Possibility of Ag_2O+$YBa_2Cu_3O_{7-X}$ Ceramics for Low Temperature Thermoelectric Refrigeration

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Ag_2O doped and oxygen deficient $YBa_2Cu_3O_{7-X}$ $(0<X<1)$ ceramics with various Ag_2O concentrations up to 40wt.% were studied for the thermoelectric refrigeration use in the temperature range from 10K to 260K. The amount of the oxygen deficiency (X) was controlled by varying the thermal quenching temperature. The Seebeck coefficient S, the electrical resistivity ρ and the thermal conductivity κ were measured and the systematic dependence of these quantities and the figure of merit (Z) on Ag_2O doping were observed.

INTRODUCTION

The development of cryogenic Peltier coolers at low temperatures is useful for special scientific experiments which are easily damaged by vibrations or are performed for a long time without using a coolant in a space laboratory. In the temperature range from 50 to 200K, the most effective thermoelectric material is the n-type $Bi_{1-X}Sb_X$ single crystal with 9-12 at.% of Sb content, of which the figure of merit (Z) as large as $5.5-10 \times 10^{-3}\ K^{-1}$ has been attained at 100K.[1] The Z value of the p-type materials which are based on the BiTe-Sb alloys is, however, smaller than $2 \times 10^{-3}\ K^{-1}$ and decreases rapidly with decreasing temperature, [1] so that the discovery of a new p-type material is desired. Instead of p-type thermoelectric semiconductors, the use of oxide superconductors for a p-type leg as a passive thermoelement below the superconducting transition temperature (T_c) was recently proposed. The maximum cooling ability of this element was reported to be ΔT_{max}=13.4K without magnetic field when T_{hot} was 79K. [2] We also investigated the use of the low thermal conductive Bi-2223 oxide superconducting tapes sheathed with the Ag-Au alloy as a passive thermoelement. [3] For oxide superconductors, the figure of merit Z $(=S^2/\rho\kappa)$, which is calculated from the values of the Seebeck coefficient S, the electrical resistivity ρ and the thermal conductivity κ, is considered to take a low value because of very small S values in the normal state.[4] However, the highly oxygen deficient samples which do not show superconductivity such as $YBa_2Cu_3O_{7-X}$ $(X\approx1)$ show large positive S values which are as large as several hundreds $\mu V/K$ at about 100K. There may be a fair chance to prepare active materials in place of p-type thermoelectric semiconductors. In this case, the larger electrical resistivity of oxygen deficient samples is a serious barrier to increase the figure of merit. The possibility of the use of the oxide superconductors as an active thermoelement was pointed out by Macklin et al. [5] but the objection was interposed by Mason. [6] However, the detailed and systematic experimental research has not been performed.

In this paper, the Seebeck coefficient S, the electrical resistivity ρ and the thermal conductivity κ of the $YBa_2Cu_3O_{7-X}$ (YBCO) materials were measured for various amounts of oxygen deficiency. The effect of Ag doping into the oxygen deficient $YBa_2Cu_3O_{7-X}$ ceramics was also investigated and the systematic relation between the Ag_2O concentration, the oxygen deficiency and the figure of merit of the materials was observed.

EXPERIMENTAL

The samples were fabricated as follows. $YBa_2Cu_3O_{7-X}$ (YBCO) superconducting powder and Ag_2O powder with concentrations of 0, 10, 20, 30 and 40wt.% were mixed and pressed into pellets and sintered at 935°C for 48h in air. The oxygen deficiency X of the samples was varied by changing the quenching temperature T_q; the samples were quenched from T_q=600, 800 and 900°C into liquid nitrogen. The values of S and κ were measured from 10K to 260K using an automatic measuring system of our making which employed a GM refrigerator as a cryostat. [7] The electrical resistivity was measured by a four-probe method using the GM refrigerator or liquid nitrogen. The distribution of the silver in the sample was analyzed by a scanning electron microscope (SEM) and an electron probe microanalyzer (EPMA).

