Thermal conductivity of Ag-doped Bi-2212 superconducting materials prepared by the floating zone method

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The thermal conductivity κ of Ag-doped Bi-2212 superconducting materials prepared by the floating zone method has been measured between 15 and 200 K. Ag-doping into the superconducting matrix yields a large enhancement of κ over a wide range of measured temperatures, and the thermal conductivity of a 15 wt% silver-doped sample in the low temperature region becomes about one order of magnitude larger than that of an undoped sample. This behaviour is discussed in terms of the percolation theory. From the viewpoint of cryogenic engineering, it is found that the Ag grains operate as 'intrinsic stabilizers' in the Bi-2212 superconducting materials.

Keywords: Bi-Sr-Ca-Cu-O; silver doping; thermal conductivity; percolation

Thermal transport studies of high T_c oxide superconductors give us important information about the nature of thermal carriers, such as charge carriers and phonons, and their scattering processes[1,2]. From an application point of view, the thermal conductivity of superconductors is a basic parameter, needed not only to estimate the thermal stability in terms of the minimum propagating zone (MPZ)[3], but also to evaluate the heat intrusion through the current leads of high T_c materials[4].

Recently, the effects of silver (Ag) doping on the superconducting properties of high T_c oxide materials have been discussed by many workers. In particular, Ag doping in $Y_1Ba_2Cu_3O_{7-\delta}$ (YBCO) sintered samples enhanced the critical current densities J_c; a change which is considered to be due to improvement of the weak links between superconducting grains[5,6]. In the $Bi_2Sr_2CaCu_2O_y$ (Bi-2212) melted samples prepared by the floating zone (FZ) method, a slight improvement of the weak links by Ag doping has been reported[7–9]. However, doping to over 10 wt% Ag causes disordering of the orientated microstructures and degrades J_c.

The effect of Ag doping on the superconducting properties has been extensively studied, but the contribution of Ag doping to the thermal properties in high T_c oxide materials is not well known. As far as we know there is only a report on the thermal conductivity of an YBCO sintered sample[10].

In this paper, the thermal conductivity κ of Ag-doped Bi-2212 superconducting materials prepared by the floating zone method has been measured between 15 and 200 K. The effect of Ag doping on thermal conductivity is examined in terms of the percolation theory.

Experimental details

Bi-2212 bulk samples with 0, 10 and 15 wt% Ag doping were prepared by the FZ method at Japan Fine Ceramics Center (JFCC). The details of sample preparation have been reported in reference 7. The sample size for thermal conductivity measurements is typically $2.0 \times 2.0 \times 15.0\,mm^3$. The thermal conductivity of the Bi-2212 bulk samples was measured in the range 15–200 K using a steady state heat-flow method. One end of the sample is attached by indium solder to the copper block in the cold head of the helium refrigerator. The heater (chip resistor) is also attached with GE7051 varnish to another end of the sample.

The temperature gradient is monitored by differential thermocouples (Au + 0.07 at%Fe alloy-Chromel) with a terminal distance of $\approx$8 mm. The heat flow is applied along the longitudinal direction of the sample. The FZ sample consists of large superconducting grains with dimensions of the order of a centimetre by a millimetre in the *a-b* plane and $\approx 10\,\mu$m in the *c*-axis plane. Moreover, the sample has a textured structure with the *c*-axes of the 2212 crystal nearly parallel to

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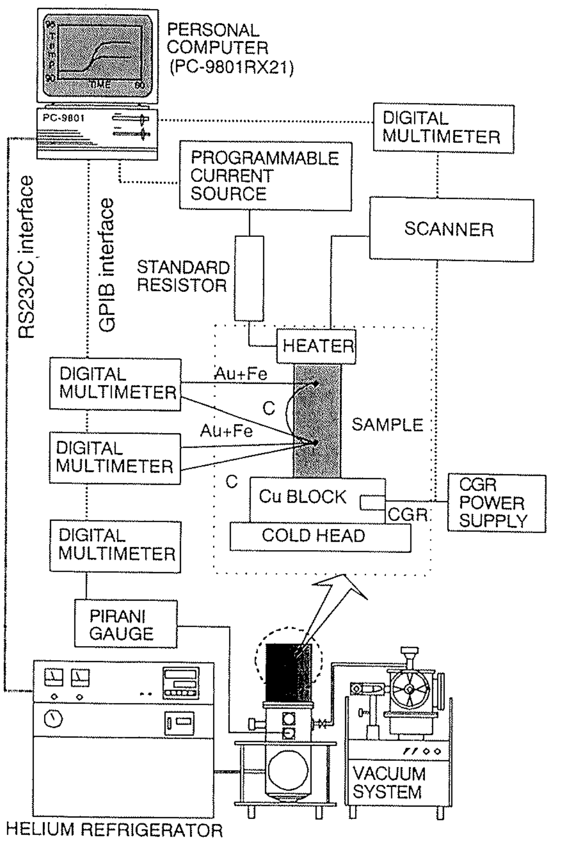

