Functional Materials 18, No.4 (2011)

Thermal conductivity of pure and Cr^{3+} and Ti^{3+} doped Al_2O_3 crystals in 50–300 K temperature range

P.A.Popov, V.D.Solomennik, P.V.Belyaev, L.A.Lytvynov*, V.M.Puzikov**

Bryansk State University, 14 Bezhitskaya Str., 241036 Bryansk, Russia
*Institute for Single Crystals, STC "Institute for Single Crystals"
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

Received July 7, 2011

Thermal conductivity of pure and chromium- and titanium-doped α–Al_2O_3 crystals is studied within 50–300 K temperature interval. It is shown that the additions of chromium and titanium as well as high-temperature annealing essentially effect the thermal conductivity of the investigated crystals.

Исследована теплопроводность чистых и легированных хромом и титаном кристаллов α–Al_2O_3 в интервале температур 50–300 К. Показано значительное влияние добавок хрома, титана и высокотемпературного отжига на теплопроводность кристаллов.

1. Introduction

The crystal lattice of α–Al_2O_3 is anisotropic and belongs to the ditrigonal-scalenohedral symmetry class 3 *m* [1]. The pure crystals (leucosapphire) possess high thermal conductivity. Therefore, leucosapphire coatings are used as elements removing heat from some laser crystals which have low thermal conductivity. The temperature dependences of the thermal conduction of leucosapphire are well-known [2–5]. Al_2O_3:Me crystals are widely used as active media of solid lasers. Up to now, the influence of their doping additions and crystallographic features on value of the thermal conductivity has been studied insufficiently. The existing theory [6, 7] does not allow to reliably calculate such a kinetic characteristic of the material. That is why experimentally determined temperature dependence of thermal conductivity $k(T)$ is a useful certification characteristic of the crystal connected with its structure and composition. This information is also necessary for revision and development of the theory of heat transfer in dielectric single crystals with different content of defects.

The goal of the present research was to experimentally determine the thermal conductivity of pure and doped corundum crystals within 50–300 K temperature interval.

2. Experimental procedure

The study was performed on the samples of leucosapphire grown by the Kyropoulos method [8], the Verneuil ruby Al_2O_3:Cr [9] and ticor Al_2O_3:Ti, grown by the Czochralski method [10]. All the samples had the dimensions 4×4×40 mm^3, their long axes were oriented along the crystallographic directions <0001>, <10$\bar{1}$2> and <11$\bar{2}$0> to an accuracy of to 1°.

To reveal the influence of oxygen vacancies on the thermal conduction of the crystals, we studied the leucosapphire samples annealed under reductive conditions (4 h, 1800°C) and in vacuum (6.5 h, 1950°C). The

annealing in $CO + CO_2$ atmosphere at the reduction potential of the medium equal to 230 kJ/mole raises the density of anionic vacancies up to 10^{17} cm^{-3} [11].

The value of thermal conductivity in 50–300 K temperature interval was determined experimentally by the method of longitudinal heat flow using the facilities and measurement procedure described in [12]. The error of the determination of the absolute thermal conductivity value in the whole of the studied temperature interval did not exceed ±5 %.

3. Results and discussion

Leucosapphire. The dependence $k(T)$ for leucosapphire samples of different crystallographic orientation is shown in Fig. 1. At room temperature $k(T)$ is considerably stronger than the classical T^{-1} dependence. In all the three cases it is described by the function $T^{-1.6}$. In the vicinity of $T = 100$ K this dependence tends to $\approx T^{-3.6}$. At the lowest of the considered temperatures the curves start reaching the low-temperature

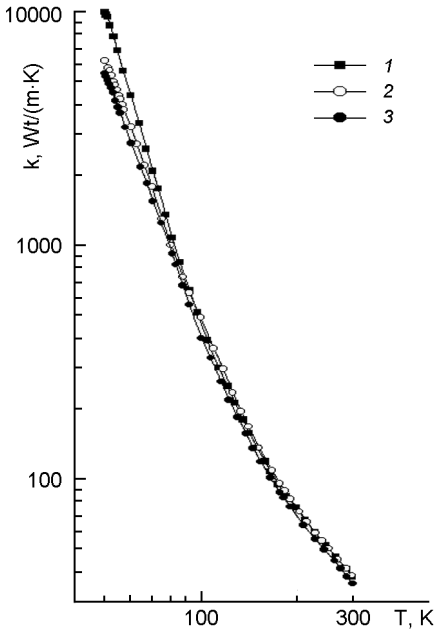

Fig. 1. Temperature dependences of thermal conductivity of leucosapphire along the crystallographic directions: *1* — <10$\bar{1}$2>; *2* — <0001> ; *3* — <11$\bar{2}$0>.

