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HIP PHASE DIAGRAM OF YBCO TYPE SUPERCONDUCTOR

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ABSTRACT

The oxygen partial pressure - temperature phase diagram of YBCO type superconductors reported before by us showed that the $YBa_2Cu_4O_x$ phase formation from $Y_2Ba_4Cu_7O_z$ with CuO, as well as from $YBa_2Cu_3O_y$ with CuO are oxidation reactions. The total gas pressure - temperature phase diagram shows that the $YBa_2Cu_4O_x$ phase formation temperature from $Y_2Ba_4Cu_7O_z$ with CuO increases with increasing the total gas pressure. On this phase boundary line, the fugacity of oxygen increases with increasing the total gas pressure even at constant oxygen partial pressure.

INTRODUCTION

Recently we have reported the total gas pressure - oxygen partial pressure - temperature phase diagram of YBCO type superconductors (P_{tot} - P_{O2} - T phase diagram)[1]. According to the P_{O2} - T phase diagram, the $YBa_2Cu_4O_x$ (124 phase) is stable at higher P_{O2} than $Y_2Ba_4Cu_7O_z$ (123.5 phase) with CuO or $YBa_2Cu_3O_y$ (123 phase) with CuO. The 124 phase formations from 123 phase with CuO and from 123.5 phase with CuO are oxidation reactions[1]. P_{tot} - T phase diagram shows that the phase formation temperature from 123.5 phase with CuO to 124 phase increases as P_{tot} increases. The objective of this study is to obtain the effects of P_{tot} on the phase equilibrium temperature and the fugacity of oxygen. In this study, 124 phase samples were synthesized at various P_{tot}, 10MPa of P_{O2} and 1300K of T. The fugacity of oxygen (f_{O2}) was calculated as a function of P_{tot} at constant P_{O2} and T, and the fugacity on the phase boundary line was also calculated.

EXPERIMENTAL

Raw materials Y_2O_3 (Shin-Etsu Chemical, Lot No. 0449-SU), $BaCO_3$ (Sakai Chemical, Lot No. 0021) and CuO (Sockawa Chemicals, Lot No. 03432A) had a purity higher than 99.9%. These powders were mixed in the atomic ratio of Y:Ba:Cu = 1:2:4 by an agate mortar in ethanol for 1.5h. After drying, the mixture was presintered at 1200K for 48h in air. The presintered powder was ground and uniaxially pressed into pellets at 20MPa, and hot isostatically pressed in oxygen - argon gas mixture (O_2-HIP) at different conditions as shown in Table I.

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Table I. The O_2–HIPping conditions.

Sample number	P_{tot}(MPa)	P_{O2}(MPa)	T(K)
A	70	10	1300
B	100	10	1300
C	140	10	1300
D	200	10	1300

The oxygen concentration of the mixture was changed to fix P_{O2} at 10MPa. (The pressure media of the sample D in Table I was the mixture of 95% argon and 5% oxygen, for instance.) Samples were heated at 400 K/h, kept at 1300K under 10MPa of P_{O2} and various of P_{tot} for 5 hours, and quenched by adiabatic expantion of the surrounding atmosphere by decreasing P_{tot} from the maximum treating pressure to 30MPa in about 2 minutes. The calculated cooling rate was about 12000K/h (3K/s) from 1300K to 1070K (800° C), and cooled at 2000K/h to room temperature. The O_2–HIPped samples were investigated by the X–ray diffraction method.

RESULTS AND DISCUSSUION

Fig. 1 shows the P_{tot} – T phase diagram at constant P_{O2} of 10MPa. The 124 phase temperature stability range increases with increasing P_{tot}. Fig. 2 shows the P_{O2} – T phase diagram at constant P_{tot} of 200MPa. 124 phase is stable at high P_{O2} region. The X–ray diffractogram of samples A, B, C and D are shown in Fig. 3. Majority of the samples are 124 phase. The intensities of (0012), (0014) and (108) diffractions increase with rising P_{tot}. The increase of these diffractions suggest the appearance of some impurity phases which have similar diffraction pattern with that of 124 phase such as 123 phase with CuO or 123.5 phase with CuO. Even at constant P_{O2}, P_{tot} gives some effects on the phase stability.

