

Transport Characteristics of Phonons and the Specific Heat of $\text{Y}_2\text{O}_3\text{:ZrO}_2$ Solid Solution Single Crystals

E. I. Salamatov^a, A. V. Taranov^{b,*}, E. N. Khazanov^{b,**},
E. V. Charnaya^c, and E. V. Shevchenko^c

^a Physicotechnical Institute, Ural Branch, Russian Academy of Sciences, Izhevsk, 426000 Russia

^b Kotel'nikov Institute of Radio Electronics, Russian Academy of Sciences, Moscow, 103907 Russia

^c St. Petersburg State University, St. Petersburg, 198504 Russia

*e-mail: taranov@cplire.ru

**e-mail: khazanov@cplire.ru

Received May 24, 2017

Abstract—The temperature dependences of the specific heat and transport characteristics of phonons in single crystals of yttrium-stabilized zirconium dioxide $\text{Y}_2\text{O}_3\text{:ZrO}_2$ solid solutions have been studied. It has been shown that the temperature dependences of the specific heat at $T > 5$ K are almost identical at the degree of stabilization of a solid solution with an Y_2O_3 content of 5–20 mol %. Differences in the temperature dependences of the specific heat of samples from different sources at $T < 5$ K are due to the presence of low-energy two-level systems. The features of the transport characteristics of thermal phonons at liquid helium temperatures reflect not only the presence of two-level systems but also the scattering of phonons on low-dimensional domains of another phase coherently conjugate to the main phase of the $\text{Y}_2\text{O}_3\text{:ZrO}_2$ solid solution.

DOI: 10.1134/S1063776117100144

1. INTRODUCTION

Single crystals and ceramic based on solid solutions of yttrium-stabilized zirconium dioxide $\text{ZrO}_2\text{:Y}_2\text{O}_3$ (YSZ) have unique physicochemical properties [1]. The possibility of variation of the phase composition of YSZ depending on the degree of stabilization and technological conditions of synthesis ensures the diversity of physical properties associated with structural features of these materials: high ion conductivity, strength, durability, and chemical and biological resistances in a wide temperature range.

It is known that the crystal structure of particles of ZrO_2 zirconium dioxide powders can be inhomogeneous and can consist of fragments of different phases stably coexisting within a single nanoparticle [2].

The X-ray diffraction analysis and high-resolution microscopy study [3] of grown YSZ crystals with an Y_2O_3 content of 2.8–5 mol % showed that their structure is a tetragonal matrix with inclusions of monoclinic-phase domains (10–20 nm in size) at the coherent conjugation of phase interfaces. The cooling of a solid solution is accompanied by the relaxation of stresses via twinning. An increase in the concentration of the stabilizing impurity results in a decrease in the amount of the monoclinic phase in the tetragonal matrix and in a more homogeneous and disperse twin structure. The study of the elastic properties of a num-

ber of YSZ solid solutions showed the instability (aging) of YSZ compounds, which is characteristic of a glassy state of the structure.

The features of the structure of YSZ-based materials and the variability of their properties, which is related to the degree of stabilization and conditions of high-temperature synthesis, can indicate a complex character and features of the own phonon spectrum.

The authors of [4] emphasized the glass-like character of the thermodynamic characteristics in YSZ single crystals containing 8 wt % (4.5 mol %) Y_2O_3 and in ferroelectrics with a dispersed phase transition (relaxors) $\text{Pb}_3(\text{MnNb}_2)\text{O}_9$ (PMN) and $\text{Pb}_2(\text{MnTa})\text{O}_6$ (PMT). The study of the specific heat in single crystals of YSZ solid solutions containing 7 and 20 mol % of Y_2O_3 at $T > 50$ K in [5] showed that the mean free paths of phonons are comparable with values observed in amorphous materials (glasses).

The diffusion coefficient of phonons in glasses (fused quartz, F-1 glass, and glasses based on pentaphosphates of rare-earth metals) and in glass-like ferroelectrics PMN and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PSN) with a dispersed phase transition, which are not amorphous but have glass-like low-temperature thermophysical properties (specific heat, thermal conductivity, and diffusion coefficient of phonons) was studied in [6].

