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Thermodynamic and electrical properties at high temperature of the Zn-substituted YBaCuO oxides with 4% Zn.

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Thermodynamic and electrical properties of $YBa_2Cu_{2.88}Zn_{0.12}O_z$ have been investigated in conditions of thermodynamic equilibria between 300 and 900°C with atmosphere of O_2-N_2 mixtures. The results have been interpreted in term of point defects and the maximum oxygen content z = 6.92 suggests oxygen vacancies localized on bridging oxygen. Electrical properties (resistivity and thermopower) measured on the same conditions are characterized by a transition n-p near the stoichiometry and two semiconducting domains

1. INTRODUCTION

A major problem is to clarify the role of Zn to explain the large reduction of T_C and T_N induced by this dopant and the departure from stoichiometry [1]. Nethertheless, no study of the electrical properties (resistivity and thermopower) related to the oxygen content has been carried out in condition of thermodynamic equilibrium at high temperature. This paper reports the determination of the oxygen content versus the oxygen pressure between 300 and 900°C and electrical properties measurements in the same conditions of oxygen pressure and temperature to relate these properties to the composition.

2. EXPERIMENTAL

Samples of $YBa_2Cu_{2.88}Zn_{0.12}O_z$ were synthesized with the standard solid-state reaction. The starting oxides were Y_2O_3(Aldrich 99.99%), $BaCO_3$ (Cerac Inc 99.999%), CuO and ZnO (Johnson Matthey Specpure). Isotherm curves of log $p(O_2)$ versus oxygen content have been recorded between 300 and 900°C and oxygen partial pressures 1 (total pressure) and 10^{-3} atm using an Ugine Eyraud B60 thermobalance having a working sensibility of 0.015 mg corresponding to a δz value equal to 2 10^{-4} for 3.5 g samples used in this study . Oxygen partial pressures were prepared using Brooks flowmeters. The electrical resistivity and the thermopower were measured also between 300 and 900°C in oxygen partial pressures between 1 and 10^{-2} atm with a device previously described [2]. The samples were bars of 2 cm of length and 0.5x0.5 cm of section.

3. RESULTS

3.1 Thermodynamics

The maximum oxygen content obtained at 300°C is $z_{max} = 6.922 \pm 0.009$. Isotherm curves log p(O2) versus the oxygen content z at 400,500 and 600°C are shown in fig 1.

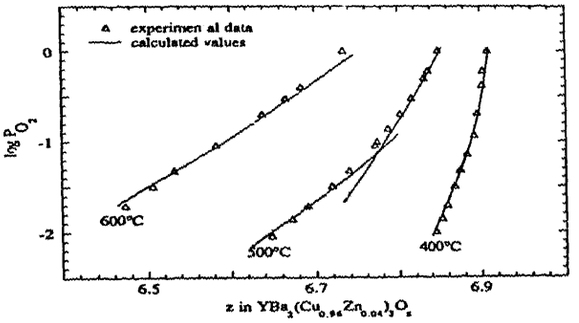

Figure 1. Isotherm curves log p(O2) vs zz and calculated values

These results are interpreted in term of point defects assuming that Zn substitutes for Cu equally in the $Cu(2)O_2$ planes and the Cu(1)O chains. If the concentrations are expressed in fraction sites, we have $[Zn] = 0.12 = [Zn'_{Cu(1)}] + [Zn^{x}_{Cu(2)}] = 0.06 + 0.06$.

At z_{max} the electroneutrality condition is $2[V_O^{oo}] = [Zn'_{Cu(1)}] + [Cu'_{Cu(1)}]$ or $2 \times 0.08 = 0.06 + 0.10$, implying the reduction of copper on chains and twice ionized oxygen vacancies. The initial hole content is $[h^{\circ}]_0 = 1 - 0.16 = 0.84$. The previous model [3] is improved, assuming that initial oxygen vacancies are

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not localized on the chains but on other sites, for exemple the bridging oxygens. With these assumptions, departures of stoichiometry are explained by two domains. For 6.92 > z > 6.75, the predominant defects are twice ionized oxygen vacancies and for z< 6.75 single ionized vacancies are the predominant defects. The calculated values are plotted in fig 1 and are in good agreement with the experimental results.