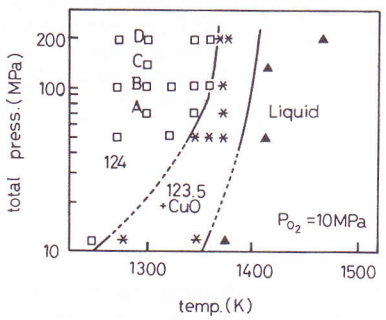

Fig. 1 Total gas pressure – temperature phase diagram of YBCO type superconductors at constant oxygen partial pressure of 10MPa. The open squares, the asterisks and the solid triangles show the condition at which the 124 phase, the 123.5 phase with CuO and the liquid phase were stable respectively. The marks A, B, C and D have the same significance as in Table I.

Fig. 2 Oxygen
at constant tot
the 123 phase
Fig. 1.

Fig. 3 X–ray dif
(0012), (0014) an

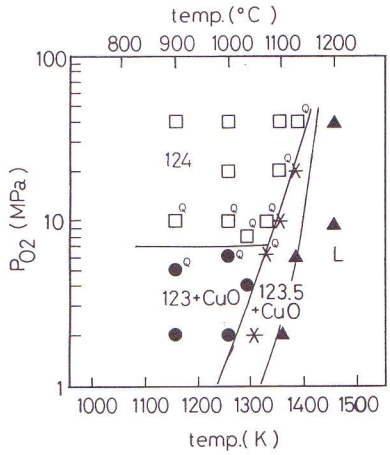

Fig. 2 Oxygen partial pressure – temperature phase diagram of YBCO type superconductor at constant total gas pressure of 200MPa. The solid circles show the condition at which the 123 phase with CuO was obtained. The other marks have the same significance as in Fig. 1.

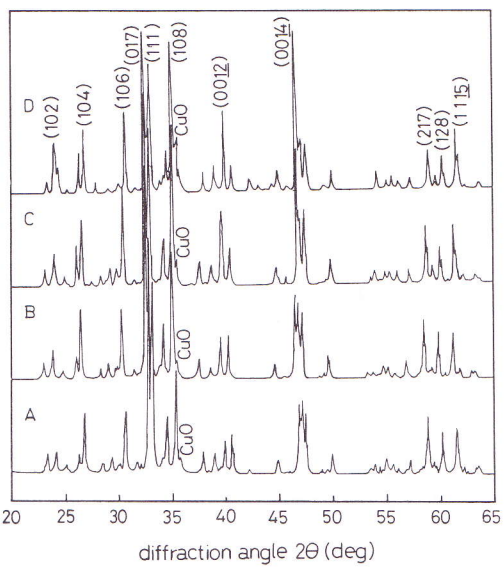

Fig. 3 X-ray diffractograms of samples A, B, C and D in Table I. The intensities of (0012), (0014) and (108) diffraction increases with rising total gas pressure.

The fugacity of oxygen (f_{O2}), calculated from generalized fugacity coefficient chart[2] for the mixture with argon, increases with increasing P_{tot} at constant P_{O2} and T as shown in Fig. 4. These changes with P_{tot} are stronger at low temperatures, and at about 1200K (around HIPping temperature) are considerably small.

As shown in Fig. 5, the iso-fugacity lines are almost perpendicular to the phase boundary line and the fugacity increases on the phase boundary line ($f_{O2,eq.}$) with rising P_{tot}. This implies that the total gas pressure modify the thermodynamic stability as an independent variable. The shifting of fugacity by the total gas pressure change can not explain the altered thermodynamic stability.

