

Low Temperature Sintering of $\text{YBa}_2\text{Cu}_3\text{O}_y$ Ceramics by Silver Compounds and Silver Ionic Conduction

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Low temperature sintering of $\text{YBa}_2\text{Cu}_3\text{O}_y$ ceramics by various Ag compounds was studied by *in situ* resistivity measurement using a four-probe method and silver ionic conductivity measurement using four silver ion conduction electrodes of $\text{Ag}-\beta''\text{-Al}_2\text{O}_3$. Even silver ionic compounds promoted sintering, indicating that the Ag^+ ion promotes sintering in the grain boundaries. From the *in situ* resistivity measurement of the pressed $\text{YBa}_2\text{Cu}_3\text{O}_y$ powders, the Ag^+ ion was assumed to attack impurities such as BaCO_3 and BaCuO_2 in the grain boundaries. The activation energies of Ag^+ ionic conductivities of the Ag-added samples (0.2–1.4 eV) were much lower than those in the $\text{YBa}_2\text{Cu}_3\text{O}_y$ bulk (2.3–2.5 eV), indicating that the Ag^+ ion easily diffuses in the grain boundaries at low temperature. © 1992 Academic Press, Inc.

Introduction

It is well known that silver doping promotes the sintering of $\text{YBa}_2\text{Cu}_3\text{O}_y$ ceramics. Some actions of silver in $\text{YBa}_2\text{Cu}_3\text{O}_y$ ceramics are proposed: introduction of oxygen (1, 2), promotion of a decomposition of BaCO_3 and hydrocarbons (1–4), catalysis in the reaction from Y_2BaCuO_5 , BaCuO_2 , and CuO to $\text{YBa}_2\text{Cu}_3\text{O}_y$ (5), reactivity with BaCuO_2 (2, 3), disruption of a Cu–O bond (6), and reduction of Cu^{2+} to Cu^+ by a substitution of the Ag^+ ion in the lattice (7). It is confirmed that silver exists as the Ag^+ ion in the Cu site as well as Ag metal in $\text{YBa}_2\text{Cu}_3\text{O}_y$ (8–10). In this paper, Ag^+ ionic conductivi-

ties in $\text{YBa}_2\text{Cu}_3\text{O}_y$ ceramics are measured and a demonstration of the low temperature sintering effect by silver compounds is presented, since Ag^+ ion seems to diffuse easily in the grain boundaries to promote the sintering.

Experimental

Y_2O_3 , BaCO_3 , and CuO were used as the starting materials for the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_y$. After calcination at 930°C , $\text{YBa}_2\text{Cu}_3\text{O}_y$ powder was prepared at 930°C for 20 hr. This powder was mixed with various silver compounds such as Ag, Ag_2O , AgNO_3 , Ag_2CO_3 , $\text{C}_3\text{H}_5\text{AgO}_3$, $\text{C}_2\text{H}_3\text{AgO}_2$,

Ag_2SO_4 , Ag_2S , AgF , AgCl , AgBr , and AgI so that the nominal composition is $\text{YBa}_2\text{Cu}_3\text{O}_y \cdot \text{Ag}_{0.3}$. The pellets of these mixtures were sintered under various temperatures for 10 hr in air or O_2 . In the case of the *in situ* monitoring of the sintering (reported by Ratto *et al.* (11)), only the resistivities of the pellets pressed under 1000 kg/cm^2 were measured by a four-probe method during the heating from room temperature to 930°C (heating rate = 12.5°C/hr). The silver ionic conductivities of the pellet samples sintered at 600 and 930°C were measured by a four-probe dc technique. The applied ion conducting electrodes consisted of the sequence $\text{Ag}/\text{Ag}-\beta''\text{-Al}_2\text{O}_3$ (12, 13). The measurements of silver ion conductivity were done according to the "van der Pauw"-4-probe technique (14). Constant voltages were reached after 10 min after current switching. These measurements were done at temperatures between 350 and 650°C .