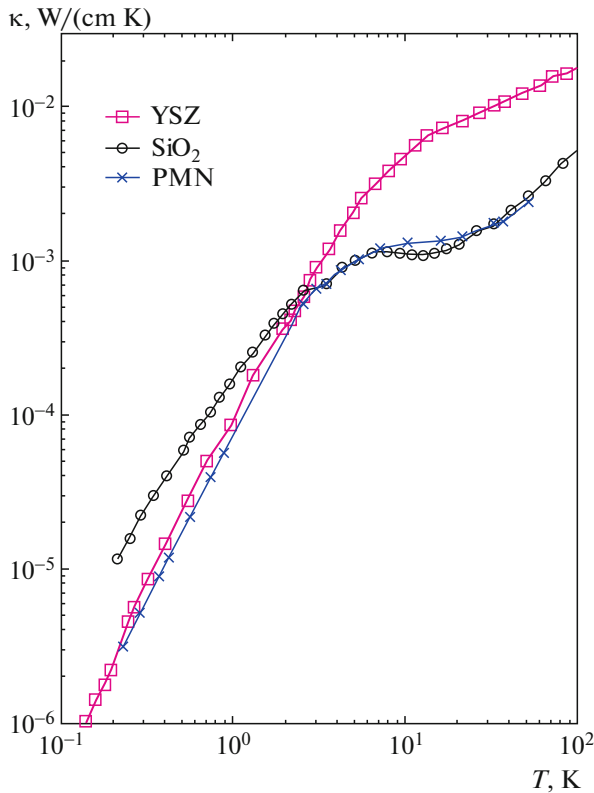


Fig. 1. (Color online) Temperature dependences of the thermal conductivity in fused quartz (SiO_2) [15] and in PMN and YSZ single crystals with the composition ZrO_2 : 4.5 mol % Y_2O_3 [4].

Such materials (glassy crystals [7]) include relaxors [8], solid alcohols [9, 10], and clathrates [11].

The theoretical model proposed in [12] is based on the assumption that the dynamic properties of amorphous materials correspond to the properties of disordered systems containing nanodefects, which resonantly scatter low-frequency phonons. It is known that the resonance scattering of phonons can lead to cross splitting of the acoustic branch, i.e., to the opening of a gap in the phonon spectrum [13, 14]. This phenomenon was used in [6] to study the effect of the gap. It was shown that the thermal conductivity and diffusion coefficient of phonons in glasses and glass-like crystals could be explained within a unified approach, where a plateau in the thermal conductivity of these systems is attributed to the position and width of the gap. One of the reasons is that the strong temperature dependence of the diffusion coefficient of phonons ($D(T) \propto T^{-5}$) below the temperature of the plateau in the thermal conductivity is due to the flattening of phonon dispersion curves near the gap. This picture was observed experimentally in various glasses and relaxors [6].

The behavior of the kinetic and thermodynamic characteristics in various glasses and relaxors can be

described within the approach developed in [6]. At the same time, the relation between the behavior of the thermodynamic characteristics and the features of the structure and phase composition of single crystals of a number of YSZ solid solutions is ambiguous and requires further study, which is the aim of this work.

2. THERMOPHYSICAL PROPERTIES OF YSZ

Figure 1 shows the temperature dependences of the thermal conductivity $\kappa(T)$ in fused quartz SiO_2 [15] and PMN and YSZ single crystals with an Y_2O_3 content of 4.5 mol % from [4]. A quadratic dependence of the thermal conductivity $\kappa(T)$ is observed in all cases at temperatures below 1 K. The dependence $\kappa(T)$ for SiO_2 and PMN exhibits a universal plateau in the temperature range of 5–10 K, whereas a certain weakening of the temperature dependence of the thermal conductivity for YSZ is observed at higher temperatures (about 20 K).

The situation with the specific heat is also uncertain. The usual glass-like behavior of the specific heat implies a linear temperature dependence of the specific heat at $T < 1$ K and a wide maximum in the reduced specific heat (in the C/T^3 representation) corresponding to the calorimetric “boson peak” in the temperature range of 5–10 K [16, 17]. This maximum on the C/T^3 dependence for YSZ samples from different sources was observed at $T = 24$ K.

Figure 2 shows the experimental temperature dependences of the specific heat of YSZ samples with different contents of Y_2O_3 . The behavior of the specific heat at temperatures above 5 K is the same for all samples and the difference in absolute values and positions of the maximum is almost independent of the concentration of the stabilizing additive. Some differences in the behavior of the specific heats of samples obtained in different laboratories are observed at lower temperatures. These differences are hardly related to the content of Y_2O_3 . The presented curves demonstrate that the boson peak near a temperature of 5 K is absent in all YSZ samples. The general behavior of the temperature dependence $C(T)$ is similar to the behavior of this characteristic in amorphous systems. However, for some reasons, the behavior of the specific heat of YSZ single crystals cannot be treated as glass-like. Below, we discuss these reasons in more detail.