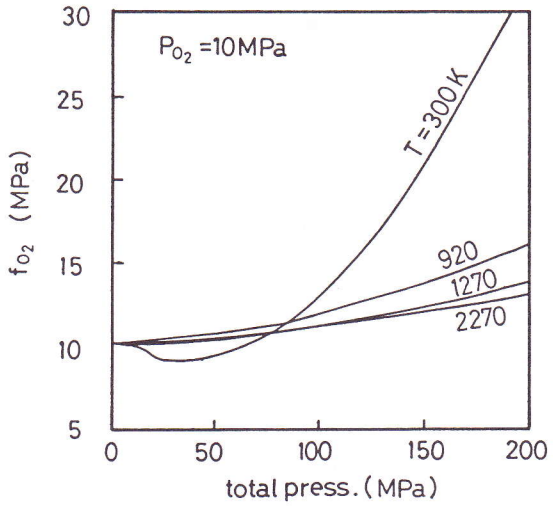

Fig. 4 The fugacity of oxygen as a function of total gas pressure at constant oxygen partial pressure of 10MPa. Data based upon the reference 3.

CONCLUSION

$YBa_2Cu_4O_x$ superconductors were synthesized by O_2-HIPping method at various total gas pressures, 10MPa of oxygen partial pressure and 1300K of temperature. In the total gas pressure – temperature phase diagram, the fugacity of oxygen on the phase boundary between $Y_2Ba_4Cu_7O_z$ with CuO and $YBa_2Cu_4O_x$ increases with rising total gas pressure at constant oxygen partial pressures. Iso-fugacity lines on the total gas pressure – temperature phase diagram are almost perpendicular to the phase boundary line. The total gas pressure modify the thermodynamic stability as an independent variable. The changing of fugacity of oxygen as a function of total gas pressure can not explain the altered thermodynamic stability.

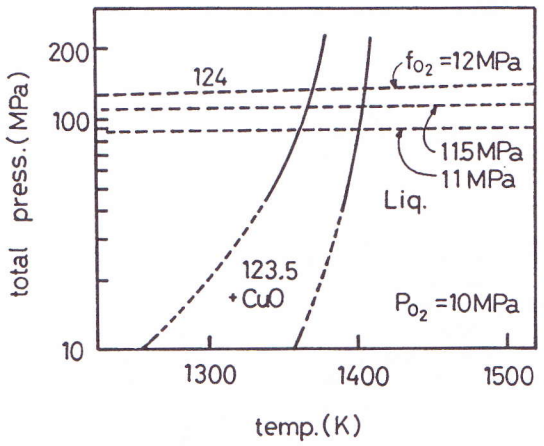

Fig. 5 Total gas pressure – temperature phase diagram with iso-fugacity lines. The fugacity on the phase boundaries increases with rising total gas pressure.

ACKNOWLEDGEMENTS

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AgO DOPED $YBa_2Cu_4O_8$ SUPERCONDUCTOR UNDER HIGH OXYGEN PARTIAL PRESSURE

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ABSTRACT

Generaly silver doping into $YBa_2Cu_3O_7$ superconductor improves the critical temperature and critical current density. In this work the silver peroxide was doped into $YBa_2Cu_4O_8$ superconductor and sintered by the Oxygen Hot Isostatically Pressing method. The critical temperature of the 124 phase increased by silver peroxide doping.

INTRODUCTION

There have been many reports of silver doping into $YBa_2Cu_3O_7$ superconductor (123 phase). The doped silver improved the critical temperature and critical current density of 123 phase[1]. Generaly the 123 phase with some silver was synthesized in air or oxygen at 1 atmosphere. The oxygen partial pressure is so low that the doped silver locates at the grain boundaries of 123 phase as metallic silver[2]. In almost all cases, silver doping did not cause any distinct microstructure changes of the 123 phase. In this study the Oxygen Hot Isostatically Pressed (O_2HIPped) $YBa_2Cu_4O_8$ (124 phase) superconductor with some silver peroxide (AgO) was obtained. The critical temperature of 124 phase was measured as a function of the amount of doped AgO[3,4].