Figure 1 Schematic diagram of fully automatic measuring system for thermal and electrical conductivity using helium refrigerator

each other[7,8]. Thus, this sample can be regarded as a quasi-single crystal and the in-plane thermal conductivity is the parameter usually measured in the present experiment.

Recently, we have developed a fully automatic measuring system for thermal and electrical conductivity using a helium refrigerator, as shown in *Figure 1*. The system is controlled by a personal computer (NEC9800 series) with RS-232C and GPIB lines, and is reported in detail elsewhere[11].

Results and discussion

The results of the electrical resistivity measurements are listed in *Table 1*. It is found that the Ag doping reduces the normal state resistivity, as reported in reference 7. In the experiment, the critical temperature T_c of the doped sample is higher than that of the undoped sample. It has also been reported[7] that the value of T_c varies between 88 and 94 K, even for undoped samples prepared by the FZ method under the same conditions. Accordingly, it is not yet clear

Table 1 Measurements of electrical resistivity for FZ Bi-2212 samples with various concentrations of Ag

Sample no.	Ag (wt%)	$T_{c\,end}$ (K)	Resistivity (at 273 K) (mΩ cm)
1	0	86.3	0.75
2	10	93.6	0.25
3	15	93.1	0.12

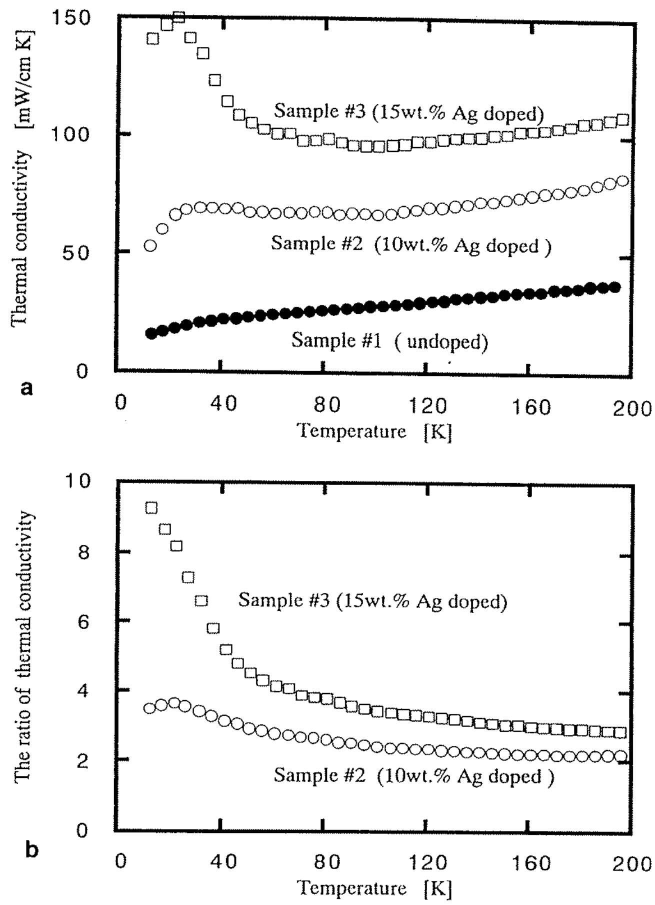

Figure 2 (a) Temperature dependence of thermal conductivity for FZ Bi-2212 samples with several concentrations of Ag. (b) Ratio of $\kappa(T)$ of doped samples to that of undoped sample

whether the enhancement of T_c is due to the effect of Ag doping or due to the preparation process.

Figure 2a shows the temperature dependence of the thermal conductivity for the FZ samples with various concentrations of Ag. The thermal conductivity of undoped sample 1 decreases monotonically as the temperature is lowered and does not show the upturn usually associated with the superconducting transition temperature. From 200 K down to the vicinity of T_c the thermal conductivities of samples 2 and 3 show qualitatively similar behaviour to that of sample 1. Then they increase slightly below T_c. Finally, the conductivity of sample 2 begins to decrease rapidly in the lower temperature region. However, the thermal conductivity of doped sample 3 increases drastically from ≈50 K down to ≈20 K. This anomaly is not associated with the T_c or the superconducting state, but seems to be related to the Ag doping effect, because the remarkable enhancement of the conductivity is qualitatively similar to that for pure Ag.

