THERMOPHYSICAL PROPERTIES OF THE HIGH-TEMPERATURE SUPERCONDUCTORS $Y_{0.8}$–$Sm_{0.2}$–Ba_2–Cu_3–O_{7-x} IN THE TEMPERATURE RANGE 4.2-380 K

B. B. Boiko, A. I. Akimov,
L. L. Vasil'ev, V. I. Gatal'skaya,
S. E. Dem'yanov, L. E. Evseeva,
E. K. Stribuk, and S. A. Tanaeva

UDC 537.312.62

We report the results of an experimental study of the thermophysical properties of high-temperature superconducting ceramic based on yttrium.

The discovery of the high-T_c superconductivity of metal-oxide ceramics has aroused great interest in the study of their physical properties in the normal and superconducting states. The behavior of such systems is attributed to their possible structural instability. Our studies of the ceramics of the system $Y_{0.8}$–$Sm_{0.2}$–Ba_2–Cu_3–O_{7-x} [1] showed that when 20% yttrium is replaced by samarium the graph of ρ(T) in the temperature range 100-170 K exhibits anomalies in the form of an abrupt (2-3 orders of magnitude) drop in resistivity, after which a complete superconducting transition is observed at T = 97 K. Analysis of the data as well as studies of the structural state and the phase composition revealed that the anomalies in the behavior of the ceramic systems due to their having more than one phase. Most researchers have noted that these anomalies have a characteristic feature: after 3-7 thermal cycles in the temperature range 77-300 K the jumps in the resistivity decreased in magnitude and disappeared altogether. The dependence ρ(T) ws linear to T_c, which is usual for such materials.

In order to detect and study the thermal anomalies of the thermophysical characteristics we measured the heat capacity c, the thermal conductivity λ, and the thermal diffusivity a of the compound $Y_{0.8}$–$Sm_{0.2}$–Ba_2–Cu_3–O_{7-x} in the temperature range 4.2-380 K.

Superconducting ceramic samples were prepared by high-temperature solid-phase synthesis from yttrium, samarium, and copper oxides and barium carbonate in the stoichiometric ratio. The synthesized material is annealed three times at 950°C for 6 h with pulverization and pressing before each anneal. The samples had a complete resistive transition to the superconducting state T = 94 K and transition width 2.5 K.

The experiments were carried out in the temperature range 4.2-400 K on apparatus for studying thermophysical characteristics by a quasistationary method [2], which allows λ, a, and c to be determined simultaneously, in a single experiment. In this method continuous heat is supplied by a constant-power internal heat source between two plates. Each sample measured 35.6 × 35.6 × 3.6 mm. Each plate weighed 24 g. The density was 5270 kg/m³. The heating rate, in accordance with the method, ranged from 1 to 3 K/min. Moreover, we made allowance for the heating-rate drift due to the nonideal nature of the adiabatic shell; this drift was recorded regularly at intervals ΔT ~ 30-50 K after the heating had been switched on. In calculating the heat capacity we took into account the heat capacity of the heater, which amounted to ~10% of the total value. An advantage of this method is the high density of experimental points and all three characteristics (λ, a, c) are obtained simultaneously on the same sample.

Experiments were also performed on the same sample to determine the heat capacity in an adiabatic calorimeter in the range 75-110 K.

Figure 1 shows the temperature dependences of the heat capacity upon the first, second, and third coolings. In all cases a distinct heat-capacity peak appears at T = 98 K, which coincides with the temperature T_s^{on} of the onset of the superconducting transition for the given system. In the temperature range 100-150 K we observe numerous heat-capacity fluctua-

Institute of Solid-State and Semiconductor Physics, Academy of Sciences of the Belorussian SSR. A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 5, pp. 709-714, May, 1990. Original article submitted April 10, 1989.