The specific heats of solid alcohols existing in both the crystal and amorphous states were presented in [19]. The wide boson peak in the amorphous and crystal states begins at $T \approx 3$ K and $T > 10$ K, respectively. The authors of that work attributed this behavior for crystal structures to the “defreezing” of phonons of narrow optical modes whose contribution to the specific heat can be described as a contribution from Einstein oscillators. The inclusion of these phonons whose group velocity is low in the heat transfer process can be responsible for the weakening of the tempera-

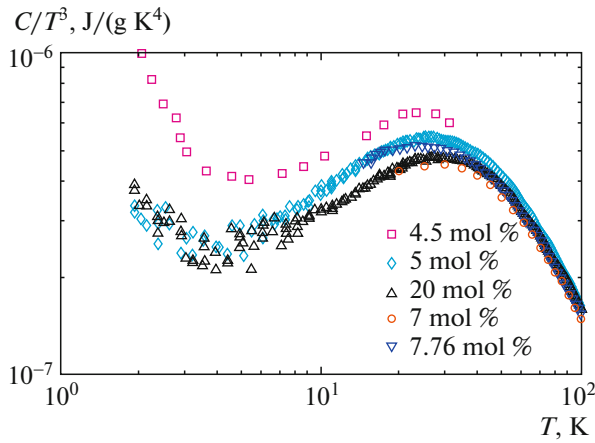


Fig. 2. (Color online) Temperature dependences of the specific heat of YSZ samples with different contents of Y_2O_3 (in mol %) 4.5 [4], 7 [5], 7.76 [18], and 5 and 20 from this work in the C_p/T^3 representation.

ture dependence of the thermal conductivity $\kappa(T)$ YSZ near a temperature of about 20 K (see Fig. 1).

In this work, this assumption is tested for single crystals of pentaphosphates of rare-earth metals and for glasses with the same composition. The boson peak on the temperature dependence of the specific heat in the C/T^3 representation in single crystals is shifted toward higher temperatures as compared to amorphous structures (Fig. 3). The results shown in Fig. 3 indicate that the assumption of the glass-like nature of the observed features of the thermodynamic characteristics of single crystals of YSZ solid solutions is not confirmed within the model developed in [6].

There are at least three possible phonon scattering mechanisms at liquid helium temperatures: (i) elastic scattering on the “mass defect” at the ion substitution $\text{Zr}^{4+} \leftrightarrow \text{Y}^{3+}$, (ii) scattering on phase inhomogeneities of the structure, and scattering on two-level systems (TLSs). Scattering of phonons on the mass defect can be neglected because the atomic masses of cations Zr (91.22) and Y (88.91) are close to each other. This fact is consistent with nearly coinciding dependences $C(T)$ at $T > 5$ K (see Fig. 2). As was shown in [20, 21], the presence of TLSs in YSZ solid solutions can be due to the distribution of vacancies over nonequivalent sites of the anion sublattice at the mutual substitution of different-valence cations. The presence of low-energy TLSs allows the explanation of a linear dependence and difference between dependences $C(T)$ at $T < 5$ K for samples synthesized in different laboratories.

The total specific heat of the system can be represented as the sum of three terms,

$$C = C_D + n_E C_E + n_{\text{tls}} C_{\text{tls}}, \quad (1)$$

where the first term is the Debye contribution, the second term is the contribution from Einstein modes

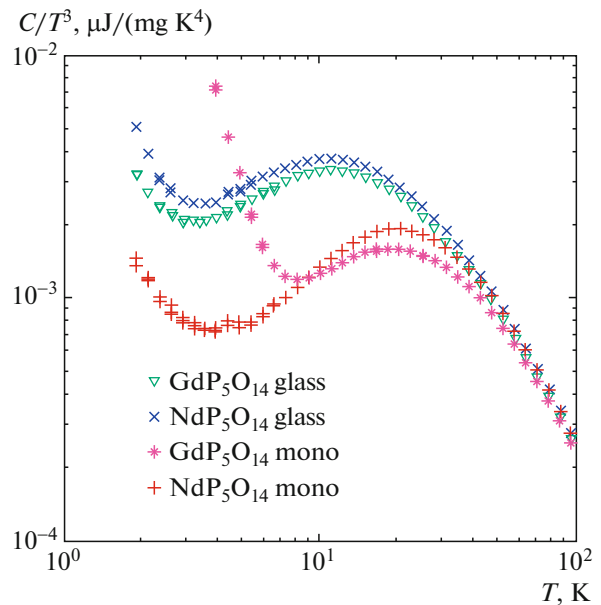


Fig. 3. (Color online) Temperature dependences of the specific heat of (mono) pentaphosphate single crystals and (glass) glasses with a similar composition.

with the concentration n_E , and the third term is the contribution from TLSs with the concentration n_{tls} . The expressions for the temperature dependence of these contributions are well known and include the energy parameters: Debye temperature T_D , Einstein temperature T_E , and the energy parameter of TLSs δ . These parameters can be determined by fitting theoretical curves to experimental data. Experimental data on $C(T)$ for the YSZ sample from [4] are shown in Fig. 4 together with theoretical curves describing the total specific heat and contributions from terms in Eq. (1). This figure also shows the dependence measured in this work at $T > 1.8$ K for the sample with an Y_2O_3 content of 5 mol % close in composition to the sample from [4].