Results and Discussion

Effect of Ag Compounds on the Low Temperature Sintering

Figure 1 shows the resistivity-temperature curves of the samples added with some Ag compounds sintered at 700°C in O_2 . All of the samples used for this measurement, as a matter of course, show a clear critical temperature of about 90 K in ac susceptibility measurements, because their bulks consist of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ superconductor. Figure 2 shows the resistivity-temperature curves of $\text{C}_3\text{H}_5\text{AgO}_3$ -added samples sintered at various temperatures in O_2 . The sintering is promoted by the addition of the $\text{C}_3\text{H}_5\text{AgO}_3$ compound even at 400°C , because a resistive transition at about 90 K is observed for this sample, not for the non-added sample. The appearance of this resistive transition indicates that a direct sintering between the $\text{YBa}_2\text{Cu}_3\text{O}_y$ particles occurs in the grain boundaries (8).

The additions of all the Ag compounds

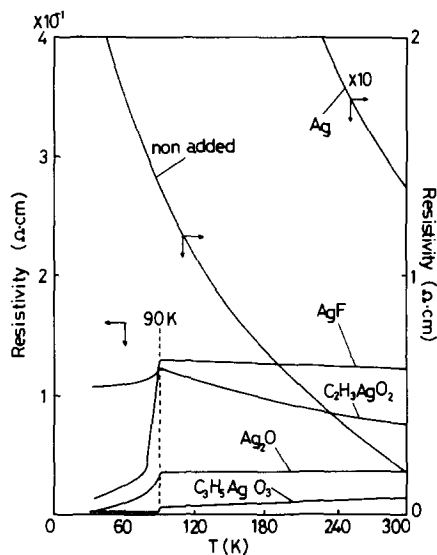


FIG. 1. Resistivity-temperature curves of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ ceramics added with various Ag compounds which were sintered at 700°C in O_2 .

except for Ag and AgI promoted sintering at temperatures lower than 700°C . In general, it is concluded that an oxygen atmosphere rather than air is preferential for sintering and that Ag compounds decomposing

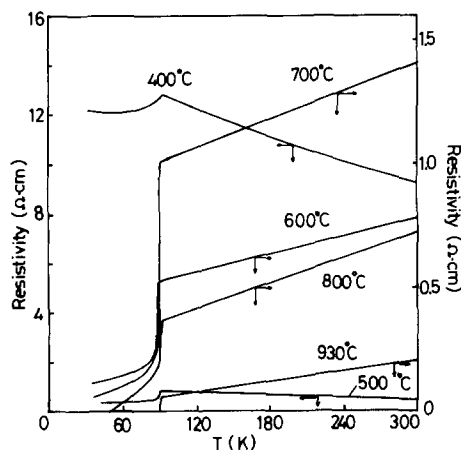


FIG. 2. Resistivity-temperature curves of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ ceramics added with $\text{C}_3\text{H}_5\text{AgO}_3$ sintered at various temperatures in O_2 .

to Ag at low temperature strongly promote sintering. Therefore, these compounds act as Ag metal which will easily produce an Ag^+ ion by a reaction of oxygen in the promotion of sintering. However, a large particle of Ag metal is not effective for sintering as shown in the results for the Ag-added samples, where about $200\ \mu\text{m}$ Ag powder is used. It should be noted that even the Ag compounds such as Ag_2SO_4 , Ag_2S , AgF , AgBr , and AgCl , which never decompose in the present sintering temperature range, promote sintering. This result indicates that these Ag compounds produce an Ag^+ ion and then promote sintering in the grain boundaries.

