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TRANSPORT AND THERMOELECTRIC PROPERTIES OF $YBa_2Cu_3O_{7-\delta}$-Ag PERCOLATION SYSTEM

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Experimental studies on the transport and thermoelectric properties of $YBa_2Cu_3O_{7-\delta}$-Ag composite ceramic system have been performed and the results are analyzed from the viewpoint of the percolation theory. The percolation threshold volume fraction f_c of Ag determined from the electrical resistivity, thermal conductivity and Seebeck coefficient measurement is f_c=0.135±0.005. This value is slightly smaller than the theoretical value f_c=0.16 for three dimensional percolation in continuous media. The critical exponent t, which is defined by $\sigma \propto (f_{Ag}-f_c)^t$ in the critical region above the percolation threshold f_c, is found to depend on the component conductivity ratio $h=\sigma_{YBCO}/\sigma_{Ag}$, which was varied by changing the oxygen deficiency δ. This dependence of t on h can be understood on the basis of the scaling hypothesis. The behavior of the Seebeck coefficient is also analyzed on the basis of the percolation theory.

1. INTRODUCTION

One main hurdle against the application of high T_c oxide superconductors (HTSC) in ceramic forms is the occurrence of the weak-links at the border of grains, which practically limit the effective critical current I_c^{eff} of bulk cuprate superconductors. The addition of Ag metal to cuprates was found often to be effectual to make up for the weak-links and a good deal of the data on the transport properties of Ag doped HTSC have been accumulated just after the discovery of HTSC. It is surely physically interesting and also useful for applicational purpose to investigate the behavior of Ag clusters on the basis of the percolation theory. However, the accumulated data and analyses from the viewpoint of the percolation theory seem hitherto to be somewhat scattered and sometimes inconsistent each other.[1-5]

In this study, we try to develop synthetic analyses about the percolative behavior of Ag clusters in $YBa_2Cu_3O_{7-\delta}$ (YBCO) by measuring the electrical resistivity, thermal conductivity and thermoelectric effect. The conductivity ratio of Ag metal and the cuprate is widely changed by varying the amount of oxygen deficiency δ of YBCO. The experimental results are analyzed on the basis of the scaling theory for the percolation of Ag clusters.

2. OUTLINE OF SCALING LAWS

In a two component random composite of M and I, clusters of M with infinite scale are at first formed when the volume fraction of M (f_M) goes beyond a certain threshold value f_c. Assuming M to be a metal and I to be an insulator, a power law applies for the bulk effective conductivity σ_E of the composite;

$$\sigma_E = A\sigma_M(f_M - f_c)^t \quad \text{for } 0 < f_M - f_c << 1. \tag{1}$$

The values of $t=1.9\pm0.1$ and $f_c \approx 0.16$ were predicted for the three-dimensional continuum media.[6] If I component is also somewhat conductive and the conductivity ratio $h=\sigma_I/\sigma_M$ is not strictly zero, the power law of eq. (1) breaks down as $\Delta f = f_M - f_c$ tends to zero. In this case, σ_E is expected to follow the scaling hypothesis,

$$\sigma_E = \sigma_M \Delta f^t \phi_+(z), \tag{2}$$

where $z = h/\Delta f^{t+s}$, s($\approx$0.73) is the critical exponent governing the divergence of conductivity in a superconductor-metal composite for $0 < f_c - f_M << 1$. The universal scaling function $\phi(z)$ can be explained in the power series of z:

$$\phi_+(z) = A^+ + B^+z + C^+z^2 + \cdot\cdot\cdot \qquad \text{for } z<1 \text{ and } f_M - f_c > 0. \tag{3}$$

For non-zero values of h, the conductivity data must be carefully handled taking proper account of region of z in which the application of eq. (3) is justified. In this paper, h dependence of the t exponent is mainly discussed.[5,7] The percolative behavior of the Seebeck coefficient is also investigated because it is an important parameter for practical application such as the thermoelectric refrigeration.[8]