The specific heat of the YSZ sample with an Y_2O_3 content of 4.5 mol % from [4] (Fig. 4) is reproduced with the parameters $T_D = 315$ K, $T_E = 125$ K, $\delta_1 = 1.8$ K, $n_E = 1.3 \times 10^{21} \text{ cm}^{-3}$, and $n_{\text{tls1}} = 6.1 \times 10^{18} \text{ cm}^{-3}$. Furthermore, according to our calculations, additional TLSs with $\delta_2 = 4.8$ K and concentration $n_{\text{tls2}} = 1.6 \times 10^{18} \text{ cm}^{-3}$ exist in this system. Our measurements in the sample with an Y_2O_3 content of 5 mol % were performed above the temperature $T = 1.8$ K. To describe them, it is sufficient to take into account TLSs with the energy parameters $T_D = 352$ K, $T_E = 125$ K, and $\delta_1 = 1.8$ K and concentrations $n_E = 1.5 \times 10^{21} \text{ cm}^{-3}$ and $n_{\text{tls1}} = 1.6 \times 10^{18} \text{ cm}^{-3}$ (theoretical dependences are not shown in Fig. 4).

According to the presented estimate, the specific heat at $T < 5$ K is determined by the presence of low-

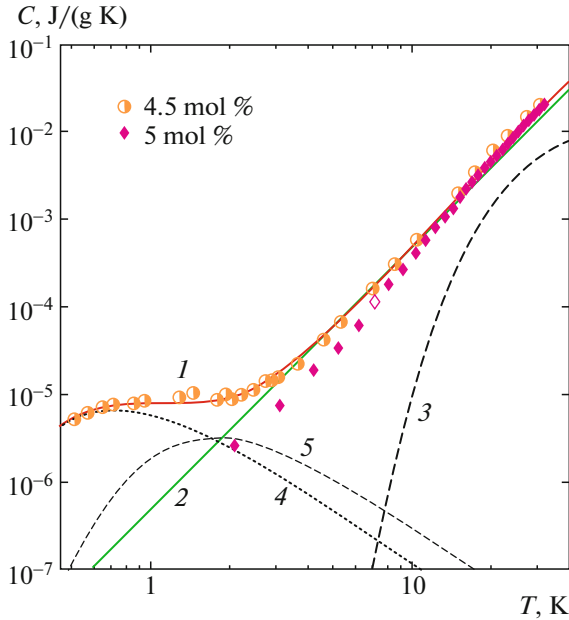


Fig. 4. (Color online) Experimental points and curves calculated by Eq. (1) for the temperature dependence of the specific heat of YSZ samples with an Y_2O_3 content of 4.5 mol % from [4] and of 5 mol % from this work: (1) total specific heat; (2) Debye contribution, (3) contribution from Einstein modes, (4) TLS_1 contribution, and (5) TLS_2 contribution.

energy TLSs whose concentration can depend on the conditions of synthesis including annealing, aging, etc. The manifestation of these TLSs can be expected in the kinetic characteristics of phonons at liquid helium temperatures.

3. ANALYSIS OF THE TRANSPORT CHARACTERISTICS OF PHONONS IN YSZ

We experimentally studied the propagation of weakly nonequilibrium thermal phonons at liquid helium temperatures when the combination of a high efficiency of scattering of phonons on defects of the structure and a small probability of inelastic phonon–phonon processes makes it possible to implement the diffusion propagation regime where weakly nonequilibrium thermal phonons after the interaction with defects of the structure are detected by a measuring system with a broadband bolometer [22]. The studied samples were plane–parallel polished plates with the thickness $L = (0.5–2) \times 10^{-2}$ cm and an area of about 0.5 cm². A gold phonon injector film and a tin detector film were deposited on the opposite faces of the samples by the vacuum thermal deposition method. The experiments were performed in liquid helium in the temperature range of 2.2–3.8 K. The temperature was varied by the evacuation of helium vapors. The working point of the bolometer was shifted by the application of a weak magnetic field.

We measured the time t_m at which the maximum of a diffuse signal of weakly nonequilibrium thermal phonons injected from the metal film heated by a short (10^{-7} s) current pulse to the temperature T_h ($\Delta T = T_h - T_0 \ll T_0$ (T_0 is the temperature of the thermostat) reaches the detector (bolometer). Such an approach allowed us, assuming that $T_h \approx T_0$ and varying the temperature of the thermostat, to obtain the temperature dependence $t_m(T)$:

$$t_m = \frac{L^2}{2D(T)}, \quad D(T) = \frac{1}{3}lv, \quad (2)$$

where D is the diffusion coefficient, v is the polarization-averaged velocity of phonons, and l is the mean free path of weakly nonequilibrium thermal phonons. Thus, the time t_m is unambiguously related to the kinetic characteristics of thermal phonons, which are due to the scattering on the structural features of the studied material.