Monitoring of the Sintering Process with Resistivity Measurement

Figure 3 shows the resistivities of the non-added sample and the samples added with Ag compounds as a function of sintering temperature. The resistive behavior mainly consists of four steps characteristic of the grain boundary during the rising of temperature as denoted by A, B, C, and D in Fig. 3. Step A is based on the semiconducting properties of impurities existing on the surface of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ grain, such as Y_2BaCuO_5 , BaCuO_2 , CuO , and BaCO_3 . Probably step B will be attributed to an oxygen release from an impurity of *p*-type semiconducting oxide in the grain boundaries, because its resistivity increases by the oxygen release. Step C is the first clear sintering process and is based on the production of $\text{YBa}_2\text{Cu}_3\text{O}_y$ from the impurities in the grain boundaries (15, 16). Therefore, the resistive transition is always observed even for the nonadded sample when the sintering temperature is higher than about 750°C . Step D (about 870°C) is based on complete sintering by the production of the liquid phase in the grain boundaries. This step is not observed for the sample with the nominal composition of $\text{YBa}_2\text{Cu}_{2.7}\text{O}_y$ which does not contain ex-

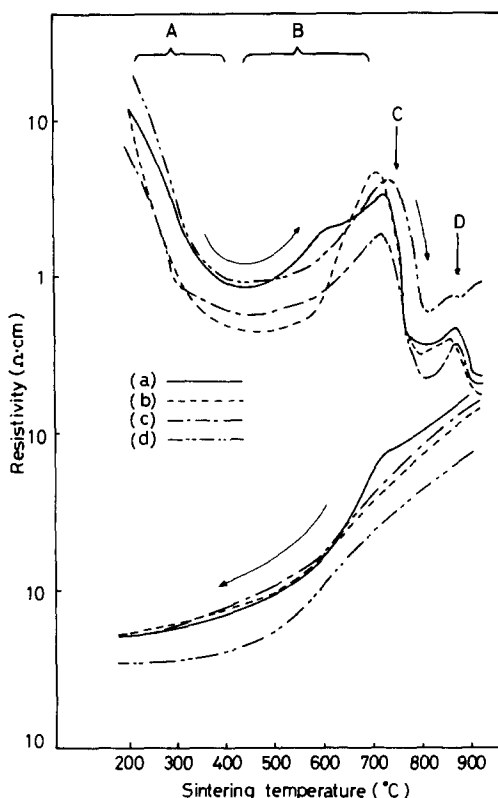


FIG. 3. Monitoring of the sintering by resistivity measurement: (a) nonadded $\text{YBa}_2\text{Cu}_3\text{O}_y$; (b) Ag_2O , added $\text{YBa}_2\text{Cu}_3\text{O}_y$; (c) $\text{C}_3\text{H}_7\text{AgO}_3$, added $\text{YBa}_2\text{Cu}_3\text{O}_y$; and (d) $\text{YBa}_2\text{Cu}_{2.7}\text{O}_y$.

cess CuO in the impurities, because the production of the liquid phase needs CuO (17).

The same measurement was made for CuO , BaCuO_2 , and Y_2BaCuO_5 pellets which are the impurities in $\text{YBa}_2\text{Cu}_3\text{O}_y$. Only BaCuO_2 shows a sintering behavior similar to that of $\text{YBa}_2\text{Cu}_3\text{O}_y$ during the rising of temperature as shown in Fig. 3, but not during the dropping of temperature, especially in the temperature region from about 500 to 800°C . This result strongly suggests that some impurities on the surface of the BaCuO_2 grain determining the resistive behavior are almost same as those of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ grain. Probably, these will be BaCO_3 and the oxides consisting of Ba and Cu.