The ratio of $\kappa(T)$ in doped sample 3 to that in the undoped sample varies in the range 3–10, as shown in *Figure 2b*. For comparison, the *a-b* plane thermal conductivity of a single crystal and the thermal conductivity of a sintered polycrystal are shown in *Figure 3*[12]. The Bi-2212 single crystal of high quality was prepared by the travelling solvent floating zone (TSFZ) method[13]. The measured values of the undoped FZ sample are about twice as high as those of the sintered sample. This result is reasonable because the FZ sample has highly *c*-axis orientated grains and fewer

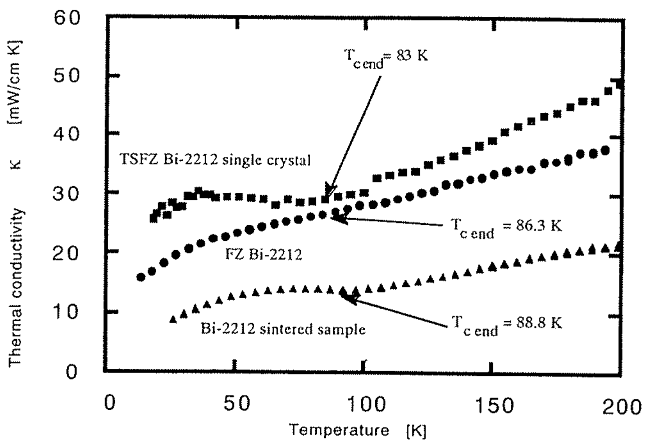

Figure 3 *a-b* plane thermal conductivity of TSFZ single crystal and thermal conductivity of sintered polycrystal

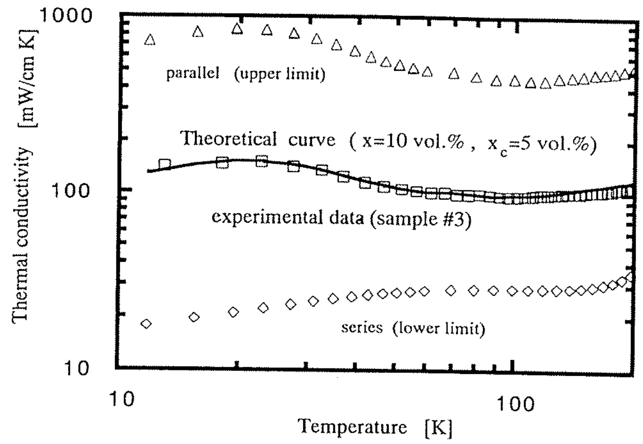

Figure 4 Theoretical curve fitted to sample 3 using the percolation model. For comparison, the lower and upper limits are also shown

crystal imperfections than the sintered sample. Moreover, the conductivity of the undoped sample is comparable with that of the single crystal except in the low temperature region. Therefore, it is difficult to explain the anomalous enhancement of the thermal conductivity of the Ag-doped sample only in terms of improvement of crystalline orientation or crystallinity in the superconducting grains.

To analyse our results, first we determine the lower and upper limits of the measured thermal conductivity, using the series and parallel models of composite conductors such as superconductors and normal metals. The upper and lower limits of the thermal conductivities, κ_{upp} and κ_{low}, are expressed in terms of the thermal conductivities of undoped Bi-2212 and pure Ag, κ_{Bi} and κ_{Ag}, as follows

$$\kappa_{upp} = (1-x)\kappa_{Bi} + x\kappa_{Ag} \qquad (1)$$

and

$$\frac{1}{\kappa_{low}} = \frac{(1-x)}{\kappa_{Bi}} + \frac{x}{\kappa_{Ag}} \qquad (2)$$

where x denotes the volume fraction of the doping metal, Ag. These primitive models do not reproduce the experimental results, as the calculated curves for the lower and upper limits show in *Figure 4*.