Figure 5a shows the dependences $D(T)$ for YSZ solid solutions with different lengths and different contents of Y_2O_3 . Figure 5b shows the dependences $D(T)$ for fused quartz and PMN and PSN relaxors, as well as for solid solutions based on them. It is seen that this dependence for relaxors and fused quartz behaves as $D(T) \propto T^{-5}$, which is characteristic of the resonance scattering of weakly nonequilibrium thermal phonons at temperatures below the temperature of beginning of the plateau in amorphous materials [6]. The dependences $D(T)$ in Fig. 5a in the long-wavelength limit behaves as $D(T) \propto T^{-4}$. The absolute values of $D(T)$ and, hence, the mean free paths of weakly nonequilibrium thermal phonons in the YSZ solid solution are about two orders of magnitude larger than the respective parameters in PMN, PSN, and fused quartz. The dependence on the length of a sample (manifestation of the scattering of weakly nonequilibrium thermal phonons on TLSs) was observed only for the YSZ solid solution with an Y_2O_3 content of 5 mol %, which made it possible to estimate the mean free path of weakly nonequilibrium thermal phonons with respect to capture on TLSs as 0.05 cm $< l < 0.08$ cm. According to the general theory of diffusion, the effective length of expansion of diffusion in the time of observation is given by the expression $l = \sqrt{D_0\tau_R}$, where D_0 is the diffusion coefficient for elastic scattering and τ_R is the scattering time (capture on TLSs). At $T = 3$ K, the scattering time is $\tau_R < 10^{-4}$ s, which is comparable with the time of detection of the maximum of phonon nonequilibrium detected by the bolometer. Consequently, the presence of low-energy TLSs determines the character of not only the dependence $C(T)$ but also the dependence $D(T)$ at low temperatures. The effect of TLSs on the dependence $D(T)$ for the sample with an Y_2O_3 content of 20 mol % was not observed. It was shown in [20] that, as the stabilization of the YSZ solid solution (with the content of Y_2O_3 from 5 to 20 mol %)