3. EXPERIMENTAL

The Ag+ $YBa_2Cu_3O_{7-\delta}$ samples were prepared through the following procedure: YBCO powder and Ag_2O powder (Dowa Mining Co. Ltd.) were mixed with an approximate weight ratio and pressed into pellets. The pellets were pre-sintered at 935°C for 15h in air and furnace cooled. The pre-sintered pellets were crashed, mixed and again pressed into pellets. They were sintered at 930°C for 30h in air and then furnace cooled in 15h. After the obtained pellets were cut into square pillars (~3x3x15mm^3), they heated again and quenched into liquid N_2 from various temperatures to prepare 'quenched samples'. The electrical resistivity was measured by a four-probe method between 10K to 260K using a GM refrigerator as a cryostat. The thermal conductivity κ and the Seebeck coefficient S were automatically measured in the same GM refrigerator.[9] The distribution of silver clusters was observed by a scanning electron microscope (SEM) and an electron probe microanalyzer (EPMA).

4. EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of the electrical resistivity $\rho(T)$ of YBCO, non-quenched and quenched from 700°C, 800°C and 900°C. $\rho(T)$ increases with increasing quenching temperature T_q. In the figure, $\rho(T)$ of Ag+0.22at.%Au alloy whose residual resistivity ratio (RRR) is roughly equal to estimated RRR of Ag clusters in YBCO[10] is also shown. Figure 2 shows, as an example, $\rho(T)$ of (Ag+YBCO) non-quenched samples for various Ag volume fractions f_{Ag} and Fig. 3 shows the temperature

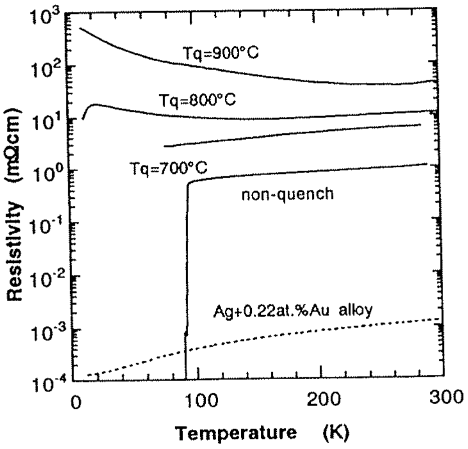

FIGURE 1
Temperature dependence of the electrical resistivity $\rho(T)$ of YBCO non-quenched and quenched from 700°C, 800°C and 900°C.

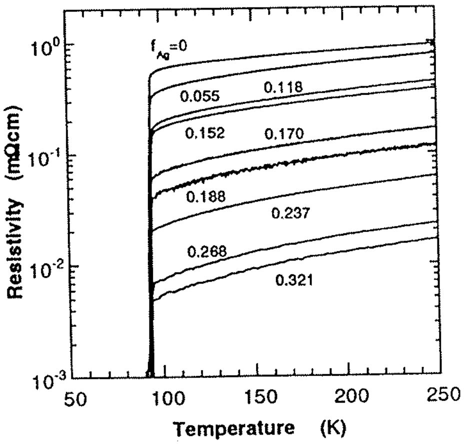

FIGURE 2
Temperature dependence of the electrical resistivity $\rho(T)$ of (Ag+YBCO) non-quenched samples for various Ag volume fractions f_{Ag}.

dependence of the thermal conductivity $\kappa(T)$ of $(Ag+YBCO)_{Tq=800°C}$ for various f_{Ag}. As is expected, $\rho(T)$ decreases and $\kappa(T)$ increases with increasing f_{Ag}. Figures 4(a) and 4(b) show the temperature dependence of the Seebeck coefficient S of $(Ag+YBCO)_{Tq=900°C}$ and $(Ag+YBCO)_{Tq=800°C}$, respectively.