RESULTS AND DISCUSSION

Figures 1 to 3 show the temperature dependence of the electrical resistivity ρ, the Seebeck coefficient S, and the thermal conductivity κ of the YBCO samples without Ag_2O doping. The non-quenched sample and the oxygen deficient sample with T_q=600°C showed a sharp resistive transition at T_c=94K and 62K, respectively. The samples with T_q=800 and 900°C showed a semiconductive resistance: The electrical resisitivity increased with increasing T_q. In Fig. 2, the non-quenched sample showed a small Seebeck coefficient S (<10μV/K) in the normal state. S values of the quenched samples increased with increasing T_q. For example, S value of the sample with T_q=900°C was 285μV/K at 200K, which was about sixty times larger than that of the non-quenched sample. In Fig. 3, the thermal conductivity of the non-quenched sample showed larger κ values because of the reduction of phonon scattering due to oxygen vacancies and also because of the larger contribution of the electronic thermal conductivity than other samples. The enhancement of the conductivity below T_c which was observed for the non-quenched and the 600°C quenched samples was caused by the reduction of the phonon-electron scattering below T_c since the Cooper pairs do not scatter phonons.

Figure 4 shows the temperature dependence of the figure of merit Z which was calculated using the ρ, S and κ data. The Z(T) curves take a maximum at a temperature T_m. The maximum value of Z and T_m increased with the increase of T_q. The Z values of the oxygen deficient YBCO samples were less than 10^{-4} K^{-1} and about one order smaller than that of conventional p-type thermoelectric semiconductors. [1]

It is theoretically predicted that Z value of a composite medium does not exceed the largest component value of Z. [8,9] On the other hand, the superconducting characteristics are known to be remarkably improved in composites of the ceramic high-T_c compound and silver; the addition of Ag significantly influence the crystallinity and the grain size of oxide superconductors. In order to investigate the possibility of improving the thermoelectric properties, Ag_2O-doped YBCO ceramics up to 40 wt.% were fabricated and quenched from 800°C. Figure 5 presents area analysis patterns of Ag identified by EPMA for the Ag_2O-doped YBCO samples with various concentrations of Ag_2O. The doped Ag_2O powder were dispersed uniformly in the form of Ag metal particles and the content of Ag particles (white images) increased with increasing Ag_2O concentration. When the content is larger than 30 wt.%, we can also notice connected Ag particles.

Figures 6, 7 and 8 show the temperature dependence of the electrical resistivity ρ, the Seebeck coefficient S and the thermal conductivity κ of the Ag_2O-doped YBCO samples, respectively. The data of the sample without Ag_2O doping are also shown for comparison. The electrical resistivity decreased with increasing Ag_2O content because the dispersed Ag particles act as the electric paths. In Fig. 7, the Seebeck coefficient of the samples in which Ag_2O was doped at 10 and 20 wt.% is only slightly smaller than that of the non-doped sample. The S values of the samples in which Ag_2O is doped at higher than 30 wt.% drastically decreased because the electric paths of Ag short-circuit the larger S value of YBCO. In Fig. 8, the thermal conductivity of the samples increased with increasing Ag_2O content. The Ag particles enhance also the heat conduction of the Ag-YBCO two component system.

Figure 9 shows the relation between the Ag_2O concentration and the calculated figure of merit at several temperatures. In this figure, the volume percentage (vol.%) of the doped Ag_2O concentration is also shown by the upside abscissa. The figure of merit of the samples slightly decreased with increasing Ag_2O concentration up to 20wt.% and then drastically decreased for higher Ag_2O concentrations. According to the three-dimensional percolation theory, the infinite size clusters of Ag particles are formed to provide the thermal and electrical paths through the matrix phase over the critical value of Ag content (≈16 vol.% which corresponds to ≈26 wt.% in this case). [10] In our study, the ρ, S and κ values of the Ag_2O-doped samples drastically changed at the Ag_2O content between 20 and 30wt.%. This result is consistent with the prediction of the percolation theory and also seems to be consistent with our observation of the area analysis in Fig. 5.

In summary, the figure of merit of oxygen deficient $YBa_2Cu_3O_{7-x}$ ceramics degraded by Ag-doping in accord with the theoretical prediction. The most drastic change of the thermoelectric and transport properties occurred between Ag contents 20wt.% and 30wt.% when the Ag content passes through the three-dimensional percolation threshold. The formation of the percolative infinite path is the most dominant factor to determine the thermoelectric properties.