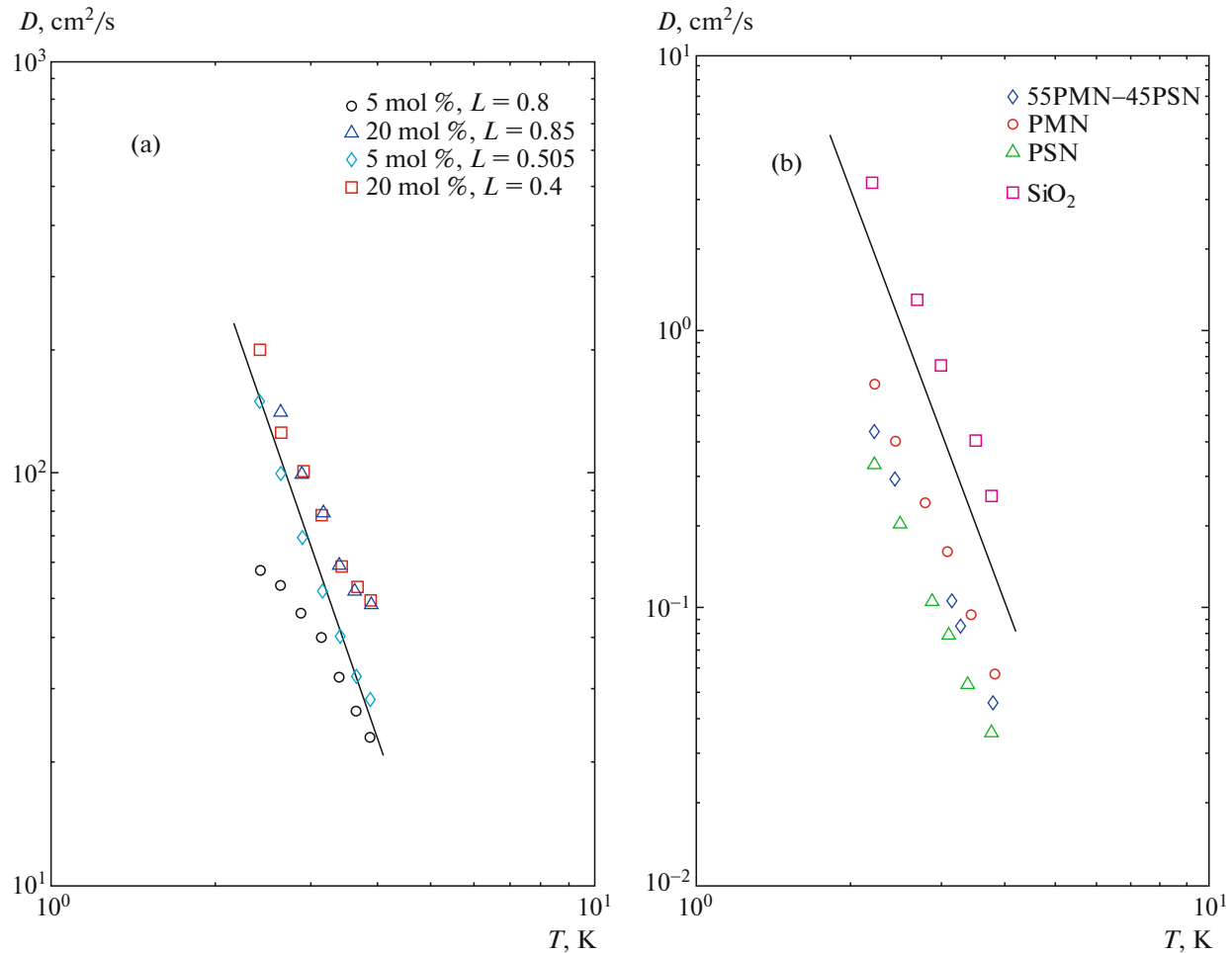


Fig. 5. (Color online) Temperature dependences of the diffusion coefficient D in (a) YSZ solid solutions and (b) fused quartz, PMN and PSN relaxors, and solid solution based on them. The solid lines are (a) $D \propto T^{-4}$ and (b) $D \propto T^{-5}$ (for an estimate of the slope of experimental curves).

increases, the ratio of the concentration of TLSs to the number of vacancies in the anion sublattice of the YSZ solid solution decreases by an order of magnitude.

Figure 6 shows the experimental dependences $D(T)$ in grown YSZ single crystals for the case where the features associated with TLSs are not observed. In all cases, the dependences are described well by the formula

$$D = A/T^4 + B, \quad (3)$$

which corresponds to the nonresonance scattering on structural inhomogeneities (inclusions) when inclusions are spherical and scattering on boundaries can be neglected. The first term in Eq. (3) with the factor

$$A = \frac{9}{2} D_0 \left(\frac{x}{1-x} \right)^2,$$

where $x = \rho_1 v_1^2 / \rho_0 v_0^2$; ρ_0 and ρ_1 are the densities of the main and additional phases, respectively; and v_0 and

v_1 are the polarization-averaged speeds of sound in the main and additional phases, respectively; describes the Rayleigh scattering and is determined by all defects of the system, which can be considered as point defects in the long-wavelength limit but can hardly be separated. Consequently, it is senseless to estimate its contribution. The second term in Eq. (3) is given by the expression

$$B = 2v_0 R / 3c,$$

and is determined by the geometric scattering on spherical inclusions of the second phase with the radius R , which have the volume fraction c . For single crystals with Y_2O_3 contents of 5 and 20 mol %, it can be accepted [23] that the main phase is the tetragonal and cubic phases, respectively, and the inclusions are the monoclinic and $Y_4Zr_3O_{12}$ phases, respectively.

Experimental data on the size of inclusions are reported only in [3] for the sample with an Y_2O_3 content of 5 mol % (domains of the monoclinic phase in the

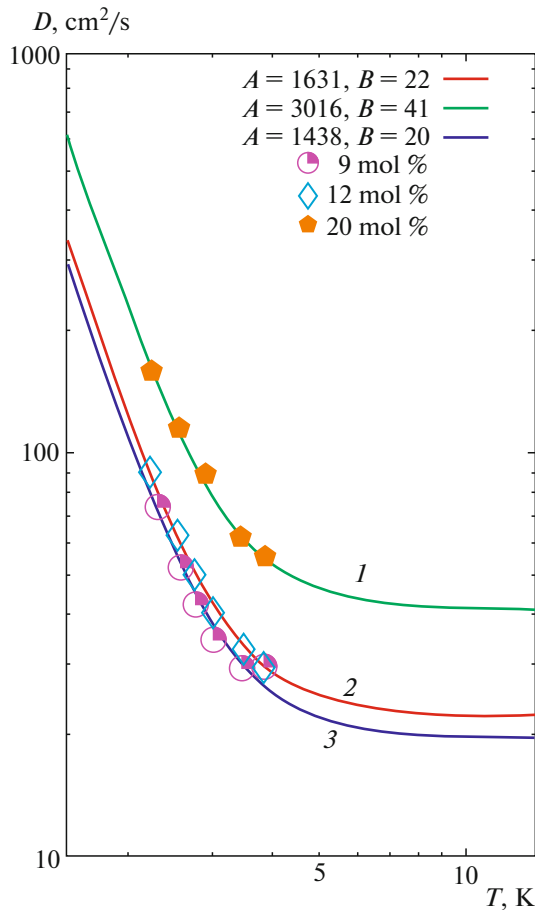


Fig. 6. (Color online) Temperature dependences of the diffusion coefficient in YSZ samples 0.1 cm long with the contents of 9, 12, and 20 mol % of the stabilizing impurity Y_2O_3 . Lines are calculated by Eq. (3) with the coefficients (1) $A = 3016$, $B = 41$; (2) $A = 1631$, $B = 22$; and (3) $A = 1438$, $B = 20$.

