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**THERMAL CONDUCTIVITIES, ELECTRICAL RESISTIVITIES,
AND SEEBECK COEFFICIENTS OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$
SUPERCONDUCTORS FROM 80 TO 300 K**

D.W. Yarbrough¹, R.K. Williams¹, and D.R. Shockley²

ABSTRACT

Thermal conductivities, electrical resistivities, and Seebeck coefficients of three polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ specimens have been measured over the temperature range 80 to 300 K in a longitudinal-heat-flow apparatus. Smoothed values for thermal conductivity, and electrical resistivity have been obtained for temperatures above the superconducting transition temperature of 90 K.

The thermal conductivity values decreased as the temperature was increased, a trend which is inconsistent with the results of some other investigators. The thermal conductivities were less than previously published values and it is suggested that these differences are due to radiative heat loss in the published values. This effect is especially important for linear heat flow measurements on low thermal conductivity materials.

The electrical and thermal conductivities of the specimens varied with Ba content and this variation was used to separate the thermal conductivity into lattice and electronic components. The compound is a mixed conductor, both the lattice and electronic components are significant. The phonon component exhibits the expected temperature variation and an analysis indicates that the electron-phonon interaction is unusually strong.

Key Words: Superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$, Thermal Conductivity, Electrical Resistivity, Seebeck Coefficients, YCBO

¹ Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN.

² DOW Chemical Company, Louisiana Division, Plaquemine, LA.

INTRODUCTION

The high- T_c rare-earth $\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ superconducting ceramics have been extensively studied since their discovery in 1986.^{1,2} These ceramics can be superconducting up to temperatures above the normal boiling point of nitrogen (77 K). Heremans et al.³ studied members of the family of superconductors containing Gd, Dy, Eu, Y, or Er and found T_c s in the range 83 to 90 K for sintered specimens.⁴ The compound $\text{YBa}_2\text{Cu}_3\text{O}_7$ was reported to have a T_c of 86 K.³ Heremans et al.¹ observed that the thermal conductivities, $k(T)$, of the five rare-earth superconductors had similar temperature dependence with $\text{YBa}_2\text{Cu}_3\text{O}_7$ having the lowest k . All five compounds have k s that increase with temperature at very low temperatures, exhibit maximums at a temperature below T_c , have an abrupt change in dk/dT at T_c , and become relatively constant or slowly decreasing for $T > T_c$. The electrical resistance, ρ , and the Seebeck coefficients, S , are zero for $T < T_c$ with S near zero for temperatures perhaps as high as 650 K.^{5,6,7}

This paper is primarily focused on experimental k -values for sintered specimens of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO). Thermal conductivities for YBCO have been previously reported for sintered specimens, single crystals, epitaxially grown specimens, and liquid-phase processed material.^{3,4,8-16}

Materials Tested

The three YBCO specimens used in this study were produced from 99.99% Y_2O_3 , CuO , and BaO_2 . The theoretical density of the product based on x-ray diffraction data was found to be 6370 kg/m³. The reactants were ground and mixed before being cold-pressed at 206.8 MPa. One of the specimens (DH2-97, No. 2) was purposely made with a small increase in Ba content to produce $\text{YBa}_{2.006}\text{Cu}_3\text{O}_{7-x}$.

The three specimens were subjected to a series of heat treatments that are described in detail by Shockley.¹⁷ Specimen one (SP7#8) was heated in air at 950°C for 72 hours and cooled to room temperature. The solid was crushed, ground to pass a 325 mesh screen, and cold-pressed into a 6.35-mm-diameter steel die at a pressure of 206.8 MPa. The cylindrical specimen was heated to 950°C in O₂ for four hours, slowly cooled to 475°C, re-heated to 875°C in 4.053 MPa O₂ for 24 hours, and then held at 500°C and O₂ pressure of 10.13 MPa for 24 hours. The initial heating step for specimen two was for 16 hours at 950°C in O₂. The material was reground, pressed into a 6.35-mm-diameter cylinder and heated in O₂ for 8 hours at 950°C. The pellet was cooled from 950°C to 700°C over a six-hour period and from 700°C to 450°C over a 48-hour period. The third specimen (DH2-93) underwent the same initial treatment as specimen one. The pelletized material was sintered in O₂ for 16 hours at 950°C, cooled to 500°C and maintained at this temperature for two hours.