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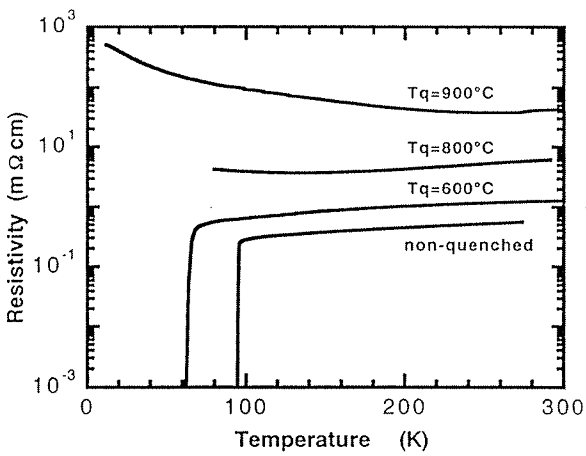

Figure 1 Temperature dependence of the electrical resistivity of oxygen deficient YBCO samples.

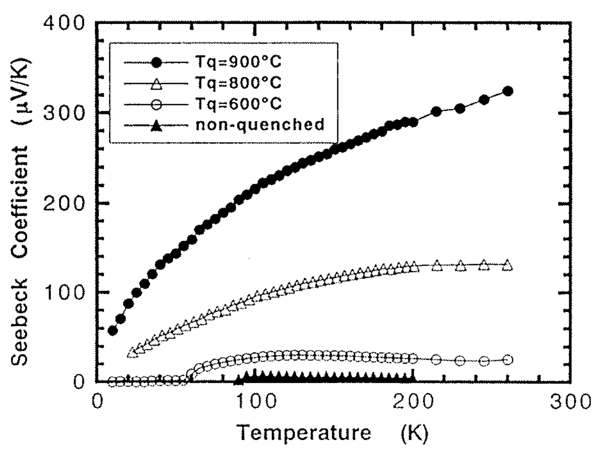

Figure 2 Temperature dependence of the Seebeck coefficient of oxygen deficient YBCO samples.

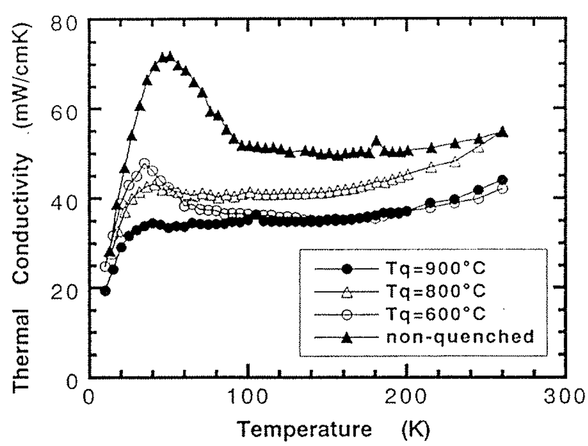

Figure 3 Temperature dependence of the thermal conductivity of oxygen deficient YBCO samples.

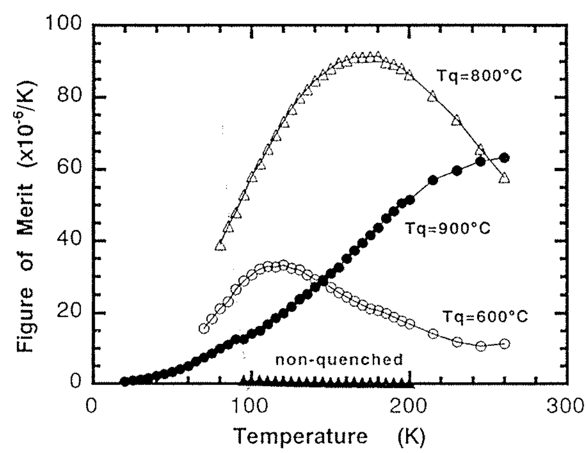

Figure 4 Temperature dependence of the figure of merit of oxygen deficient YBCO samples.

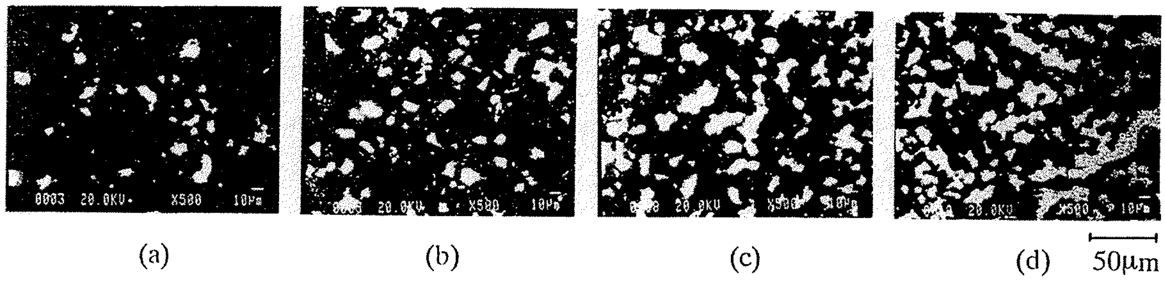

Figure 5 Area analysis patterns of Ag for the samples of (a) 10wt.%, (b) 20wt.%, (c) 30wt.% and (d) 40wt.% Ag_2O doping, respectively.