tetragonal matrix). Taking the value $v_0 = 4.5 \times 10^5$ cm/s for the polarization-averaged speed of sound and assuming that the geometric scattering factor B depends quite weakly on the concentration of the solid solution (see Fig. 6), one can carefully estimate the volume fraction c of domains of the monoclinic phase in the tetragonal matrix. At the average size of inclusions of the monoclinic phase $R = 15$ nm, the concentration of inclusions is $c \approx 3 \times 10^{-3}$. It is noteworthy that these estimates are qualitative because all reported data on the phase composition of YSZ (see, e.g., [23]) refer to room temperature and above it.

4. CERAMIC

The phase composition of crystallites (grains) in an YSZ-based polycrystalline ceramic can be determined to a significant extent by the technological conditions of synthesis. The presence of domains of different phases in the structure of ceramic grains can be

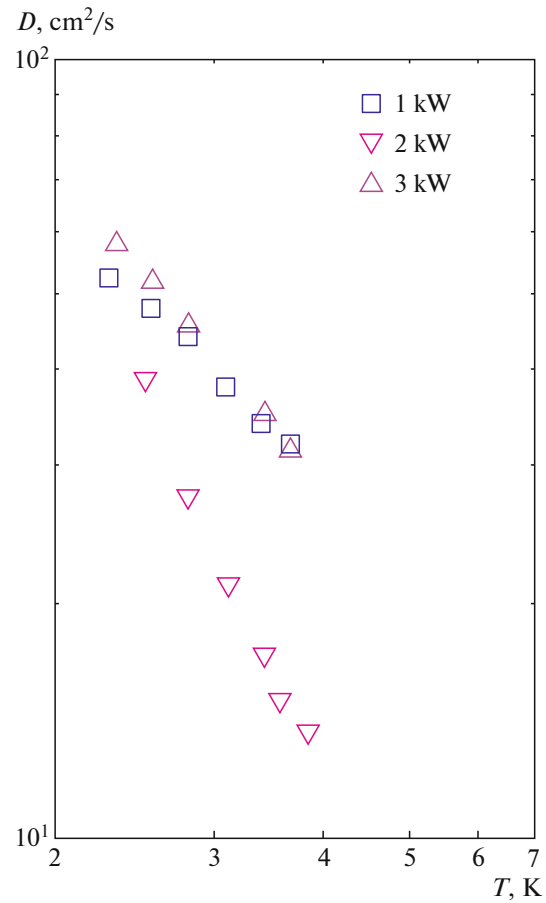


Fig. 7. (Color online) Temperature dependences of the diffusion coefficient in YSZ polycrystalline ceramic samples (2.8 mol % Y_2O_3) at various powers of ultrasonic irradiation. The synthesis temperature is $T = 1650^\circ\text{C}$.

responsible for a sharp change in the transport characteristics of weakly nonequilibrium thermal phonons in the studied temperature range.

Figure 7 shows the temperature dependences of the diffusion coefficient of weakly nonequilibrium thermal phonons in ceramic samples subjected to ultrasonic irradiation with different powers at the stage of pressing. It has been established that the preliminary ultrasonic irradiation led to the intensification of diffusion of yttrium from the bulk of grains to the surface in the process of sintering, to the deviation of the distribution of yttrium ions from the homogeneous distribution, to the reduction of the content of Y_2O_3 , and to the formation of domains of the monoclinic phase inside grains. According to the X-ray photoelectron spectroscopy data, ultrasonic irradiation led to the partial destruction and removal of adsorbed C–O and C–O–O–H hydrocarbonyl groups from the surface of grains and, as a result, to the equilibrium state of grain boundaries, stabilizing and reducing their thickness. The size of grains depended only weakly on the ultra-

sonic irradiation power. The X-ray diffraction analysis shows that polycrystalline ceramic samples in the absence of ultrasonic irradiation had the tetragonal modification. At the ultrasonic irradiation powers of 1 and 2 kW, the amount of the monoclinic phase in the bulk was 5 and 12 mol %, respectively [24]. At a power of 3 kW, the monoclinic phase was not observed, whereas the presence of carbide-like carbon was detected. The transition of free carbon to the carbide-like phase with the formation of zirconium carbide on the surface of grains stimulated the diffusion of yttrium from the bulk of grains in the process of sintering. An increase in the volume fraction of the monoclinic phase in $\text{ZrO}_2 : 2.8 \text{ mol } \% \text{ Y}_2\text{O}_3$ ceramic samples led to the decrease in the diffusion coefficient of thermal phonons. The absolute values of the diffusion coefficient corresponded within the order of magnitude to the values measured in single crystal samples.

