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OXYGEN EXCHANGE STUDY IN PHASE TRANSFORMATIONS OF SUPERCONDUCTING BISMUTH CUPRATES (Pb2212 AND Pb2223)

M. Mansori, C. Favotto, K. Jardet, M. Roubin, A. Sebaoun and P. Satre

Laboratoire de Physico-Chimie du Matériau et du Milieu Marin, Matériaux à Finalité
Spécifique (E.A. 1356), Faculté des Sciences et Techniques, Université de Toulon et du Var
B.P. 132, 83957 La Garde Cedex, France

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Abstract

The oxygen exchange between the condensed phase(s) and the gas phase was studied as a function of temperature for superconducting phases of the system (Bi,Pb)–Sr–Ca–Cu–O.

An oxygen probe apparatus allowed confirmation that the variation in oxygen composition in the Pb2212 and Pb2223 superconducting phases is a reversible phenomenon on heating and cooling. It was demonstrated that the mass loss of both phases, for the 905 and 980°C isotherms, was due to the oxygen composition variation and to PbO loss (this latter phenomenon begin irreversible).

Keywords: bismuth cuprates, DTA-DTG, oxygen partial pressure, X-ray diffraction, zirconia sensor

Introduction

Three high-T_c superconducting oxides have been reported in the system Bi_2O_3–SrO–CaO–CuO, and considerable efforts have been directed to their practical use. In our samples, the bismuth was partially substitued by lead to achieve the compositions $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8\pm\alpha}$ (denoted Pb2212) and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10\pm\beta}$ (denoted Pb2223), in order to stabilize the 2223 phase.

The lack of thermodynamic data as a function of both temperature and oxygen partial pressure prevents a prediction of the stability fields of coexisting phases in order to produce pure superconducting phases. Numerous recent works [1–5] demonstrated a reversible exchange of oxygen between the ceramics and the surrounding atmosphere during heating and cooling between 750 and 980°C. Thus, in the description of phase equilibria, the oxygen partial pressure is a sensitive parameter.

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The purpose of this work is to follow the variations in oxygen stoichiometry during phase transformations of superconducting bismuth cuprates (Pb2212 and Pb2223) by means of isothermal thermogravimetric measurements and oxygen pressure determinations. The phases $(Bi_{1.6}Pb_{0.4})Sr_2Ca_1Cu_2O_{8\pm\alpha}$ and $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_3O_{10\pm\beta}$ were chosen in order to understand the influence of the $(Sr_xCa_{1-x})_2PbO_{4\pm\delta}$ and $(Sr_xCa_{1-x})_2CuO_{3\pm\varepsilon}$ phase competition on the oxygen exchanges.

Experimental

The use of an electrochemical solid-electrolyte sensor (yttrium-doped ZrO_2) permitted investigation of the oxygen exchange.

Figure 1 shows a diagram of the P_{O_2} measuring device. A zirconia sensor is sealed to an alumina tube to prevent any oxygen transfer with the open atmosphere.

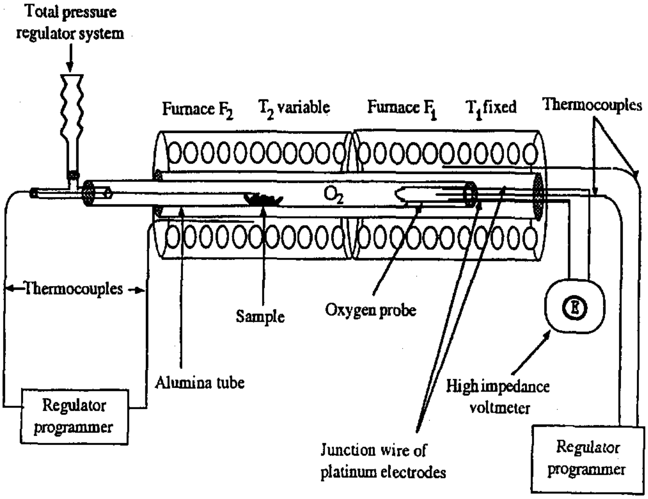

Fig. 1 Scheme of the experimental device

Furnace F_1 allows the probe temperature to be maintained constant at the selected temperature. The powder sample is placed inside furnace F_2, in a gold crucible.

The temperature of furnace F_2 is controlled by a Eurotherm 900HP regulator-programmer.