Table. Smoothed values of thermal conductivity (W/(m·K))

T, K	Al_2O_3			Al_2O_3:Cr		Al_2O_3:Ti		
	<10$\bar{1}$2>	<0001>	<11$\bar{2}$0>	Cr 0.05 %	Cr 1 %	Ti 0.06 %	Ti 0.08 %	Ti 0.2 %
50	9970	6200	5400	5200	402	190	177	85
60	4470	3270	2800	2900	328	196	185	91
70	2160	1800	1600	1620	274	194	185	95
80	1150	1020	990	930	232	187	180	97
90	700	668	607	590	195	176	172	97
100	468	490	403	410	163	161	159	96
110	332	360	306	308	136	147	145	93
120	257	277	233	231	119	134	132	88
130	202	210	185	187	103	119	119	84
140	164	171	153	156	90.0	105	106	79.6
150	137	142	128	130	79.7	95	96	75.0
160	118	121	109	114	70.1	86	87	70.2
170	102	105	95	100	63.2	79	80	65.8
180	90	92	85	87	58.0	72	73	61.1
190	82	83	77	77	53.6	66.4	68	57.2
200	75	76	69.7	70	49.4	61.5	62	54.2
210	68.3	69	63.5	64	46.2	57.3	58	51.4
220	63.0	63.4	59.1	58.5	43.0	53.7	54.3	48.3
230	58.6	58.9	54.9	54.1	40.6	50.7	51.3	45.7
240	54.6	54.8	51.5	50.5	38.4	47.5	48.4	43.6
250	51.1	51.2	48.2	47.5	36.0	44.6	45.5	41.9
260	48.1	48.1	45.3	44.9	33.9	42.1	43.2	40.0
270	45.4	45.3	42.6	42.2	32.3	39.7	40.9	38.2
280	42.9	42.9	40.1	40.0	30.9	37.6	38.7	36.5
290	40.3	40.7	37.7	38.1	29.6	35.7	36.8	35.1
300	37.9	38.7	35.9	36.3	28.4	34.0	35.2	33.9

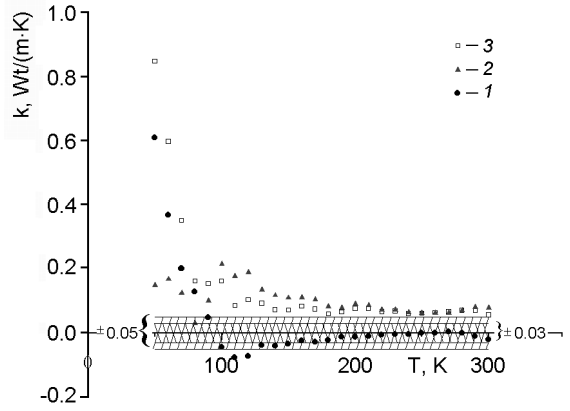

Fig. 2. Temperature dependences of anisotropy of thermal conductivity for leucosapphire: *1* — ε_1; *2* — ε_2; *3* — ε_3.

maximum characteristic of single crystals. For corundum crystals this maximum is observed at relatively high temperature $T \approx 40$ K [13]. However, all the mentioned features are typical of the crystals with high melting temperature ($T_m^{Al_2O_3} = 2327$ K [5]) and, consequently, high characteristic Debye temperature (according to the calorimetric data [14], for Al_2O_3 $\Theta_D = 1000$ K at $T = 300$ K).