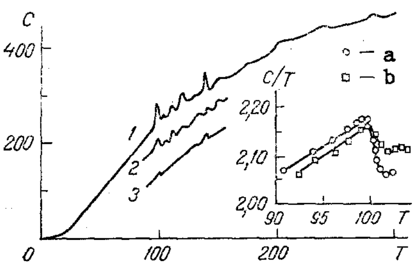

Fig. 1

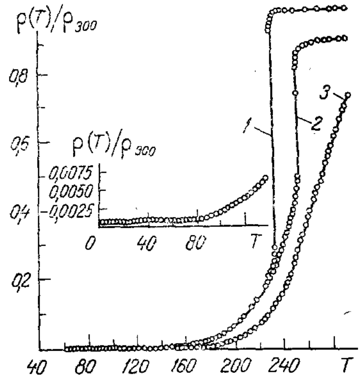

Fig. 2

Fig. 1. Temperature dependence of the heat capacity of $Y_{0.8}$–$Sm_{0.2}$–Ba_2–Cu_3–O_{7-x} during thermocycling: 1) first cooling; 2) three cycles; 3) five cycles; dependence c/T = f(T); a) quasistationary method; b) adiabatic calorimeter method; c) $J \cdot kg^{-1} \cdot K^{-1}$; c/T) $J \cdot kg^{-1} \cdot K^{-2}$; T, K.

Fig. 2. Relative temperature dependence of the resistivity of the component $Y_{0.8}$–$Sm_{0.2}$–Ba_2–Cu_3–O_{7-x}: 1, 2, 3) after one, two, and three thermal cycles, respectively.

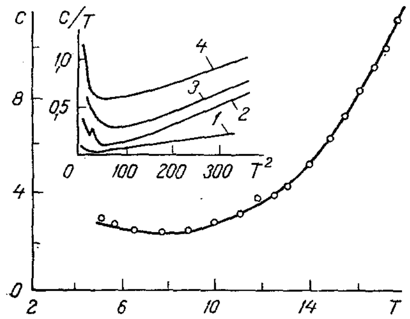

Fig. 3

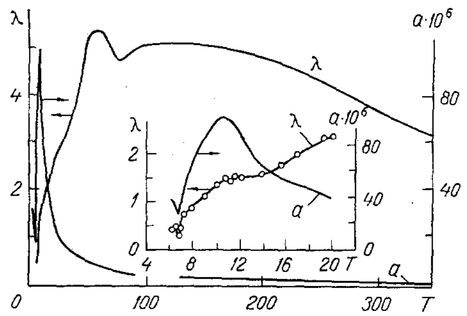

Fig. 4

Fig. 3. Temeprature dependence of the heat capacity of $Y_{0.8}$–$Sm_{0.2}$–Ba_2–Cu_3–O_{7-x} in the temperature range 4.2-20 K and the dependence c/T = f(T): 1) Y–Ba_2–Cu_3–O_{7-x} [11]; 2) Sm–Ba_2–Cu_3–O_{7-x} [14], 3) $Y_{0.8}$–$Sm_{0.2}$–Ba_2–Cu_3–O_{7-x}; 4) Ba–Cu_{2+x} [12].

Fig. 4. Temperature dependences of the thermal conductivity λ and thermal diffusivity a of $Y_{0.8}$–$Sm_{0.2}$–Ba_2–Cu_3–O_{7-x}. a) $m^2 \cdot sec^{-1}$; λ, $W \cdot m^{-1} \cdot K^{-1}$.

tions and only slight anomalies of c exist at higher temperatures (180, 215, 240 K). With the next thermal cycle the amplitude of the anomalous jumps in the heat capacity decreases and the curves flatten out. Similar tendencies appear on the temperature dependence of the resistivity with a jump in the region of 230 K (Fig. 2, curve 1). After three thermal cycles (curve 3) $\rho(T)/\rho_{300}(T)$ becomes monotonic as usual.

Comparison of the results obtained by different methods as well as the data of [3-5] permit the conclusion that the measuring method affects the temperature dependence of the thermophysical characteristics. Junod et al. [5] demonstrated that when the heating rate is increased the heat capacity shifts to higher values and the jump Δc in the region of the superconducting transition decreases. In general the jumps Δc, according to published data, vary from 3.5 to 6.5 J/kg·K under pulsed heating [6] and from 9 to 36 J/kg·K under slow heating [4]. In our experiments the value of Δc was 6 J/kg·K in the adiabatic calorimeter regime and 12.5 J/kg·K under uniform heating at a rate of 2 K/min.

This influence of the measuring method on the temperature dependence of the thermophysical characteristics is attributed to relaxation processes during the propagation of heat in high-T_c superconductors. Voronel et al. [4] proved the existence of two relaxation times in the neighborhood of T_c, and while $\tau \sim 500$-700 sec for the entire temperature region, apart from T_c, $\tau \sim 3000$ sec only in the region of the superconducting transition. Such a long relaxation time can have a significant effect on the thermophysical characteristics and other properties during continuous measurements, leading to fluctuations in these properties at $T > T_c$ [5, 7], and the influence of the relaxation is longer when the heating rate is higher.