To summarize, it has been shown that the nature of thermodynamic dependences $\kappa(T)$ and $C(T)$ in YSZ solid solutions at $T > 5 \text{ K}$ is determined by processes characteristic of the crystal state of the lattice. The thermal conductivity is low because statistically distributed domains of an additional phase are present in the crystal lattice of the corresponding YSZ solid solution. The low-temperature features of the dependence $C(T)$ are significantly controlled by two-level states associated with vacancies of oxygen complexes in the environment of cations.

ACKNOWLEDGMENTS

The YSZ samples for studies (“Fianit”) were taken from Prokhorov General Physics Institute, Russian Academy of Sciences and the pentaphosphate samples were placed at our disposal by Prof. S.N. Ivanov. The specific heat was measured with the equipment of the Resource Center of Diagnostics of Functional Materials for Medicine, Pharmacology, and Nanoelectronics, Science Park, St. Petersburg State University at a PPMS-9+EverCool-II facility (Quantum Design). This work was supported by the Russian Foundation for Basic Research (project nos. 13-07-01006 and 15-07-02563).

REFERENCES

1. E. C. Subbarao, in *Science and Technology of Zirconia*, Ed. by A. H. Heuer and L. W. Hobbs, Vol. 3 of *Advances in Ceramics* (Am. Ceram. Soc., Ohio, 1981), p. 1.
2. V. Ya. Shevchenko, A. E. Madison, and V. B. Glushkova, *Glass Phys. Chem.* **27**, 400 (2001).
3. M. A. Borik, V. T. Bublik, A. V. Kulebyakin, E. E. Lomonova, F. O. Milovich, V. A. Myzina, V. V. Osiko, S. V. Seriyakov, and N. Yu. Tabachkova, *Phys. Solid State* **55**, 1690 (2013).
4. D. A. Ackerman, D. Moy, R. C. Potter, et al., *Phys. Rev. B* **23**, 3886 (1981).
5. S. N. Ivanov, G. V. Egorov, and P. A. Popov, *Sov. Phys. Solid State* **34**, 1928 (1992).
6. E. I. Salamatov, A. V. Taranov, and E. N. Khazanov, *J. Exp. Theor. Phys.* **121**, 267 (2015).
7. Hiroshi Suga, *J. Phys.: Condens. Matter* **15**, S775 (2003).
8. S. N. Ivanov, E. P. Smirnova, A. V. Taranov, and E. N. Khazanov, *J. Exp. Theor. Phys.* **88**, 342 (1999).
9. A. I. Krivchikov, A. N. Yushchenko, O. A. Korolyuk, et al., *Phys. Rev. B* **77**, 024202 (2008).
10. G. Ross, P. Andersson, and G. Backstrom, *Nature (London)* **290**, 322 (1981).
11. A. I. Krivchikov, B. Ya. Gorodilov, O. A. Korolyuk, et al., *Phys. Rev. B* **73**, 064203 (2006).
12. E. I. Salamatov, *J. Non-Cryst. Solids* **202**, 128 (1996).
13. A. P. Zhernov, E. I. Salamatov, and E. P. Chulkin, *Phys. Status Solidi B* **168**, 81 (1991).
14. A. P. Zhernov, E. I. Salamatov, and E. P. Chulkin, *Phys. Status Solidi B* **165**, 355 (1991).
15. R. C. Zeller and R. O. Pohl, *Phys. Rev. B* **4**, 2029 (1971).
16. M. A. Ramos, C. Talon, R. J. Jimenez-Rioboo, et al., *J. Phys.: Condens. Matter* **15**, S1007 (2003).
17. M. A. Ramos, S. Vieira, F. J. Bermejo, et al., *Phys. Rev. Lett.* **78**, 82 (1997).
18. T. Tojo, T. Atake, T. Mori, and H. Yamamura, *J. Therm. Anal. Calorim.* **57**, 447 (1999).
19. M. Hassaine, M. A. Ramos, A. I. Krivchikov, et al., *Phys. Rev. B* **85**, 104206 (2012).
20. S. Ostanin and E. Salamatov, *Phys. Rev. B* **68**, 172106 (2003).
21. V. V. Ivanov, E. I. Salamatov, A. V. Taranov, and E. N. Khazanov, *J. Exp. Theor. Phys.* **110**, 34 (2010).
22. S. N. Ivanov, A. V. Taranov, and E. N. Khazanov, *Sov. Phys. JETP* **72**, 731 (1991).
23. C. Pascal and P. Duran, *J. Am. Ceram. Soc.* **66**, 23 (1983).
24. O. V. Karban', E. N. Khazanov, O. L. Khasanov, E. I. Salamatov, and O. Yu. Goncharov, *Perspekt. Mater.*, No. 6, 76 (2010).

Translated by R. Tyapaev