The bulk densities of the specimens one, two, and three were 5840, 5650, and 5750 kg/m³, respectively. The calculated porosities were 0.0832, 0.1133, and 0.0976. The magnetic susceptibility data shown in Figure 1 confirmed T_cs to be 91 K, 92.5 K, and 93 K for specimens one, two, and three, respectively. Seebeck coefficients were zero below T_c.

Test specimens approximately 5 mm in diameter and 22 mm in length were used for property measurements. Stainless steel cylinders were attached with good thermal contacts to each end of the specimens to provide room for a heater and material to clamp to the low-temperature heat sink.

Physical Property Measurements

Thermal conductivity, electrical resistivity, and Seebeck coefficient measurements were performed on the three YCBO specimens described in the preceding section. Thermal conductivities for specimens one and three were obtained for mean temperatures from 95 K to 305 K. All of the k measurements were made at temperatures above T_c . The temperature range over which k -values for specimen two were measured was 166 to 304 K. Electrical resistance data were obtained for the three specimens over the range 92 K to 305 K. Seebeck coefficients were measured for specimens one and three over the temperature range 82 K to 305 K. The S data include a few points for temperature below T_c .

Thermal conductivity measurements were made with a longitudinal heat flow apparatus that has been previously described.^{18,19} Electrical resistivities and Seebeck coefficients were determined from voltage differences between known points on the test specimen with constant DC current for the ρ measurements. The circuitry associated with this measurement is discussed by Shockley¹⁷ and Moore et al.¹⁸ Measurement uncertainties estimated by Shockley¹⁷ are $\pm 2.5\%$ for k , $\pm 1.5\%$ for ρ , and $\pm 0.08 \mu\text{V/K}$ for S when the temperature is above 95 K. These estimates are consistent with previous estimates for this apparatus.^{19,20} Figure 2 contains a drawing of the apparatus used to make property measurements. The drawing shows the locations of the stainless steel cylinders used to extend the length of the test specimens.

The measured k and ρ values were corrected for the presence of voids (porosity) using Maxwell's equation²⁰

$$R = R_m(1 - P)/(1 + 0.5 P) \quad (1)$$

where the subscript m indicates a measured value and P is the volume fraction of pores. The experimental data were fit to polynomials obtained by applying the Method of Least Squares. The differences between the polynomial descriptions and the data were plotted to provide a small correction to the polynomial at spaced temperatures. The results of this procedure are values for k , ρ , and S at evenly selected temperatures. The smoothed k , ρ , and S values are given in Tables 1, 2, and 3.

Table 1. Thermal Conductivities for Three YBCO Specimens

T(K)	k (W/m•K)		
	Specimen One	Specimen Two	Specimen Three
95	4.35	6.01	5.06
100	4.34	5.96	5.04
120	4.33	5.76	4.86
140	4.28	5.56	4.68
160	4.22	5.36	4.48
180	4.15	5.14	4.29
200	4.07	4.93	4.17
220	3.95	4.75	4.01
240	3.84	4.51	3.82
260	3.74	4.30	3.65
280	3.63	4.20	3.47
300	3.50	3.98	3.30

Table 2. Electrical Resistivities for Three YBCO Specimens

T(K)	ρ ($\mu\Omega\cdot\text{cm}$)		
	Specimen One	Specimen Two	Specimen Three
95	386.7	--	375.2
100	405.8	--	409.5
120	478.4	--	491.5
140	535.7	--	553.9
160	588.1	--	614.1
180	642.2	371.4	667.8
200	687.5	415.5	723.2
220	741.9	458.1	786.7
240	794.3	482.4	856.5
260	835.7	516.9	926.0
280	897.0	560.6	987.5
300	917.8	599.5	1040.3

Table 3. Seebeck Coefficients for Two YBCO Specimens

T(K)	S(μ V/K) Specimen One	T(K)	S(μ V/K) Specimen Two
81.3	0.0	82.1	0.0
84.9	0.0	86.4	0.0
87.8	0.7	90.0	0.0
90.4	2.9	96.4	-3.6
95.5	5.7	100.4	-3.8
107.0	5.7	112.2	-4.0
128.2	5.4	129.2	-3.9
154.7	4.9	145.3	-3.6
179.3	4.8	162.0	-3.4
205.8	4.9	184.7	-2.6
231.2	5.0	205.4	-2.4
254.0	4.9	251.8	-1.8
280.4	4.8	304.6	-1.5
304.3	4.7		