The results are difficult to interpret uniquely at present because the samples are multiphase and in a ceramic state, especially in the case of large samples, as well as because the crystal and electronic structures of multicomponent metal oxides are complex. These anomalies can be determined either by the structural transitions, associated with vacancy ordering in the oxygen sublattice of the sample, or by an instability in the lattices. Moreover, since they were rather large, the samples were not sufficiently homogeneous. Our experiments to determine at different points on the surface of the samples, using the vortex-current LFF (low-frequency fluctuations) method [8], revealed that the resistivity is appreciably inhomogeneous. This means that a macrostructural (technological) inhomogeneity can also affect the properties of the material.

Of particular interest is the heat capacity in the low-temperature range (Fig. 3). Starting from $T < 7$ K, the heat capacity becomes an increasing function of the temperature. Such behavior of c(T) was noted in [9] for the compounds Yb–Ba–Cu–O and Ho–Ba–Cu–O and was attributed to the existence of a magnetic moment in rare-earth elements. Ferreira et al. [10] indicated that for these materials these anomalies are associated with the Schottky electron anomaly and not with magnetic ordering and, moreover, magnetic ordering exist in the impurity phase.

At low temperatures the heat capacity of high-T_c superconductors can be written as

$$c = \gamma T + \beta_1 T^3 + \beta_2 T^5 + \Delta c,$$

where γT is the linear part of the heat capacity, $\beta_1 T^3$ is the lattice heat capacity, $\beta_2 T^5$ is the dispersion lattice heat capacity, Δc is the contribution from the antiferromagnetic ordering of the paramagnetic ions of the rare-earth metals in the composition of the material (Sm) or of the magnetic impurities (Fe, Dy, etc.) and/or crystal-field effects (Schottky effect). For $T < 12$ K the contribution $\Delta c \sim T^{-2}$, which is evidently due to the Schottky effect of the impurity phase, e.g., $Ba–Cu–O_{2+x}$, since antiferromagnetic ordering of Sm^{3+} occurs at $T = 0.6$ K [11]. Magnetic impurities that contribute to the heat capacity at higher tempeatures can exist, however (Dy [11]).

Traces of the phase $Ba–Cu–O_{2+x}$ were observed by Vasil'ev et al. [12]. Eckert et al. [13] showed that the presence of small amounts of $Ba–Cu–O_{2+x}$ can result in anomalous behavior of the heat capacity at low temperatures, especially affecting the linear term c. Many authors believe that γ correlates with large amounts of secondary phases, especially $Ba–Cu–O_{2+x}$. Sasaki et al. [12] asserted that $\gamma = 0$ for the ceramic Bi–Sr–Ca–Cu–O while $\gamma \neq 0$ for the thallium ceramic $Tl_2–Ca_2–Ba_2–Cu_3–O_{10}$ since the phase $Ba–Cu–O_{2+x}$ also exists there.

In general, the existence of a linear term in the heat capacity is an interesting property of high-T_c superconductors, which is also important from the theoretical standpoint. At this stage it is still not clear whether or not it is a consequence of resonant valence bonds or of tunneling two-level systems. The linear term is difficult to determine exactly because it is masked by the increase in c/T at low temperatures. But it is already clear that the linear term is related to paramagnetic phase impurities ($Ba–Cu–O_{2+x}$) and/or with paramagnetic chemical impurities (rare-earth and transition metals), and is larger when the inpurity content is higher.

All the coefficients of Eq. (1) were determined and the heat capacity can be written as

$$c = (45{,}66T^{-2} + 0{,}1445T + 0{,}001T^3 + 2\cdot 10^{-7}T^5)\ \mathrm{J\cdot kg^{-1}\cdot K^{-1}},$$

which describes the experimental c/T data well for $5 < T < 14$ K. The values of c/T for the ceramics $Sm–Ba_2–Cu_3–O_{7-x}$ and $Ba–Cu–O_{2+x}$ and $Y–Ba_2–Cu_3–O_{7-x}$ have been plotted on the graph of $c/T = f(T^2)$ (Fig. 3). As we see, the contribution of $Ba–Cu–O_{2+x}$ may be very substantial. Moreover, the presence of the paramagnetic ion Sm^{3+} also makes a contribution to the heat capacity, causing it to increase because of magnetic fluctuations below 7 K, as was Escribe–Fillippini et al. [14] noted for $Sm–Ba_2–Cu_3–O_{7-x}$, where they found a heat-capacity peak at

$T = 5.5$ K and postulated the existence of two sublattices with different magnetic ordering temperatures. But in this situation it is most natural to attrribute such behavior of an impurity magnetic phase, as was done in [11, 12].