The studied samples are solid phases in the system Bi–Pb–Sr–Ca–Cu–O and more precisely in the isoplethic cut $(Bi_{1.6}Pb_{0.4})_2Sr_2CuO_{6+z}$–$CaCuO_{2+x}$, schematically denoted Pb2201–0011. The general formula for mixtures in this section is $(Bi_{1.6}Pb_{0.4})Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ (where δ is the oxygen stoichiometry content in the phase and *n* represents the number of copper planes associated with 2Bi; *n* varies from 1 to ∞) [1–3, 6, 7].

The phase denoted Pb2212 for n=2 and Pb2223 for n=3 were synthesized in the laboratory by a coprecipitation method [8]. A previous study by TG (Figs 2a and 2b, respectively) demonstrated that the isothermal course of the mass variations of these phases is reversed between 905 and 980°C.

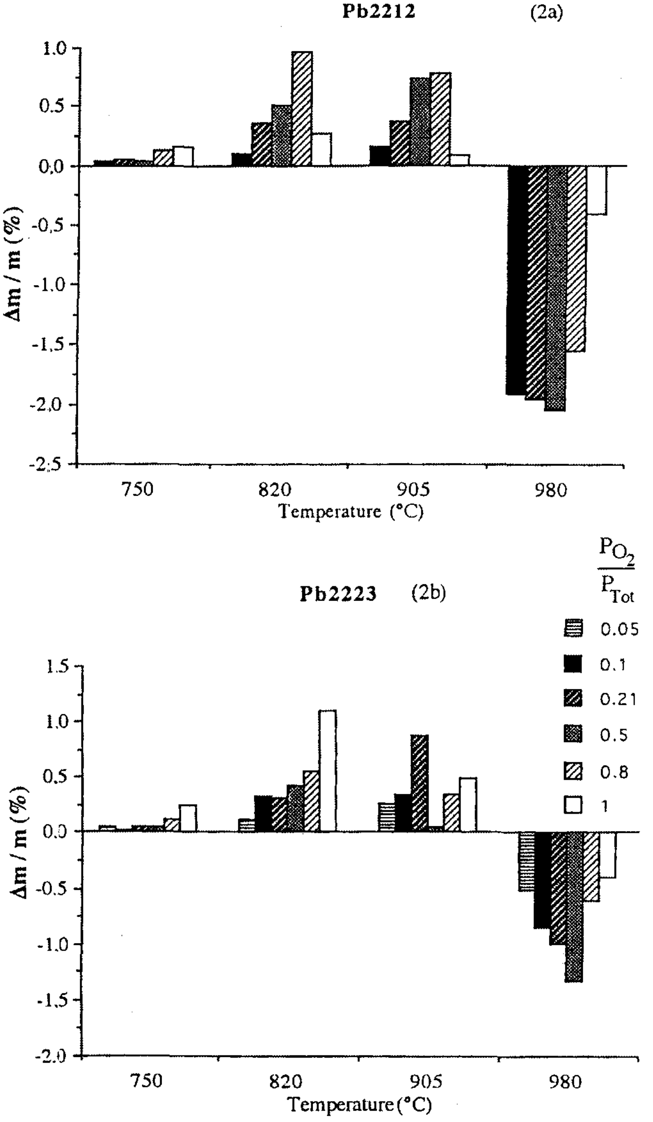

Fig. 2 Histograms of relative mass variations of Pb2212 (a) and Pb2223 (b) mixtures at fixed temperatures (3 h) for $0.05 \leq P_{O_2}/P_{Tot} \leq 1$

This change in behaviour is linked to the mass variations associated with the reversible oxygen exchange and the irreversible PbO loss. This PbO loss increases since the proportion of liquid becomes important for T>930°C. In that stage, it was essential to follow the changes in the equilibrium oxygen partial pressure P_{O_2} on both sides of this temperature. The P_{O_2} follow-up by potential measurement with the normal atmosphere as reference (P_{O_2}=0.21) atm) allowed a precise determination of which variation corresponds to the oxygen exchange.

The selected thermal cycle for the potential measurement study is the same as that of the previous TG study: sample heating at 10°C min^{-1} is followed by annealing for 3 h (at 905 or 980°C) and then cooling at 10°C min^{-1} down to room temperature [4, 5].