At $T = 300$ K the absolute values of thermal conductivity (see Table) lie within the limits of the known literature data for leucosapphire [5, 13]. At $T = 50$ K the value of thermal conductivity for the crystallographic direction $<10\bar{1}2>$ is close to 10 kWt/(m·K) that testifies that the crystal has high chemical purity and structure perfection (the absence of a large number of point defects).

The obtained results also permit to estimate the anisotropy of thermal conductivity of leucosapphire. Presented in Fig. 2 are the points $\varepsilon(T)$ of the temperature dependence of the relative difference of the thermal conductivity along the crystallographic directions calculated from the formulae:

$$\varepsilon_1 = (k_{10\bar{1}2} - k_{0001})/k_{0001},$$
$$\varepsilon_2 = (k_{0001} - k_{11\bar{2}0})/k_{11\bar{2}0},$$
$$\varepsilon_3 = (k_{10\bar{1}2} - k_{11\bar{2}0})/k_{11\bar{2}0}.$$

The said figure shows the presence of two bands with the boundaries $\varepsilon = Const(T) = \pm 0.05$ (corresponding to the error of the determination of the absolute thermal conductivity value) and $\varepsilon = Const(T) = \pm 0.03$ (corresponding to reproducibility of the measured thermal conductivity value and, consequently, the possibility of the experimental procedure in samples comparison).

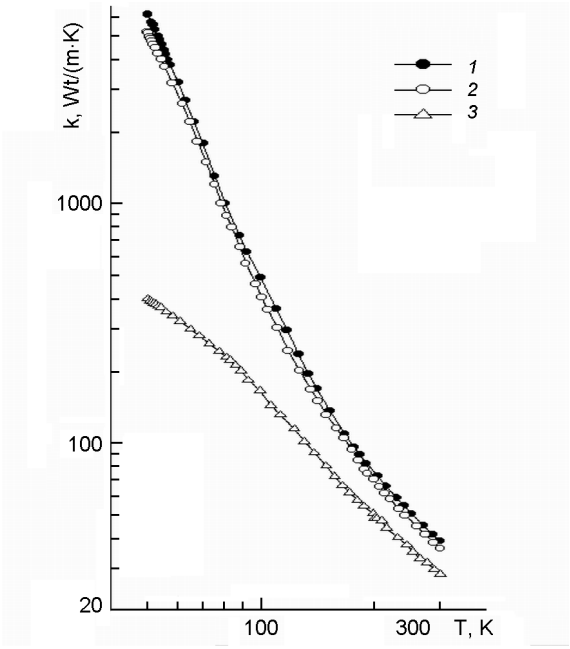

Fig. 3. Temperature dependences of thermal conductivity of ruby crystals with different chromium content: *1* — nominally pure, *2* — 0.05 %, *3* — 1 %.

The thermal conductivity of leucosapphire is anisotropic in a wide temperature region. At $T = 50$ K the value of thermal conductivity for the directions $<10\bar{1}2>$ is twice as high in comparison with that for $<11\bar{2}0>$. For this pair of the directions the anisotropy index $\varepsilon > 0$ within the whole of the investigated temperature interval.

Another situation is observed for the pair of the directions $<10\bar{1}2>$ and $<0001>$. At the lowest of the studied temperatures the thermal conductivity along the direction $<10\bar{1}2>$ is essentially higher than the one along the third-order axis $<0001>$. However, in the vicinity of $T = 110$ K the relation between the thermal conductivity values becomes reversed; with the rise of the temperature the obtained $k(T)$ values turn out to be the same.

The thermal conductivity for the direction $<11\bar{2}0>$ is the lowest among all the investigated values, at least in 50–300 K range.

A zigzag location of the points of the graph ε_2 in the region of 50–150 K seems to be caused by high sensitivity of the efficiency of phonon scattering to different structure defects (inevitably present in small quantities even in undoped crystals), as well as by the character of this scattering depending on the temperature.

