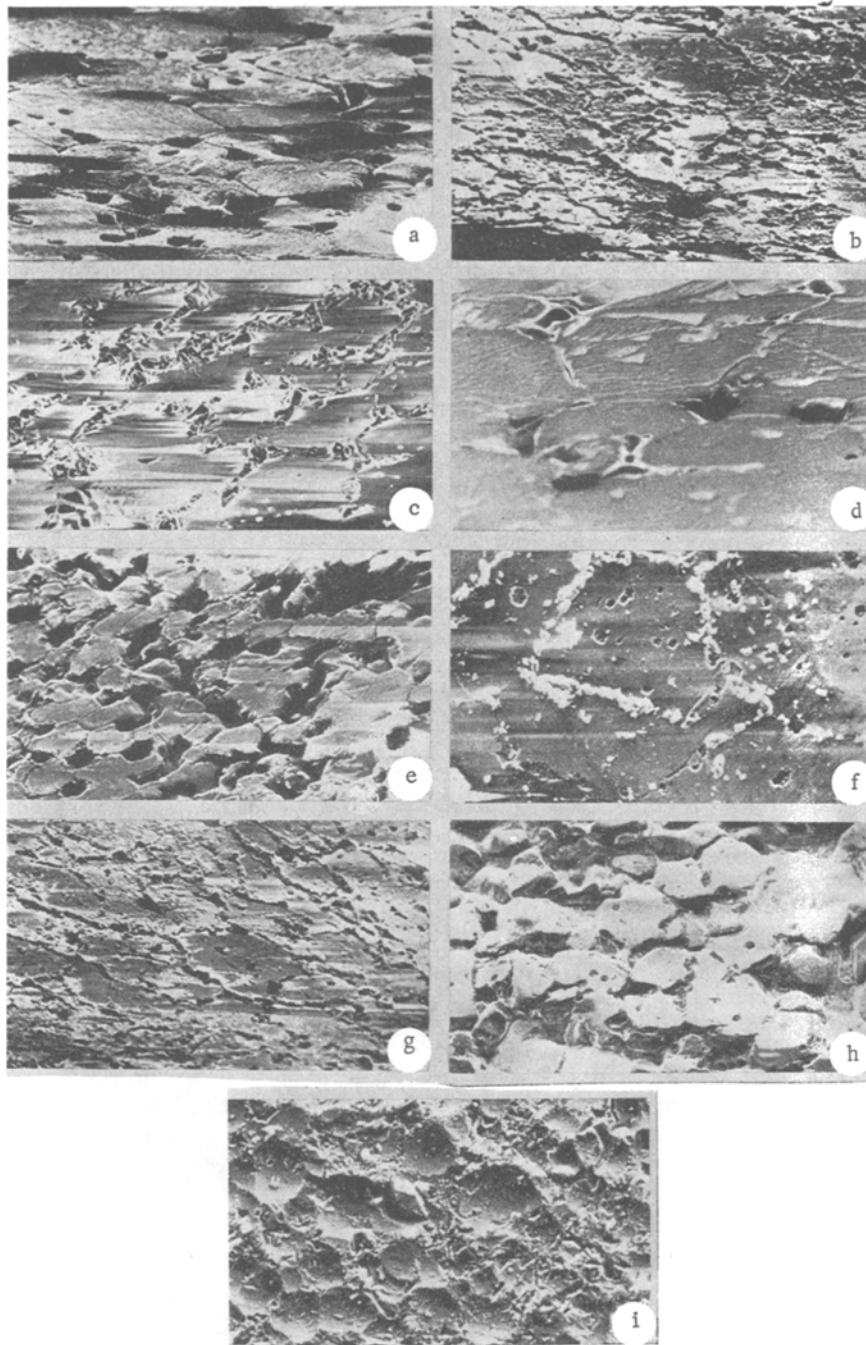


Fig. 1. Microstructure of specimens: a) BeO; b) BeO+0.7%  $Y_2O_3$ ; c) BeO+5% MgO; d) BeO+5%  $Fe_2O_3$ ; e) BeO+5%  $TiO_2$ ; f) BeO+5%  $Al_2O_3$ ; g) BeO+5%  $SiO_2$ ; h) BeO+3% glass; i) BeO+5%  $ZrO_2$ ;  $\times 340$ .