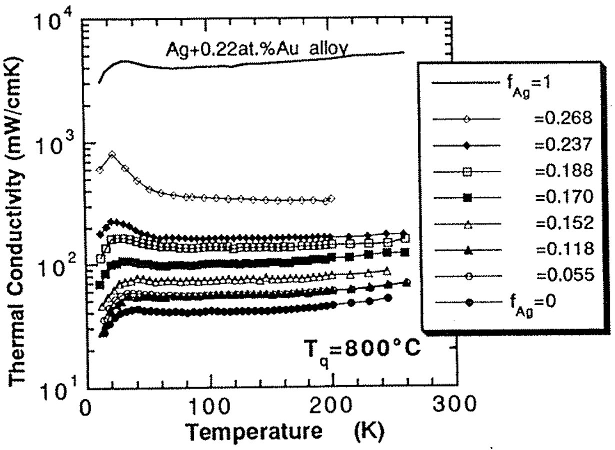

FIGURE 3 Temperature dependence of the thermal conductivity $\kappa(T)$ of $(Ag+YBCO)_{Tq=800°C}$ for various f_{Ag}.

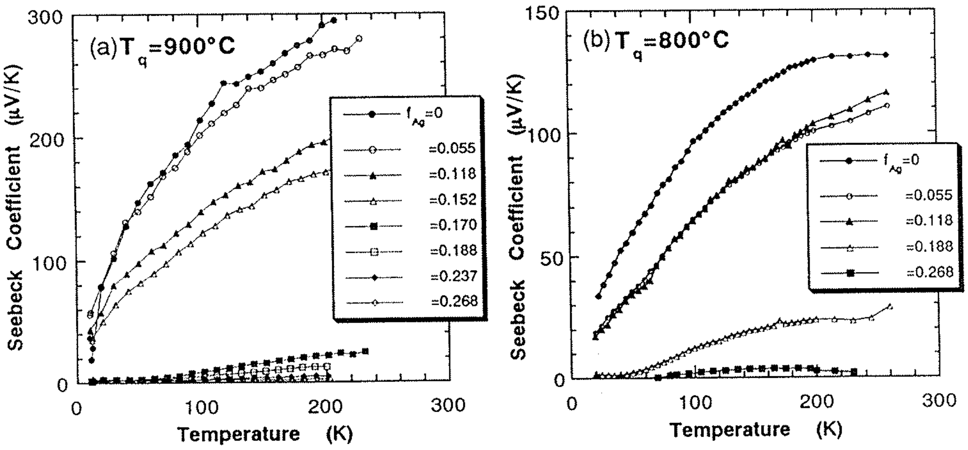

FIGURE 4 Temperature dependence of the Seebeck coefficient S of (a) $(Ag+YBCO)_{Tq=900°C}$ and (b) $(Ag+YBCO)_{Tq=800°C}$.

5. DISCUSSION

Figures 5(a)-5(c) show the typical plots of log σ_E vs log $(f_{Ag}-f_c)$ to determine experimental values of critical exponent t_{ex} and the percolation threshold f_c. The conductivity values at 150K were used because RRR of Ag cluster is verified to depend on f_{Ag} to some extent[10] and $\sigma_{YBCO}/\sigma_{Ag}$ values become dependent on RRR of Ag cluster at low temperatures. The most suitable value of f_c was determined to be 0.135 for the present Ag+YBCO ceramics system. This f_c value is slightly smaller than the generally accepted value of $f_c \approx 0.16$ for a 3D continuum media. The smaller value of observed f_c might reflect selective segregation of Ag clusters into grain boundary regions of YBCO. The determined t_{ex} values depend on the conductivity ratio h and are larger for smaller h as shown in Fig. 6. In the following, we estimate the relation between observed t_{ex} value and h on the basis of the scaling law given by eqs. (2) and (3).[5,7]