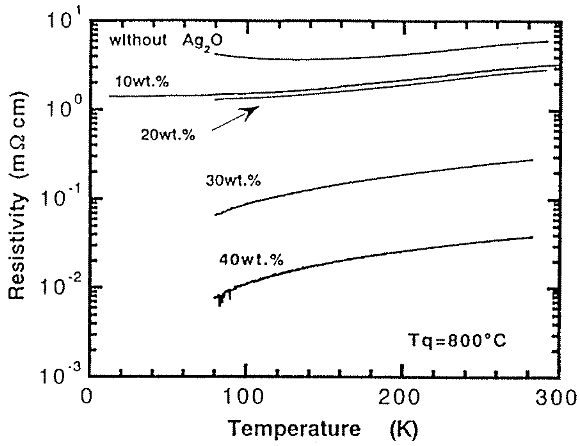

Figure 6 Temperature dependence of the electrical resistivity of Ag_2O-doped YBCO samples.

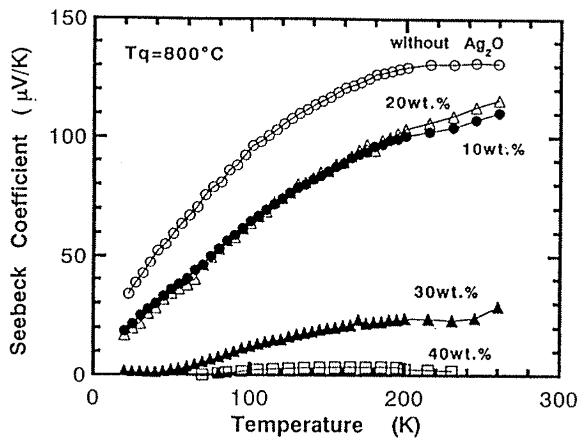

Figure 7 Temperature dependence of the Seebeck coefficient of Ag_2O-doped YBCO samples.

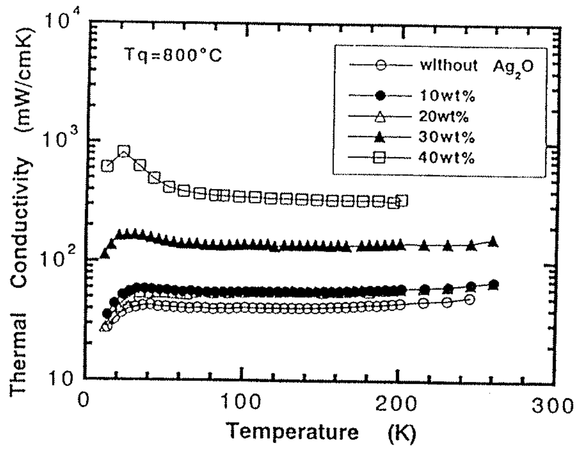

Figure 8 Temperature dependence of the thermal conductivity of Ag_2O-doped YBCO samples.

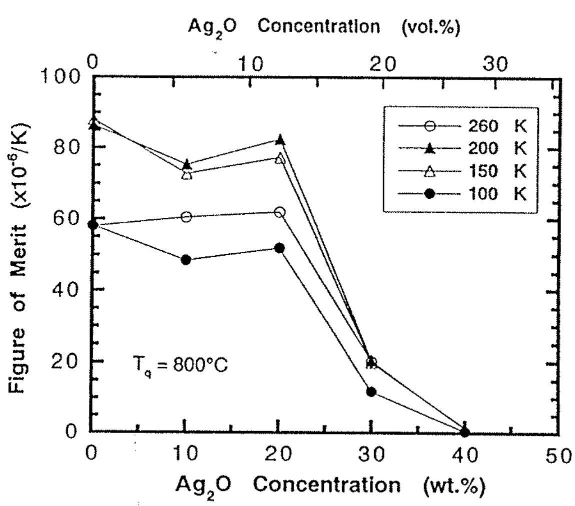

Figure 9 Figure of merit of Ag_2O-doped YBCO samples.