Figure 2 shows the heat conductivity of beryllia without the additions (purity 99.5%, density 95% of theoretical, grain size  $\sim 15 \mu m$ ). There is a heat conductivity maximum of about  $400 \text{ W/m}\cdot\text{deg}$  at about  $170^\circ K$ . For comparison, the data of Pryor et al. [8] is also shown (beryllia 99.8% pure, density 98%, grain size  $\sim 12 \mu m$ ). As can be seen from Fig. 2, an increase in the density and purity of the material leads to an increase in heat conductivity and a shift in the maximum to the side of lower temperatures.

Both empirical dependences are described well by the earlier-proposed [6] formula for calculating the heat conductivity of dielectrics:

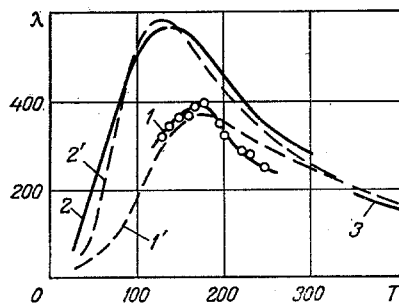


Fig. 2. Heat conductivity of beryllia in relation to temperature: 1, 3) our data; 2) Pryor's data [8]; 1', 2') calculated from Eq. (1) at  $K_n = 8 \cdot 10^{-4}$  and  $K_n = 2 \cdot 10^{-4}$ , respectively.  $\lambda$ , W/m·deg; T, °K.

$$\lambda = 2.3 \cdot 10^{-4} c \Theta \frac{d}{f} \left( K_n + \frac{uxz}{3E_u} \right)^{-1}, \quad (1)$$

where  $\Theta$  is the Debye temperature, °K; c, u, Debye thermodynamic functions: heat capacity, J/g-atom·deg, and internal energy, J/g-atom; d and f, distance between atoms, Å, and the area per atom in the perpendicular cross section, Å<sup>2</sup>;  $E_u$ , bond energy, J/mole; x, number of atoms in a molecule; z, coordination number;  $K_n$ , concentration of irregularities in the structure;  $\lambda$ , heat conductivity, W/m·deg.

The values of d, f, and z pertain to the sublattice of larger atoms (ions); for an oxygen fcc sublattice,  $z = 12$ ,  $f = d^2/\sqrt{2}$ . Substitution of the handbook values for beryllia (see Table 1) in Eq. (1) along with the values of  $K_{n1} = 8 \cdot 10^{-4}$ ,  $K_{n2} = 2 \cdot 10^{-4}$  gives the curves 1' and 2', which are close to the empirical curves. Both the calculations and experiment show that a change in the flow content of the structure changes the heat conductivity and shifts its maximum. The left branches of the theoretical curves correspond to a limitation of heat conductivity by structural defects ( $K_n \gg uxz/3E_u$ ), while the right branches correspond to a limitation of heat conductivity by thermal oscillations.

The very high thermal conductivity of beryllia — 3-6 times greater than that of its "neighbors" with respect to the periodic table, MgO and Al<sub>2</sub>O<sub>3</sub> — is explained with reference to Eq. (1) by the higher Debye temperature and greater bond forces ( $E_u/xz$  69 for BeO and 25 and 28 for MgO and Al<sub>2</sub>O<sub>3</sub>, respectively). The heat conductivity of these three oxides as calculated from Eq. (1) is in much better agreement with the data in the literature than the heat conductivity obtained from the Liebfried-Schliemann formula with a Grüneisen constant equal to 2 (Table 1).