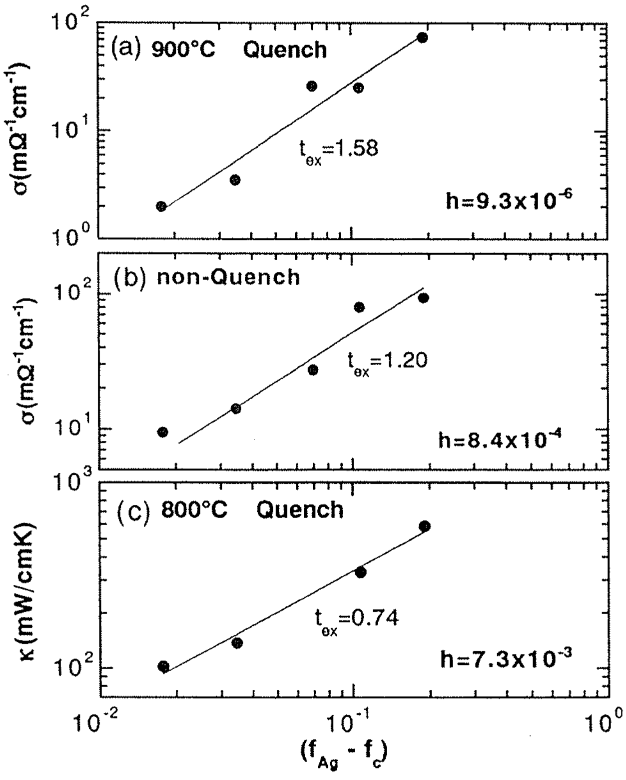

FIGURE 5 The typical plots of log σ_E vs log $(f_{Ag}-f_c)$ to determine experimental values of critical exponent t_{ex} and the percolation threshold f_c for (a) T_q=900°C, (b) non-quenched and (c) T_q=800°C, respectively. Note that (c) is for the thermal conductivity.

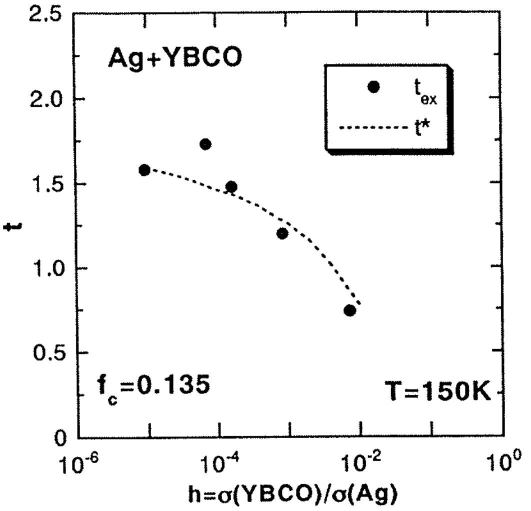

FIGURE 6 The experimentally determined t_{ex} values and calculated t^* values as a function of conductivity ratio h=σ(YBCO)/σ(Ag) (see text).

To calculate σ_E based on eq. (2), the scaling function ϕ_+ must be known. As a trial function, we set $\phi_+(z)=A^+(1+z)$ and calculated σ_E in the range up to z=1. Then average slope between $f_{Ag}-f_c=0.2$ and z=1 was defined as t^* and thus obtained t^* is given by the dotted line in Fig. 6. In the present calculation, t value of 1.8 and s value of 0.73 were used. We see in Fig. 6 that t^* values agree fairly well with experimental t_{ex} values. The parameter values used for the calculation are summarized in Table I.

Finally in Fig. 7 we plot log (1/S) vs log $(f_{Ag}-f_c)$ for $(\mathrm{Ag+YBCO})_{Tq=900^\circ C}$ and $(\mathrm{Ag+YBCO})_{Tq=800^\circ C}$. f_c value is set to be 0.135, the same value as the percolation threshold for the conductivity. The apparent value of the exponent t_{ex}' is 1.59 and 1.90, respectively. These values almost coincide with t_{ex} values determined from the effective conductivity σ_E. The Seebeck coefficient can be expressed as

$$S=\frac{\pi^2}{3}\frac{k^2T}{e}\frac{1}{\sigma}\frac{\partial\sigma}{\partial\varepsilon}, \tag{4}$$

where e is the electron charge and ε is the energy of electrons. Eq. (4) is inversely proportional to the conductivity σ and the experimental result that t_{ex}' in the f_{Ag}

dependence of S almost agrees to t determined from σ_E imply that the $\partial\sigma/\partial\varepsilon$ term is nearly independent of the value of f_{Ag}.