EXPERIMENTAL

The starting materials are Y_2O_3, $BaCO_3$, CuO and AgO which had a purity of more than 99.9%. At first Y_2O_3, $BaCO_3$ and CuO were mixed at each ratio as shown in Table I and calcined at 1243K (970° C) for 48 hours in air. Silver was added as AgO in the amount of at% corresponding to 100(Ag/(Ag+Cu)). The pre-sintered powder was uniaxially pressed into cylindrical pellets at 20MPa (10mm diameter and about 2mm thickness) and Cold Isostatically Pressed (CIPped) at 200MPa for 1 minute. Samples were, then, treated by O_2-HIP (Kobe Steel, O_2-Professor HIP.) technique. Samples were heated at a rate of 400 K/h, kept under 40MPa of P_{O2} and 200MPa of P_{tot} at 1270K of temperature for 5 hours, and quenched by adiabatic expansion of the surrounding atmosphere by decreasing the total gas pressure from the maximum treating pressure to 30MPa in about 2 minutes. The obtained cooling rate was about 12000K/h (3K/s) from the treating temperature to 1070K (800° C), and cooled at 2000K/h to room temperature.

The critical temperature, at which the resistivity turns to zero, were measured by four probe method.

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Table I. The composition of starting powders.

Sample number	Atomic ratio(Y:Ba:Cu:Ag)	AgO doping (%)
1	1 : 2 : 4 : 0	0
2	1 : 2 : 3.96 : 0.04	1
3	1 : 2 : 3.8 : 0.2	5
4	1 : 2 : 3.6 : 0.4	10
5	1 : 2 : 3.2 : 0.8	20

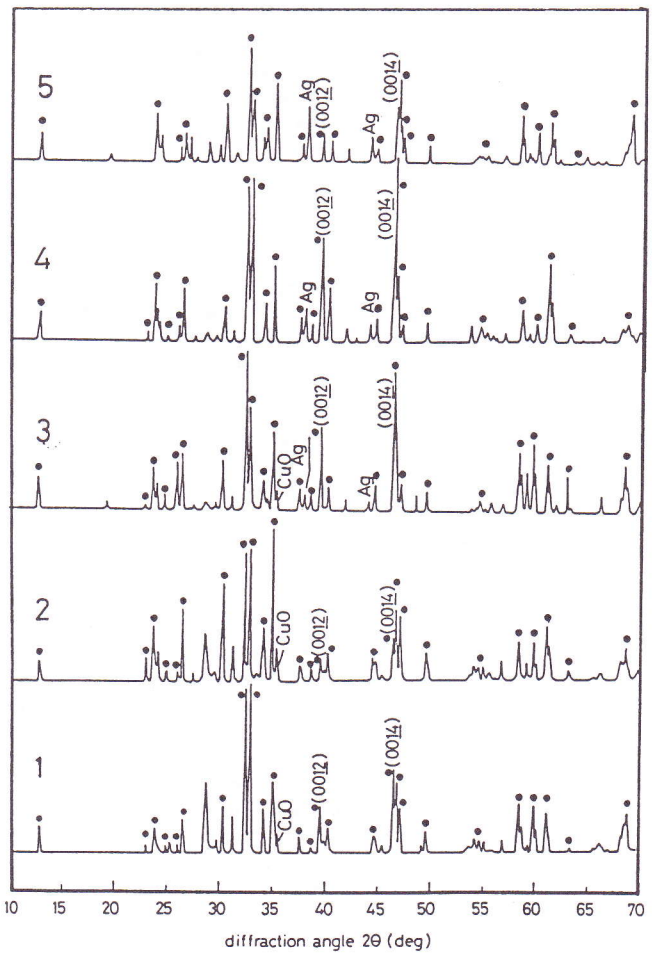

Fig. 1 The X-ray diffractogram of AgO doped samples.