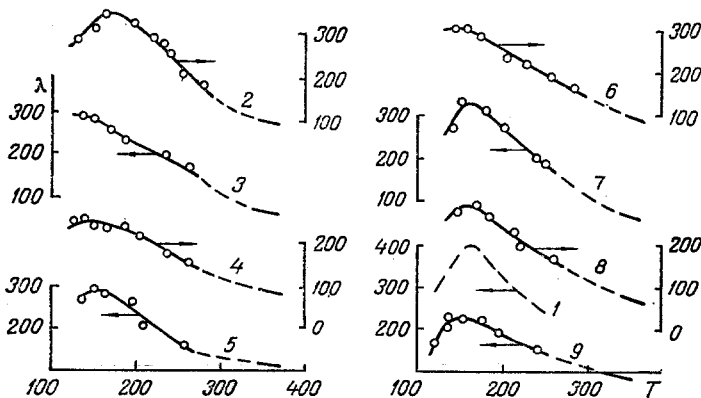


Fig. 3. Heat conductivity of beryllium oxide with additions in relation to temperature: 1) BeO; 2) BeO + 0.7% Y<sub>2</sub>O<sub>3</sub>; 3) BeO + 5% MgO; 4) BeO + 5% Fe<sub>2</sub>O<sub>3</sub>; 5) BeO + 5% TiO<sub>2</sub>; 6) BeO + 5% Al<sub>2</sub>O<sub>3</sub>; 7) BeO + 5% SiO<sub>2</sub>; 8) BeO + 3% glass; 9) BeO + 5% ZrO<sub>2</sub>.

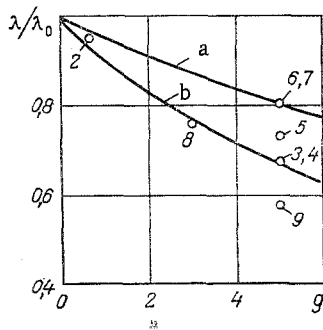


Fig. 4. Relative heat conductivity of beryllia with additions at 200°K in relation to the quantity of the additions: 2) Y<sub>2</sub>O<sub>3</sub>; 3) MgO; 4) Fe<sub>2</sub>O<sub>3</sub>; 5) TiO<sub>2</sub>; 6) Al<sub>2</sub>O<sub>3</sub>; 7) SiO<sub>2</sub>; 8) glass; 9) ZrO<sub>2</sub>; a, b) calculated from Eq. (2) at λ<sub>0</sub>γ<sub>0</sub>/λ<sub>s</sub>γ<sub>s</sub> = 5 and 10, respectively; g, wt. %.

Additions of the other oxides substantially lower the heat conductivity of beryllia (Fig. 3). Almost all of the relations  $\lambda = f(T)$  in Fig. 1 have a maximum at 150–170°K. The low-temperature measurements satisfactorily "join" with the measurements made above room temperature. The greatest reduction in heat conductivity is caused by additions of ZrO<sub>2</sub>, MgO, and Fe<sub>2</sub>O<sub>3</sub> (35–45%), while the least reduction occurs in the case of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (by 20%). Attention should be given to the large reduction in heat conductivity that occurs with a relatively small addition (up to 5 wt. %). It may be suggested that the additions (or a eutectic of the addition and beryllia) envelop the grains of the base, thereby creating significant heat-transfer resistance. A similar proposal was made in [5]: "...additions of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> form barriers which impede the transfer of heat from the grains." Eutectic points which are low compared to the sintering temperature [9] and the use of the salt method of introducing additions favor the enveloping of the grains. The two-phase system consisting of beryllia and an intergranular substance can be regarded as an aggregate of layers which are perpendicular to the flow of heat and have a heat conductivity expressed by the relation [10]:

$$\lambda = \frac{\lambda_0 \lambda_s}{v \lambda_0 + (1-v) \lambda_s}, \quad (1a)$$

where  $\lambda_0$  is the heat conductivity of the base (beryllia);  $v$  and  $\lambda_s$  are the volume percentage and heat conductivity of the intergranular substance.