Figure 4 shows the measured values of the thermal conductivity and thermal diffusivity in the temperature range 4.2-370 K and separately in the range 4.2-20 K. In the range 120-370 K the thermal conductivity varies little as the temperature increases and is determined by the electron-phonon and phonon-phonon scattering. In [15] we showed that λ_{el} is 5-7% of the total thermal conductivity, the electron-phonon interaction is rather weak and the decrease in $\lambda(T)$ is due to an increase in the phonon-phonon interaction as the temperature is raised. Moreover, the behavior of $\lambda(T)$ will in many ways be determined by the behavior of $u(T)$. From [16] we know that the velocity of sound in $Y-Ba_2-Cu_3-O_{7-x}$ varies nonmonotically, increasing slightly from 100 to 125 K, and then falls off markedly according to an almost linear law. As the temperature decreases below 100 K the heat transfer decreases at T_c because part of the electrons pass into the superconducting state and the total thermal conductivity decreases slightly until the reduction of the electron-phonon scattering causes the thermal conductivity to grow and at $T = 50$-60 K it passes through a maximum, which is characteristic of all high-T_c superconductors.

As the temperature is lowered further scattering on defects, impurities, and structural inhomogeneities of the lattice and in the case of superconducting ceramic, scattering on pore and grain boundaries, becomes the determining factor and the thermal conductivity decreases. The magnitude and nature of the maximum λ depend on the oxygen content and the porosity of the sample [17, 18]. The lower the oxygen content in the material, the more the lattice changes and, evidently, the more "normal"; electrons in it since the material $Ba_2-Cu_3-O_6$ is already nonsuperconducting, which means more normal electrons remain in it below T_c and for a "longer time" [3] and, therefore, the temperature of the maximum λ and the temperature of the inflection of $\lambda(T)$ decrease. The porosity of high-T_c superconductors affects the thermal conductivity and thermal diffusivity in two ways: phonons can be scattered from pore boundaries; and the porosity reduces the effective cross section for electron and phonon transport. The absolute values of λ and a, therefore, are smaller when the porosity is greater.

Unusual behavior of thermal diffusivity is observed at low temperatures. At $T = 8.5$ K the function $a(T)$ passes through a maximum. Since $a = {}^1/_3 ul$, the behavior of $a(T)$ is determined by $u(T)$ and $\ell(T)$. At $T > 9$ K impurity scattering and defect scattering are substantial and, therefore, $\ell \sim T^{-1}$ and if u = const or decreases slightly, then $a(T)$ decreases more rapidly than T^{-1}. At lower temperatures the mean free path for ordinary materials becomes constant and is determined by boundary scattering, then $a(T)$ should also be constant. In the given processes sharply reducing the mean free path begin at low temperatures. They may increase both phonon-magnon interaction on chemical paramagnetic impurities and scattering secondary phases ($Ba-Cu-O_{2+x}$). An abrupt increase in $a(T)$ is observed at $T_c = 97$ K and then in the region 100-150 K the variations in $a(T)$ are fluctuational with flattening of the curves after thermocycling.

In summary, we have made a comprehensive study of the thermophysical properties of $Y_{0.8}-Sm_{0.2}-Ba_2-Cu_3-O_{7-x}$ over a wide range of temperatures. A correlation is observed between the temperature dependences of the electrical resistivity and the thermophysical properties. The temperature dependences of the thermal properties are affected by the measuring method. Paramagnetic chemical and physical impurities have been found to have an effect on the thermophysical properties at low temperatures.

NOTATION

Here ρ is the electrical resistivity; T is the absolute temperature; T_c is the superconducting transition temperature; c is the heat capacity; λ is the thermal conductivity; a is the thermal diffusivity; τ is the relaxation time; u is the velocity of sound; λ_{el} is the electronic part of the thermal conductivity; and ℓ is the phonon mean free path.

LITERATURE CITED

1. B. B. Boĭko, F. P. Korshunov, G. V. Gatal'skii, et al. Vestsi Akad. Navk BSSR. Ser. Fiz.-Mat. Navuk, No. 2, 39 (1988).
2. L. L. Vasil'ev, S. A. Tanaeva, and G. I. Borbova, Porous Materials in Cryogenic Engineering [in Russian], Minsk (1979).
3. R. A. Butera, Phys. Rev. B, 37, No. 10, 5909 (1988).