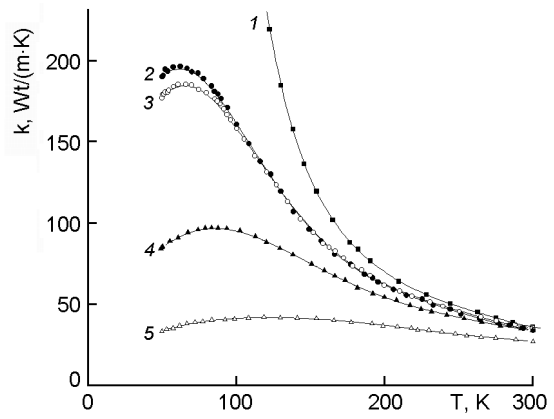

Fig. 4. Temperature dependences of thermal conductivity of ticor with different titanium content: *1* — nominally pure, *2* — 0.06 %; *3* — 0.08 %; *4* — 0.2 %; *5* — 0.5 %.

The spread of the points $k(T)$ with respect to the approximating values may be explained by the use of rounded-off tabulated values of thermal conductivity in the calculations of $\varepsilon(T)$.

Al_2O_3:Cr *crystals (rubies).* We compared the values of thermal conductivity of two ruby crystals with different content of chromium. In one of the samples the concentration of chromium was typical of laser rubies (0.05 at. %). The other sample contained 1 at. % of chromium, which was close to the limiting chromium concentration in dark-red ruby. Shown in Fig. 3 are the temperature dependences of thermal conductivity for ruby with low and high concentrations of chromium. Presented for comparison is the curve $k(T)$ for leucosapphire grown by the Kyropoulos method. As is seen, low quantity of Cr (0.05 at.%) is responsible for small diminution of the thermal conductivity of ruby in comparison with that of the undoped sapphire sample within the whole of the investigated $k(T)$ interval. On the contrary, 1 at. % content causes a cardinal decrease of the considered characteristic. At $T = 50$ K the difference between the values of thermal conductivity of the reference sample and the doped one (containing 1 at. % of Cr) is more than an order of magnitude, at room temperature such a difference is a quarter of an order.

Al_2O_3:Ti *crystals.* The results of the study of the thermal conductivity of Al_2O_3:Ti^{3+} (ticor) single crystals in comparison with the data obtained for $k(T)$ of Sample 5 in [16] are shown in Fig. 4.

As is seen, the doping of corundum with titanium gives rise to a considerable decrease of the thermal conductivity value.

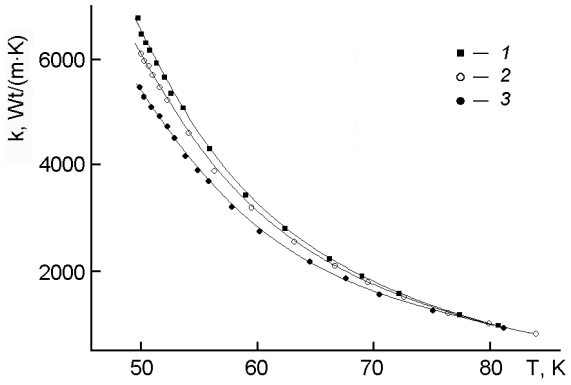

Fig. 5. Temperature dependences of thermal conductivity of leucosapphire: *1* — after reducing annealing; *2* — after vacuum annealing; *3* — without annealing.

The obtained $k(T)$ dependences characterize this material as a highly concentrated solid solution. Such a form of the curves testifies to the crystal structure imperfection. The degree of temperature maximum diffuseness increases with the rise of the doping addition concentration, and this maximum shifts towards higher temperatures, which is typical of dielectric single crystals with different degree of structure imperfection [7].

The decrease of the quantity of Ti^{3+} ions (which isomorphically replace Al^{3+} ions in Al_2O_3 lattice) gives rise to a noticeable increase of the degree of crystal structure imperfection. This is explained by the fact that the coefficient of titanium incorporation into the crystal lattice ($\approx$0.2) is essentially lower than that of chromium [16]. We assume that non-uniform distribution of Ti^{3+} ions in the bulk of the investigated sample is connected with crystal growth peculiarities leading to the appearance of local stress maxima [17] which may cause considerable phonon scattering in a wide temperature range and the corresponding decrease of the thermal conductivity.