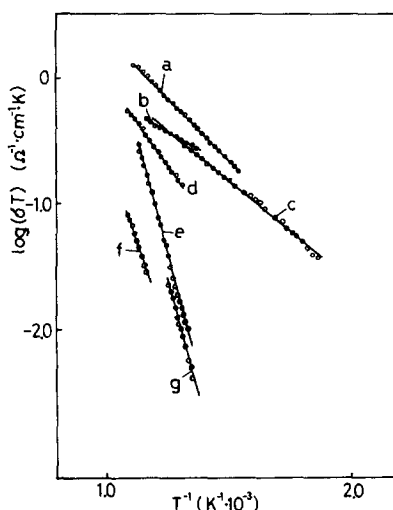


FIG. 4. Ag ionic conductivities (σT) of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ ceramics added with various Ag compounds, as a function of temperature: (a) $\text{C}_3\text{H}_5\text{AgO}_3$, added $\text{YBa}_2\text{Cu}_3\text{O}_y$, sintered at 600°C ; (b) Ag_2O , added $\text{YBa}_2\text{Cu}_{2.7}\text{O}_y$, sintered at 600°C ; (c) Ag_2O , added $\text{YBa}_2\text{Cu}_{2.7}\text{O}_y$, sintered at 930°C ; (d) $\text{C}_3\text{H}_5\text{AgO}_3$, added $\text{YBa}_2\text{Cu}_3\text{O}_y$, sintered at 930°C ; (e) Ag_2O , added $\text{YBa}_2\text{Cu}_3\text{O}_y$, sintered at 930°C ; (f) Ag_2CO_3 , added $\text{YBa}_2\text{Cu}_3\text{O}_y$, sintered at 600°C ; and (g) Ag_2CO_3 , added $\text{YBa}_2\text{Cu}_3\text{O}_y$, sintered at 930°C .

Therefore, the Ag^+ ion will affect these impurities in the grain boundaries and then will promote sintering in the low temperature region.

Silver Ionic Conduction in $\text{YBa}_2\text{Cu}_3\text{O}_y$ Ceramics

Figure 4 shows the Ag^+ ionic conductivities as a function of temperature. The samples sintered at 930°C contain Ag^+ ions in the Cu site in the bulk as well as the grain boundaries, but Ag^+ ions exist only in the grain boundaries for the samples sintered at 600°C (8). However, the ionic conductivities are not strongly dependent on the sintering temperature as shown in Fig. 4. Therefore, the Ag^+ ion will move at the surface of $\text{YBa}_2\text{Cu}_3\text{O}_y$ grain in the grain boundaries. The fact that the activation energies of Ag ionic conductivity for the present samples (0.2–1.4 eV as listed in Table I) are much

TABLE I
ACTIVATION ENERGIES OF Ag^+ IONIC CONDUCTIVITY OF $\text{YBa}_2\text{Cu}_3\text{O}_y$ CERAMICS ADDED WITH VARIOUS Ag COMPOUNDS

Sample	Sintering temperature ($^\circ\text{C}$)	Activation energy (eV)
$\text{YBa}_2\text{Cu}_3\text{O}_y(\text{C}_3\text{H}_5\text{AgO}_3)_{0.3}$	600	0.39
	930	0.52
$\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag}_2\text{CO}_3)_{0.15}$	600	1.16
	930	1.44
$\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag}_2\text{O})_{0.15}$	930	1.43
$\text{YBa}_2\text{Cu}_{2.7}\text{O}_y(\text{Ag}_2\text{O})_{0.15}$	600	0.23
	930	0.32

lower than those of the Ag diffusion in $\text{YBa}_2\text{Cu}_3\text{O}_y$ bulk (2.3–2.5 eV) (18) also supports the grain boundary diffusion of Ag^+ ion.

Table I summarizes the activation energies of Ag ionic conductivity. The activation energies are roughly classified into two values. One is 0.2–0.5 eV, which is a little larger than that of RbAg_4I_5 (19), and the other is 1.2–1.4 eV. This suggests that there are two kinds of processes for the Ag^+ ionic diffusion at the surface of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ grain. For the consideration of this process, it will be very useful if the activation energy of the Ag^+ ionic conductivity is lower for the sample with a nominal composition of $\text{YBa}_2\text{Cu}_{2.7}\text{O}_y \cdot 0.3(\text{Ag}_2\text{O})$ (substituted type for Cu) than for that with a nominal composition of $\text{YBa}_2\text{Cu}_3\text{O}_y \cdot 0.3(\text{Ag}_2\text{O})$ (added type). Probably, the Ag^+ ion will diffuse via the Cu vacancy of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ surface for the former sample, but at the $\text{YBa}_2\text{Cu}_3\text{O}_y$ surface containing no vacancy for the latter sample. In conclusion, the Ag^+ ion will diffuse at the $\text{YBa}_2\text{Cu}_3\text{O}_y$ surface in the grain boundaries by the above two-type process and promote sintering even in the low temperature range.

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