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Preparation of $YBa_2Cu_4O_8$ Superconductor Using Polymer-Gelation Method with Polyvinyl Alcohol

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Calcination and sintering of the precursor gel prepared from polyvinyl alcohol and metal nitrates gave pure $YBa_2Cu_4O_8$ superconductor. Using this method, pure phase of $YBa_2Cu_4O_8$ superconductor can be prepared in a short heat treatment time compared with the conventional method.

Among Y-Ba-Cu-O superconductors, $YBa_2Cu_4O_8$ (Y124)[1] is getting focused on by many researchers due to its thermal and chemical stability compared to those of $YBa_2Cu_3O_{7-x}$(Y123).[2] Even though the superconducting transition temperature (Tc) of Y124 (80 K) is lower than that of Y123 (90 K), stable superconducting property of Y124 suggests the possibility to put superconducting oxides to practical use. However, synthesis of bulk sample of Y124 by solid state method requires the applications of quite high oxygen pressure and long thermal treatments.[3] Recently, Mazaki *et al* [4] have reported that the preparation of Y124 was successful using sol-gel method under an ambient oxygen pressure, where 200 h of heat treatment time was necessary. Fujihara *et al* [5] synthesized a single phase of $YBa_2Cu_4O_8$ by sintering the gel obtained from corresponding metal acetates, water, and tartaric scid at 780 °C for 30 h in flowing oxygen.

We report here that the pure Y124 can be prepared easily by using polymer-geration method with polyvinyl alcohol(PVA) in a short heat treatment procedure.

The metal nitrate solution was prepared by dissolving the prescribed amount of commercial powders of $Y(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$, and $Cu(NO_3)_2 \cdot 3H_2O$ in water. PVA (polymerization degree:2000) was autoclaved at 120 °C for 20 min. By repetition of freezing (-20 °C) and melting the mixture sol, the gelation proceeded step by step and slightly turbid blue precursor gel was obtained.

At first, the precursor gel was heat-treated in O_2 at 500 °C for 10 h until pyrolysis of PVA and nitrate anion was completed. The XRD analysis revealed that the precursor powder obtained by the above pyrolysis was a mixture consisting of Y_2O_3, $BaCO_3$, and CuO. The precursor powder was heat-treated with several conditions under an ambient oxygen pressure. Figure 1 represents the XRD patterns of the heat-treated samples of the pyrolyzed powder. When the precursor powder was calcined at 750 °C for 2 h under an ambient oxygen pressure, the obtained powder contained $Y_2Cu_2O_5$, Y123, $BaCO_3$, and CuO (Fig. 1a). Calcination of the precursor powder at 800 °C for 2 h gave a mixture of Y123 and CuO (Fig. 1b), and the 24 h calcination at 800 °C gave Y124 as a main product (Fig. 1c). Pure Y124 was obtained when the calcined powder (800 °C, 24 h) was heat-treated at 820 °C for 30 h under an ambient oxygen pressure (Fig. 1d). Of special interest is the fact that Y124 can be prepared easily by using the present polymer-gelation method, which is in contrast to the reported method [3,4] that required high oxygen pressure and long thermal treatments.

It may be anticipated that metal ions are dispersed in an atomic level in the present PVA based precursor gel. Moreover, SEM result suggests that the particle size (ca.5mm) of the mixed powders obtained by pyrolysis of precursor gel at 500 °C is small enough. These facts may contribute to the facility in forming Y124.

Figure 2 demonstrates the observed electric resistivity and ac susceptibility as a function of temperature for the Y124 sample. For the measurements, the powder heat-treated at 800 °C for 24 h was pulverized, pressed into disk shape, and then sintered at 820 °C for 30 h under an ambient oxygen pressure. The electric resistivity curve showed Tc(onset)=82 K and Tc(R=o)=79 K with a sharp superconducting transition. Sharp superconducting transition was also observed around 80 K in the ac susceptibility measurement. These results are characteristic for the Y124 sample.

Further investigations are undertaken to elucidate the formation process of the Y124 using PVA based polymer-gelation method.

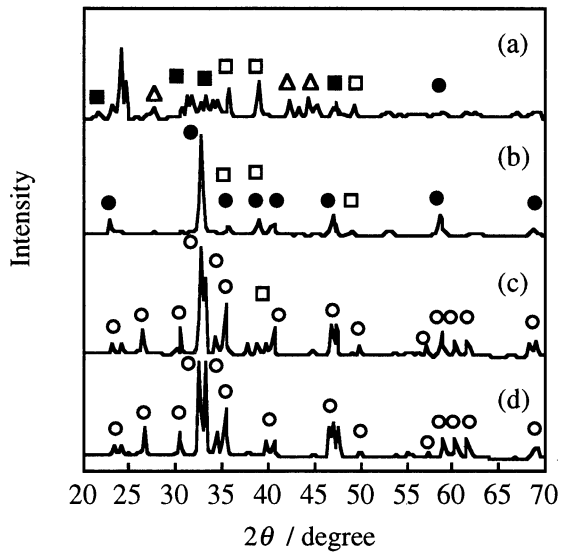

Fig.1. XRD patterns of the powder heat-treated in O2 at 750 °C for 2 h (a), at 800 °C for 2 h (b) and 24 h (c) and then at 820 °C for 30 h (d). ○Y124, ●Y123, △$BaCo_3$, □CuO, ■$Y_2Cu_2O_5$

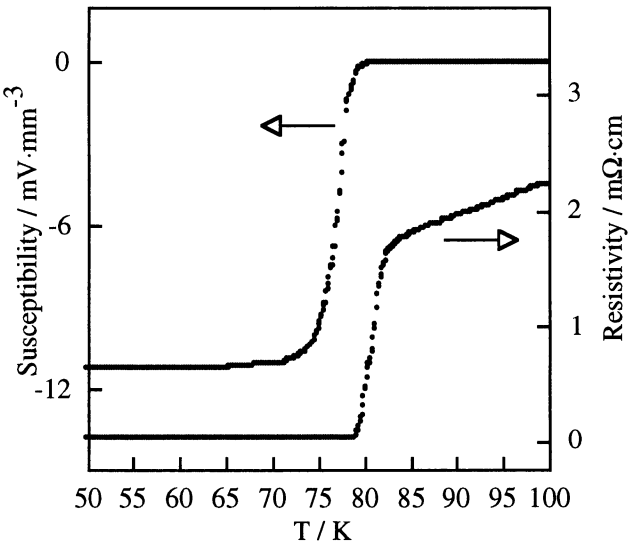

Fig. 2. Temperature dependence of resistivity and ac susceptibility for the Y124 sample sintered at 820 °C for 30 h.

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