Next, we discuss the present experimental data using the percolation theory to address the conductivity problem in different media. The Ag particles are homogeneously distributed in the superconducting matrix of Bi-2212, and randomness of Ag particle distribution is assumed in this model. According to the precolation theory, a cluster of Ag particles of infinite size is formed, so that the heat path of the Ag particles passes through the matrix above a critical value of Ag (x_c in terms of volume fraction). The effective conductivity is then given in the following form[14]

$$\frac{\Lambda}{\Lambda_{Ag}} = S_1 + \nu\left(\frac{\Delta S}{1-(1-\nu)l_2} + \frac{2S_3}{1-(1-\nu)l_1} + S_4\right) \qquad (3)$$

where: $\Delta S = S_2 - S_1$; $S_1 = l_1^2$; $S_2 = l_2^2$; $S_3 = (1-l_2)l_1$; $S_4 = 1 - S_2 - 2S_3$; $l_1 = [(x-x_c)/(1-x_c)]^{0.8}$; $l_2 = x_c^{1/3}$; and $\nu = \Lambda_{Bi}/\Lambda_{Ag}$.

If $S_1 \geqslant S_2$, then $\Delta S = 0$ or $l_1 = l_2$. In this model, macroscopic cubes with equal (unit) sides are assumed in the three-dimensional space of an inhomogeneous system. Isolated clusters are modelled as separated inserted cubes with side l_2. They are located at a distance $1-l_2$ from each other and are connected via conducting paths which have a cross-sectional area equal to l_1^2. In Equation (3), replacing Λ_{Bi} and Λ_{Ag} with κ_{Bi} and κ_{Ag}, respectively, the effective thermal conductivity κ_{eff} is calculated.

The curve best fitted to the experimental data of sample 3 ($x \approx 10$ vol%) is obtained when the critical value of Ag (x_c) is determined to be 5 vol%, as shown in *Figure 4*. This result is certainly in good agreement with the experimental values. However, the critical value obtained by fitting to the experimental data is a third smaller than the theoretical value (≈ 15 vol%), which is calculated based on the random percolation model for three-dimensional continuous systems[15]. This result suggests that in the measured sample, the Ag particles are not randomly distributed but are inhomogeneously dispersed[9]. Thus, if the Ag particles are not randomly dispersed, but most of them precipitate on the grain boundaries, even below the threshold value for three-dimensional random percolation, it is possible that the Ag particles form an infinite cluster.

In *Figure 5*, the calculated curve for sample 2 is shown with that of sample 3, when the threshold value (x_c) for sample 3 and the Ag volume fraction (x) of sample 2 are 5 and ≈ 7 vol%, respectively. For comparison, a theoretical curve of 20 vol% Ag doping is also shown. The estimation using the same threshold value reproduces the data of sample 2 comparably.

From energy dispersive X-ray microanalysis (EDX) for the 10 wt% Ag-doped sample, it has been found that Ag grains exist not only on the grain boundaries but also in the superconducting grains, with an island-like shape. But it is difficult to identify the existence of the infinite clusters of Ag from observation of the microstructures. Furthermore, optical microscopy in a section parallel to the growth direction has revealed that the Ag grains are roughly aligned along the growth direction. This anisotropy is also probably related to the low threshold value in this system.

In a similar way, the effective electronic conductivity

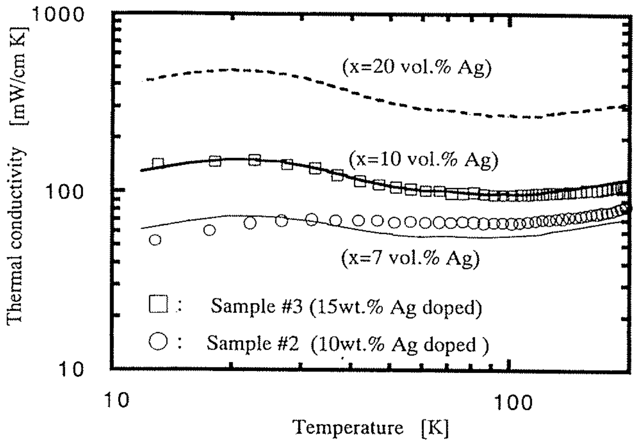

Figure 5 Theoretical curves for various concentrations of Ag

σ_{eff} at room temperature is calculated using Equation (3) for samples 2 and 3. As a result, the effective resistivities ($1/\sigma_{eff}$) are estimated to be ≈0.29 and ≈0.1 mΩ cm, for samples 2 and 3, respectively. These values are comparable with the experimental values for samples 2 and 3 listed in *Table 1*. The effective resistivity with 20 vol% Ag doping also turns out to have a very low magnitude of ≈0.02 mΩ cm.