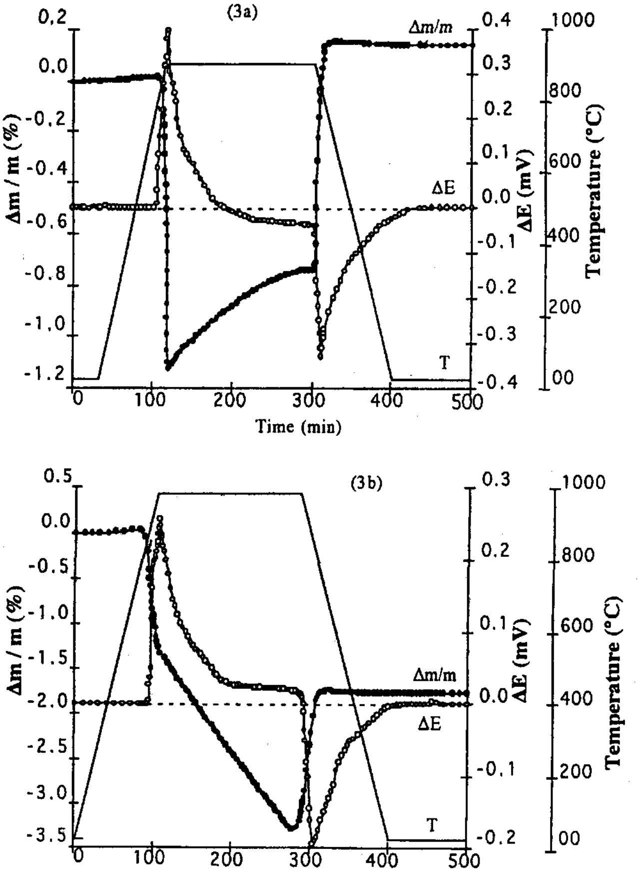

Fig. 3 Comparative results of the study, by TG and potential measurement, of oxygen exchange between the gaseous phase and the condensed phase(s) of the Pb2212 species for annealing at 905°C (a) and 980°C (b). In both cases, exchange reversibility is observed

Results

This study is first made for Pb2212 successively at annealing temperatures of 905 and 980°C (Figs 3a and 3b, respectively).

The TG curves show a mass variation from 800°C on heating, which is reversible on cooling. A mass gain is also observed on annealing at 905°C. These mass variations correspond to the condensed phases – gas phase exchanges, which bring oxygen and PbO into action. On the other hand, on annealing at 980°C, a mass loss ($\Delta m=-2.05\%$) is observed and can be explained by the simultaneous PbO loss. Oxygen non-stoichiometry in oxides during thermal treatment has also been observed [4, 5].

The potential variation curves reveal ΔE stability up to 800°C. This is the temperature from which a potential increase (corresponding to oxygen loss from

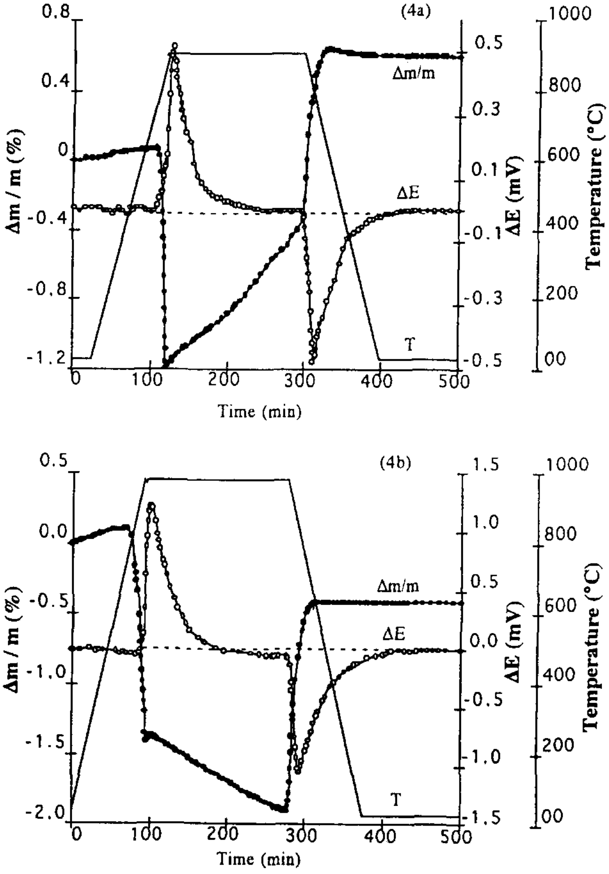

Fig. 4 Comparison of results of TG and potential measurements of oxygen exchange between the gaseous phase and the condensed phase(s) of the Pb2223 species for annealing at 905°C (a) and 980°C (b). In both cases, exchange reversibility is observed