Taking into account the relations between the volume  $v$  and weight  $g$  percentages at small quantities of the additions ( $g \ll 1$ )

$$v = \left( 1 + \frac{1-g}{g} \frac{\gamma_s}{\gamma_0} \right)^{-1} \approx g \frac{\gamma_0}{\gamma_s}$$

( $\gamma_0$  and  $\gamma_s$  are the volume weights of the base and intergranular substance, respectively), Eq. (1a) is rewritten in the form

$$\frac{\lambda}{\lambda_0} \approx \left( g \frac{\lambda_0 \gamma_0}{\lambda_s \gamma_s} + 1 \right)^{-1}. \quad (2)$$

If we construct two relations  $\lambda/\lambda_0 = f(g)$  at values of  $\lambda_0 \gamma_0 / \lambda_s \gamma_s = 5$  and 10 (Fig. 4), then the empirical points are located between these curves, except in the case of ZrO<sub>2</sub>. The empirical points were taken for a temperature of 200°K, but the ratio  $\lambda/\lambda_0$  remains about the same for other temperatures within the investigated interval. Thus a model of flat layers perpendicular to the heat flow satisfactorily describes the effect of the above additions on the heat conductivity of beryllia and allows us to evaluate the value of  $\lambda_s \gamma_s$  for the intergranular substance. The exception is zirconium dioxide — the only addition with a eutectic temperature ( $\sim 2300^\circ\text{K}$ ) which exceeds the sintering temperature of the material. In all probability, the intergranular substance in this case is pure zirconium dioxide. The value of the product  $\lambda_s \gamma_s$  for ZrO<sub>2</sub> is almost two orders less than for beryllia, and calculation by Eq. (2) yields values of  $\lambda/\lambda_0$  which are considerably lower than the empirical values. An investigation of the structure of the material showed that this discrepancy is due to the fact that only a certain percentage of the ZrO<sub>2</sub> occupies the space between the grains. The remaining portion of ZrO<sub>2</sub> forms individual inclusions.

Based on the above data, we may recommend the exclusion of ZrO<sub>2</sub>, MgO, and Fe<sub>2</sub>O<sub>3</sub> from the production of high-thermal-conductivity products based on beryllium oxide, since these oxides most significantly reduce the heat conductivity of beryllia.

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## Thermodynamic Properties of Cesium and Potassium

### at High Pressures and Temperatures

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Results are presented of PVT experiments of cesium and potassium in the gas phase. An equation of state is derived and tables of the thermodynamic properties of cesium vapor are computed. A survey is given of the PVT properties of cesium in the liquid phase.

Several experiments have been conducted to date to determine the thermophysical properties of cesium vapor. Their results may be generalized by the equation of state needed to calculate the thermodynamic properties of cesium vapor. A survey of PVT experiments on cesium is given in the monograph [1]. The most accurate of these experiments was conducted by the method of a constant-volume piezometer, in which an elastic membrane located in the hot zone serves as the pressure transducer. The membrane is unreliable at high temperatures: it changes position, corrodes, and is destroyed. Thus, the physics department at the Moscow Aviation Institute has developed a unit [2] in which the membrane is placed in the cold zone ( $t \approx 50^\circ\text{C}$ ) and the pressure of the cesium vapor is transmitted to the membrane through a column of liquid cesium in a capillary tube. Here, the limiting temperature reached in the experiment is determined only by the thermal stability of the material of the piezometer. Table 1 gives empirical values of PVT parameters obtained on this unit in four series of experiments. The computing error in these experiments for the compressibility factor  $z = PV/RT$  is  $\Delta z/z = 0.65\%$  with a confidence interval of 0.95.

Several improvements have been made to the design of the unit, the principal one being substitution of a molybdenum heater for the graphite heater. This eliminated the problem of the harmful effect of graphite vapors on the piezometer welds. The unit was used to

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