Finally, from the viewpoint of cryogenic engineering, the dynamic stability of superconductors is discussed. The dynamic stability is quantitatively estimated by the concept of the minimum propagating zone (MPZ)

$$l_m = \left\{ \frac{2\kappa(T_c - T_0)}{J_c^2 \rho} \right\}^{1/2} \quad (4)$$

where l_m, T_0 and ρ denote the length of the normal zone, the operating temperature and the normal state resistivity, respectively. This formula is easily derived by equating heat generated in the normal zone to loss dissipated by heat conduction within the sample. l_m is a function of both the thermal and electric conductivities for superconducting materials. Thus, Ag doping in superconducting materials yields higher values of the conductivities, so that an improvement in the dynamic stability is anticipated. In fact, in the low temperature region (≈20 K) the MPZ value of a 15 wt% Ag-doped sample is about eight times larger than that of the undoped sample if the superconducting properties such as T_c and J_c are independent of the Ag concentration. Furthermore, it is theoretically estimated using Equations (3) and (4) that 30 wt% Ag doping makes the MPZ value ≈33 times larger at 20 K.

Though the oxide superconductors exhibit high critical temperatures, above LN_2 temperature, there is the very serious problem of an irreversibility line in the (H–T) phase diagram for these materials. Thus, it is desirable to operate not in the higher temperature region but in the lower temperature region, for an apparatus such as a superconducting magnet designed using high T_c superconducting materials. Accordingly, it is reasonable to estimate the value of MPZ at 20 K. As Ag doping in the superconducting matrix quantitatively enhances the dynamic stability, it is found that Ag grains operate as 'intrinsic stabilizers' in Bi-2212 superconducting materials.

Conclusions

We have reported measurements of thermal conductivity for Ag-doped Bi-2212 superconducting materials prepared by the FZ method. The following points are noteworthy.

1. Ag doping in the superconducting matrix yields a large enhancement of κ over a wide range of measured temperature, and the thermal conductivity of a 15 wt% Ag-doped sample in the low temperature region becomes about one order of magnitude greater than that of an undoped sample.
2. The remarkable enhancement of thermal conductivity due to the Ag doping effect is discussed mainly in terms of the percolation theory. This model strongly supports such anomalous behaviour.
3. As Ag doping in the superconducting matrix quantitatively enhances the dynamic stability, it is found that Ag grains operate as 'intrinsic stabilizers' in Bi-2212 superconducting materials.

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References

1 **Tewordt, L. and Wölkhausen, T.** *Solid State Commun* (1989) **70** 839
2 **Matsukawa, M., Noto., K., Fujishiro, H., Todate, T.** ***et al.*** *Physica B* (1994) **194/196** 2217
3 **Matsukawa, M., Noto., K., Ikebe, M., Kashiwazaki, Y.** ***et al.*** *Physica C* (1991) **185/189** 2477
4 **Yamada, Y., Yanagiya, T., Hasebe, T., Jikihara, K.** ***et al.*** *IEEE Trans Magn* (1993) **MAG-3** 923
5 **Imanaka, N., Saito, F., Imai, H. and Adachi, G.** *Jpn J Appl Phys* (1989) **28** L580
6 **Malik, M.K., Nair, V.D., Biswasand, A.R., Raghavan, R.V.** ***et al.*** *Appl Phys Lett* (1988) **52** 1525
7 **Kubo, Y., Michishita, K., Shimizu, N., Higashida, Y.** ***et al.*** *Jpn J Appl Phys* (1989) **28** L1936
8 **Michishita, K., Shimizu, N., Sugawara, Y., Ito, W.** ***et al.*** *Jpn J Appl Phys* (1993) **32** L572
9 **Shimizu, N., Michishita, K., Hayami, Y., Hattori, K.** ***et al.*** *Cryog Eng* (1990) **25** 71 (in Japanese)
10 **Dotsenko, V.I., Kislyak, I.F., Rusanov, K.V., Tyurina, E.G.** ***et al.*** *Sov Tech Phys Lett* (1991) **17** 813
11 **Hobara, N., Matsukawa, M., Matsuura, N., Fujishiro, H.** ***et al.*** *Cryog Eng* (1993) **28** 688 (in Japanese)
12 **Fujishiro, H., Ikebe, M., Naito, T., Matsukawa, M.** ***et al.*** *Physica C* submitted for publication
13 **Shigaki, I., Kitahama, K., Shibutani, K., Hayashi, S.** ***et al.*** *Jpn J Appl Phys* (1990) **29** L2013
14 **Dul'nev, G.N. and Malarev, V.I.** *Inzh Fiz Zh* (1990) **59** 522 (in Russian)
15 **Webman, I., Jortner, J. and Cohen, M., H.** *Phys Rev* (1976) **B14** 4737