RESULTS AND DISCUSSION

The X-ray diffractograms of AgO doped samples show that the superconducting 124 phase is fromed in all cases. The peaks of impurities, such as Y_2O_3, 211 phase, 123.5 phase, CuO and some other compounds consist of Y, Ba and Cu decrease as AgO doping fraction increases. Small amount of Ag metal was detected for samples doped more than 5 at% AgO. AgO was not detected directly in any case. In the X-ray diffractogram, the intensities of (0012) and (0014) diffractions increase as the AgO doping fraction increases. The increase of these diffractions suggests the Ag substitution into Cu-sites, increase of oxygen atoms in the planes or the appearance of some impurity phases which have similar diffraction pattern with that of 124 phase such as 123 phase or 123.5 phase.

The critical temperature was measured as a function of AgO doping. The results are shown in Fig. 2. The critical temperature, at which the resistivity turns to zero, increases with increasing the amount of doped AgO up to 1%. The critical temperature begins to decrease slightly with increasing the amount of doped AgO more than 1%. It suggests that the solubility limit of Ag into Cu site is around 1 at%. Because AgO could replace CuO even CuO presented in stoichiometric 124 phase, the AgO substituted phase is reasonably stable. Fig. 3 shows the resistivity of the samples 1,2 and 4 as a function of temperature.

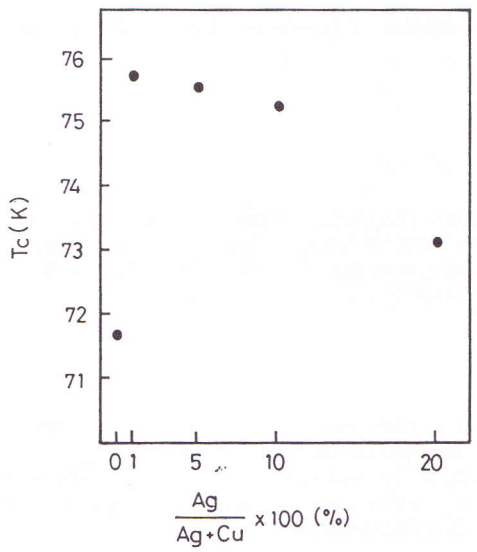

Fig. 2 The relationship between the critical temperature ($T_{c,zero}$) and Ag doping quantity mol% (=100Ag/(Ag+Cu)). The samples correspond from number 1 to 5 of Table I, and are O_2-HIPped under P_{tot}=200MPa, P_{O2}=40MPa at 1270K for 5hours.

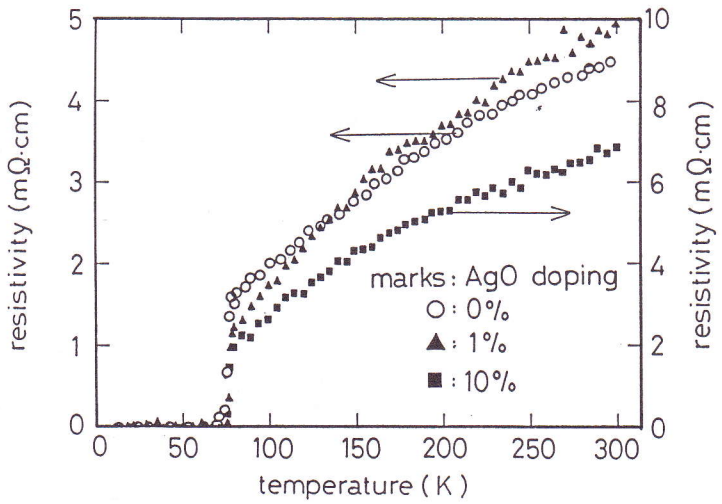

Fig. 3 The resistivity of samples as a function of temperature.

CONCLUSION

By the doping of AgO into $YBa_2Cu_4O_8$ superconductor, the critical temperature ($T_{c,zero}$) increased about 4 degrees to 75.7K by doping AgO at 1% of Cu contents. $T_{c,zero}$ begins to decrease slightly by AgO doping more than 1% of Cu contents. This result suggests that the solubility limit of Ag into Cu site is around 1%.

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