3.2 Electrical resistivity

Electrical resistivity was measured under oxygen pressures between 1 and 10-2 atm. The thermodynamic study giving the relation pO2 vs z lead to relation electrical resistivity ρ vs z. The experimental plots r vs z for various temperatures are shown on fig 2.

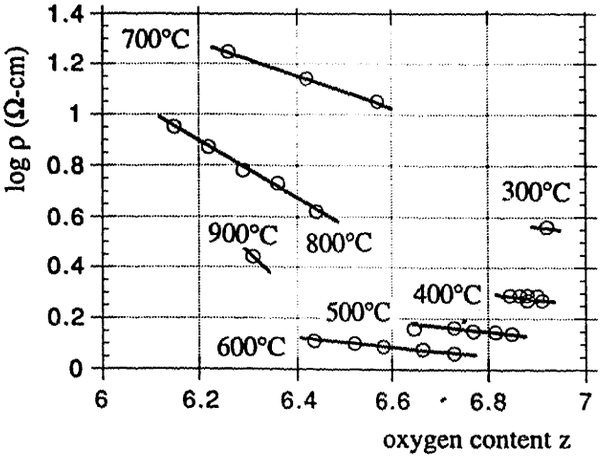

Figure 2. Electrical resistivity vs oxygen content

We see two domains: the former corresponds to the temperatures between 300 and 600°C with a semiconducting behaviour and an activation energy of 0.06 eV and the later corresponds to the temperatures higher than 600°C with a second semiconducting behaviour and an activation energy of 0.4 eV. In both the cases, ρ increases when z decreases indicating a decrease of the concentration of the charge carriers.

3.3 Thermopower

Thermopower was measured in the same conditions than ρ and the results are plotted on fig 3 where measurements between z= 6.92 and z= 6.75 are detailed. These results show a transition n-p for z= 6.85 contrary to pure YBaCuO [4]. The whole results are plotted on fig.4 and we see a continuous decrease of the concentration of the charge carriers.

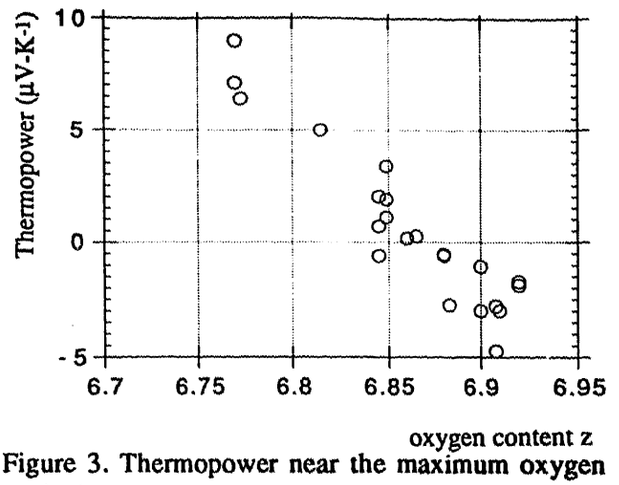

Figure 3. Thermopower near the maximum oxygen content.

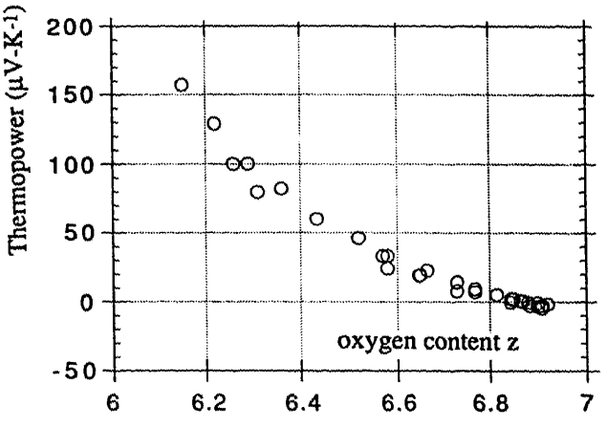

Figure 4 Thermopower ws 6.15<z< 6.92

4 CONCLUSION

Thermodynamic and electrical properties have been measured at high temperature under various oxygen pressures. Electrical resistivity is characterized by two semiconducting domains and thermopower indicates a n-p transition near the maximum oxygen content contrary to pure YBaCuO.

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