Discussion of the Property Measurements

Published k data for YBCO specimens show considerable variation even for similarly prepared specimens. The k for YBCO reported by Heremans et al.⁴ for $T > T_c$ are about $0.5 \text{ W/m}\cdot\text{K}$ and are about a factor of ten less than the values reported here. The specimen porosities reported by Heremans are in the range 0.4 to 0.7, values that are much greater than those for the present work. Thermal conductivities for a high- T_c YBCO specimen reported by Jezowski et al.⁹ are in the range 5.0 to $5.2 \text{ W/m}\cdot\text{K}$ in the temperature interval from T_c to 300 K . These k are in reasonable agreement with the present values. The temperature coefficient, dk/dT , for Jezowski's data, however, changes from negative to positive around 250 K while the present data have $dk/dT < 0$ over the entire temperature range. The dk/dT change in sign could be due to radiative losses (heat shunting) at the higher temperatures. The k for "crystals" of YCBO reported by Hagen et al.²¹ are about a factor of two above the present results. Jezowski et al.¹⁴ obtained $k(T)$ for $x = 0.19, 0.46$, and 0.90 (x is a measure of oxygen deficiency in the YBCO). These x values correspond to a continuous loss of oxygen from the specimens. The k obtained for small x are in the range 4 to $5 \text{ W/m}\cdot\text{K}$ while for $x = 0.9$ the k are significantly lower, i.e. in the range 2 to $3 \text{ W/m}\cdot\text{K}$ for $T > 100 \text{ K}$. The k were obtained at temperatures where the material is in the "normal" state. Thermal conductivities reported by Cohn et al.¹⁵ for YBCO crystals and "liquid-phase" processed specimens show $dk/dT < 0$ for $T > T_c$. The k -values, however, are two to three times the k found in this work for sintered specimens. Ambient temperature k for a YBCO specimen obtained by Williams et al.⁸ agree to within about 10% before the specimen was subjected to an additional step of heat treatment. The additional heat treatment reduced the 300 K

k-value from about 3.2 W/m•K to 2.5 W/m•K. The average k at 300 K for specimens one and three in this work was 3.4 W/m•K.

The alloy separation technique developed by Williams and Fulkerson²² was used to obtain k for the YBCO specimens. The data from specimens one and three were averaged and taken as the alloy material while specimen two was treated as the pure material.¹⁷ The results shown in Table 4 indicate that the electronic contribution to k is about 24% of the total. Peacor et al.¹⁶ found that an electronic contribution of about 30% was needed to "fit" YCBO k data. Cohn et al.¹⁵ found the electronic contribution to be from 1 to 30% of k. Jezowski et al.¹² report the electronic component to be 20% of k. Shockley¹⁷ applied Callaway's model²³⁻²⁵ to the calculation of the lattice contribution to k. The calculated values were 10 to 20% greater (17% average) than the values obtained by the alloy separation technique.

The thermoelectric power reported by others^{5,7} vary a lot depending on how a specimen was prepared and annealed. The S, however, all tend to be small, 0-20 μ V/K, and positive.

Table 4. Lattice Conductivity Obtained by Alloy Separation

T (K)	k-lattice (W/m•K)	$(k_1 + k_2)/2$ (W/m•K)	% lattice
180	3.23	4.22	77
200	3.13	4.12	76
220	2.98	3.98	75
240	2.95	3.83	77
260	2.86	3.70	77
280	2.64	3.55	74
300	2.52	3.40	74
		Ave.	76

Summary

The thermal conductivities reported here for three YBCO specimens agree with previously reported k to within about 25% with the exception of one set of data for high porosity specimens. Good agreement between the present data for k at 300 K and some recent k data for $T > 300$ K was observed. The electronic contribution to k was found to be about 24% and this agrees with the range of 20 to 30% found in the literature.

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Figure Captions

- Figure 1. Magnetic Susceptibility as a Function of Temperature for Three YBCO Specimens.
- Figure 2. Diagram of Apparatus Used to YBCO Property Measurements.

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Fig. 1

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