4. A. V. Voronel, D. Linsky, A. Kisljuk, and S. Drishlikh, Physica, 153-155, 1086 (1988).
5. A. Junod, A. Bezinge, and J. Muller, Physica, 152, 50 (1988).
6. M. V. Nevitt, G. W. Crabtree, and T. E. Klippert, Phys. Rev. B, 36, No. 4, 2398 (1987).
7. V. G. Bessergenev, Papers Read at Eighth All-Union Conference of Thermophysical Properties of High-Temperature Superconductors [in Russian], Novosibirsk (1988).
8. V. F. Zinchenko, V. I. Krylovich, V. I. Alekseenko, et al., Mekh. Kompoz. Mater., No. 5, 891 (1987).
9. O. V. Ershov, A. A. Minakov, V. G. Veselago, et al., Abstracts of Papers Read at Eighth All-Union Conference of Thermophysical Properties of High Temperature Superconductors, Part II [in Russian], Novosibirsk (1988).
10. J. M. Ferreira, B. W. Lee, Y. Dalichaouch, M. S. Torikachvili, et al., Phys. Rev. B, 37, No. 4, 1580 (1988).
11. B. W. Lee, J. M. Ferreira, Y. Dalichaouch, M. S. Torikachvili, et al., Phys. Rev. B, 37, No. 4, 2368 (1988).
12. T. Sasaki, O. Nakatsu, N. Kobayashi, A. Tokiawa, et al., Physica, 156, 395 (1988).
13. D. Eckert, A. Junod, T. Graf, and J. Muller, Physica, 153, 1038 (1988).
14. C. Escribe-Fillippini, K. Konate, R. Buder, J. Marcus, et al., Physica, 153, 1030 (1988).
15. B. B. Boĭko, A. I. Akimov, L. L. Vasil'ev, et al., Inzh. Fiz. Zh., 57, No. 6, 885 (1989).
16. T. Landgreid, K. Fossheim, and F. Vassanden, Physica, 153-155, 1096 (1988).
17. A. Jesowski, K. Rogacki, R. Horyn, and J. Klamut, Physica, 153-155, 1347 (1988).
18. J. Heremans, D. T. Morelli, G. W. Smith, and S. C. Strite, Phys. Rev. B, 37, No. 4, 1604 (1988).

CONDUCTIVE THERMAL CONDUCTIVITY OF FIBROUS MATERIALS UNDER TRANSIENT GAS FLOW

N. A. Bozhkov and A. A. Ivanov

UDC 536.2.01

The results are reported from computational studies of the conductive thermal conductivity of fibrous materials working at pressures correspnding to transient gas flow in pores.

Energy transfer through a layer of fibrous material is determined by such elementary processes as thermal conductivity through a framework and a gas, radiative heat transfer, and forced and free convection. The intensity of these processes depends in many ways on the external conditions [1]. The region of application of highly porous thermal insulation materials is characterized by variation of the pressure from hundreds of atmospheres to space vacuum, a temperature range from 20 to 2000 K, and different compositions of the gas filling the pore. The contribution of one elementary process or another to the overall heat transfer process will vary, depending on the parameters indicated above. Thus, radiative heat transfer is virtually absent at low temperatures and the effect of free convection is negligible at pressures $P < 100$ kPa while its role is decisive at pressures of the order of 100 MPa [1]. Of great interest is the range of pressures where transient gas flow conditions in a porous medium are realized. A number of applications of heat-insulation coatings typically have the pressure-time characteristic shown in Fig. 1. In the indicated pressure range heat transfer in the pores is determined by the interaction of gas molecules with each individual fiber (a similar situation arises when radiation interacts with the elements of a fibrous framework).

Analysis of the mathematical models in [1, 2] for heat transfer through the gas and framework permit the conclusion that for structures formed by fibers with different diameters, lengths, orientations, and thermophysical characteristics (TPC's) the thermal conductivity will depend on the anomalies in the fiber distribution according to size, orientation, and thermophysical properties as well as on such integrated indices as porosity and average fiber diameter. The effect of the distribution on the TPC's can manifest itself most in transient pressure regimes.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 5, pp. 714-721 May, 1990. Original article submitted March 13, 1989.