Table I. The parameter values used for the calculation of t^* and experimental t_{ex} values.

measurement	T_q	conductivity at 150K	$h(=\sigma_{YBCO}/\sigma_{Ag})$	t_{ex}	t^*
κ	800°C	κ_{Ag}=4300mW/cmK κ_{YBCO}=31.3mW/cmK	7.3×10^{-3}	0.74	0.78
ρ	non-Q	σ_{Ag}=1621mΩ^{-1}cm^{-1} σ_{YBCO}=1.36mΩ^{-1}cm^{-1}	8.4×10^{-4}	1.20	1.27
ρ	700°C	σ_{Ag}=1621mΩ^{-1}cm^{-1} σ_{YBCO}=0.26mΩ^{-1}cm^{-1}	1.6×10^{-4}	1.48	1.43
ρ	800°C	σ_{Ag}=1621mΩ^{-1}cm^{-1} σ_{YBCO}=0.114mΩ^{-1}cm^{-1}	7.0×10^{-5}	1.73	1.49
ρ	900°C	σ_{Ag}=1621mΩ^{-1}cm^{-1} σ_{YBCO}=0.015mΩ^{-1}cm^{-1}	9.3×10^{-6}	1.58	1.99

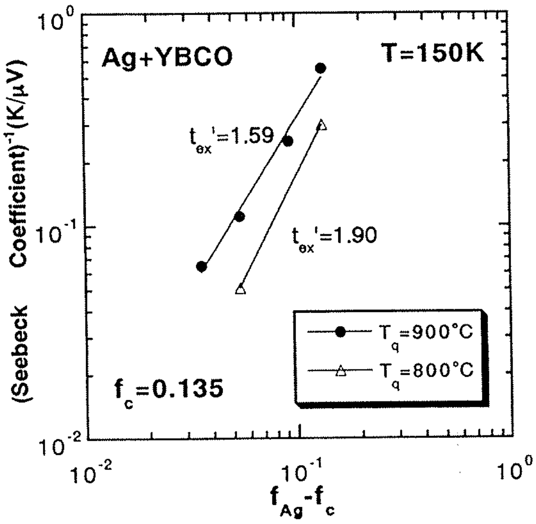

FIGURE 7 The plots of log (1/S) vs log (f_{Ag}-f_c) for (Ag+YBCO)$_{Tq=900°C}$ and (Ag+YBCO)$_{Tq=800°C}$ samples.

5. SUMMARY

(1) The electrical resistivity ρ, the thermal conductivity κ and the Seebeck coefficient S were measured for Ag+$YBa_2Cu_3O_{7-\delta}$ ceramics composite and the results were analyzed from the viewpoint of the percolation theory. The percolation threshold volume fraction f_c of Ag is determined to be 0.135, which is a little smaller than 0.16 generally accepted for random binary alloys in 3D continuum media.

(2) Observed critical exponent t_{ex} for $f_{Ag}>f_c$ is dependent on the conductivity ratio $h=\sigma(YBa_2Cu_3O_{7-\delta})/\sigma(Ag)$, which was varied by quenching the ceramics composite from various temperatures.

(3) The trial scaling function, $\phi_+(z)=A(1+z)$ explains fairly well the h dependence of observed t_{ex} values.

(4) The critical exponent t_{ex}' of the Seebeck coefficient for $f_{Ag}>f_c$ almost agrees to t_{ex} values determined from the electrical conductivity. This means that $\partial\sigma/\partial\varepsilon$, the electron energy dependence of the conductivity, is almost constant irrespective of the f_{Ag} values.

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