Influence of high-temperature annealing. The results of the study of thermal conductivity for two annealed leucosapphire samples in comparison with that of the initial sample which has the same crystallographic direction of the long axis — $<11\bar{2}0>$ — are presented in Fig. 5 in linear scale for $T <$ 90 K.

A weak effect of the annealing is observed at the lowest among the studied temperatures. In both cases the low-temperature thermal conductivity increases in comparison with $k(T)$ of the non-annealed sample. This may be explained by the effect

of structure normalization at high-temperature annealing, as well as by the decreased level of the total and local stresses.

4. Conclusions

The thermal conductivity of nominally pure α—Al_2O_3, as well as of chromium and titanium-doped crystals, is studied experimentally. The obtained results allow to conclude that the additions of chromium and titanium considerably influence the thermal conductivity of the crystals. High-temperature annealing increases the low-temperature thermal conductivity.

The work was supported in part by the grant 2.1.1/10747 in the frame of the program "Development of scientific potential of higher school" of Ministry of Education and Science of Russian Federation.

References

1. I.V.Belov, *Izv.AN SSSR*, 238,53 (1947).
2. A.M.De Goer, *J. de Physique.*, No.30, 389 (1969).
3. G.A.Slack, *J. Phys. Rev., No.126, 427 (1962).*
4. R.Berman, E.L.Foster, J.M.Ziman, *J. Proc. Royal Soc. London, Ser. A, Mathem. and Phys. Sci.*, A 231, 130 (1955).
5. E.R.Dobrovinskaya, L.A.Lytvynov, V.V.Pishchik, Sapphire in Science and Engineering, NASU, STCU, Kharkov (2007), p.480.
6. R.Berman, Thermal Conduction in Solids, Clarendon Press, Oxford (1976).
7. V.S.Oskotskiy, I.A.Smirnov, Defects in Crystals and Thermal Conductivity, Nauka, Leningrad (1972) (in Russian).
8. M.I.Musatov, Thermostable Dielectrics, Atomzidat, Moscow (1980) (in Russian).
9. E.R.Dobrovinskaya, L.A.Lytvynov, V.V.Pishchik, Encyclopedia of Sapphire, ISC, Kharkov (2004) [in Russian].
10 Ye.Kryvonosov, L.Lytvynov, The Growth of Al_2O_3:Ti in Carbon-containing Environtment, First Workshop on Technological Bottlenecks in Compact High Intensity Short Pulse Lasers, Paris (2003), p.14.
11. V.S.Kanevskiy, Ye.V.Krivonosov, L.A.Litvinov, *Izv.AN SSSR. Neorg.Mater.*, No.25, 1486 (1989).
12. N.N.Sirota, P.A.Popov, I.A.Ivanov, *J.Cryst. Res.Technol.*, **27**, 535 (1992).
13. Thermal Conductivity of Solids, Reference book, edited by A.S.Okhotin, Energoatomizdat, Moscow (1984) [in Russian].
14. Landolt-Bornstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik. 6 Auflage. Band II. Eigenschaften der Materie in ihren Aggregatzustanden. Teil 4. Kalorische Zustandsgrossen, Springer-Verlag, Berlin, Germany, (1961), p.863.
15. P.A.Popov, V.D.Solomennik, D.A.Vinnik et al., *Bull. of South Urals State Univ. Math. Mech., Phys.*, **4**, 102 (2011).
16. T.A.Bazilevskaya, N.V.Gritsenko, V.T.Gritsina, *Ukr. Fiz. Zh.*, **26**, 1032 (1986).
17. S.Vishnevskiy, Ye.Krivonosov, L.Litvinov, *J. Crystallography*, **53**, 156 (2008).

Теплопровідність чистих і легованих Cr^{3+} і Ti^{3+} монокристалів Al_2O_3 в інтервалі температур 50–300 К

П.А.Попов, В.Д.Соломеннік, П.В.Бєляєв, Л.А.Литвинов, В.М.Пузіков

Досліджено теплопровідність чистих та легованих хромом та тітаном кристалів α–Al_2O_3 у температурному інтервалі 50–300 К. Показано значний вплив домішок хрому, тітану та високотемпературного відпалу на теплопровідність кристалів.