the condensed phase) is observed. This phenomenon can be noted up to temperature levels fixed at 905 and 980°C, respectively. It corresponds to a reduction state of the superconducting oxide. On the isotherms, the potential decreases until it asymptotically reaches constant values. This potential decrease at 905 and 980°C corresponds to a return to the equilibrium associated with the fixing of oxygen by the superconducting oxide. The 905°C phenomenon corresponds to an oxygen chemical potential which is greater in the gas phase than in the condensed one; it is the opposite at 980°C. On cooling, the reverse reaction of that observed on heating (and stopped since the isothermal treatment started) occurs; it corresponds to the fixing of oxygen by the superconducting oxide. The potential measurement results confirm those of thermogravimetric analysis and follow the reversible transfer of oxygen; thus, it is possible to differentiate the PbO loss from the O_2 mass variations.

A study was carried out under the same conductions for the superconducting oxide Pb2223 at the 905 and 980°C isotherms (Figs 4a and 4b). The phenomena were similar, but this time the oxygen exchange was more visible. A very small oxygen pressure variation induces a large mass variation. An X-ray diffraction study for both the 905 and the 980°C isotherms permitted characterization of the crystallized solid phases corresponding to the compositions of the Pb2212 and

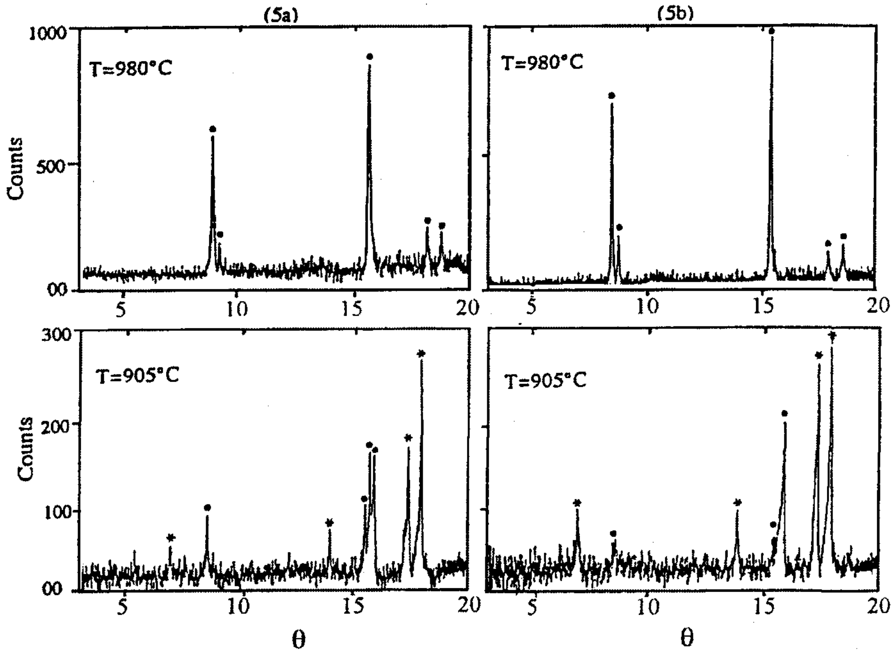

Fig. 5 X-ray diffraction diagrams of the mixtures corresponding to the composition of Pb2212 (a) and Pb2223 (b) under P_{O_2}/P_{Tot}=0.21 at 905 and 980°C. * $(Sr_xCa_{1-x})_2CuO_{3\pm\varepsilon}$, and • $(Sr_xCa_{1-x})_2PbO_{4\pm\delta}$

Pb2223 mixtures (Figs 5a and 5b). Between the 905 and 980°C isotherms, the phase $(Sr_xCa_{1-x})_2CuO_{3\pm\varepsilon}$ disappears and the phase $(Sr_xCa_{1-x})_2PbO_{4\pm\delta}$ increases. At both temperatures, crystallized phases are in equilibrium with the liquid phase [9].

Conclusion

The partial oxygen pressure variation as a function of temperature, $P_{O_2}(T)$, was followed in a monovariant path of the system Bi–Pb–Sr–Ca–Cu–O, using an oxygen zirconia probe.

The results confirmed that the oxygen stoichiometry variation in the superconducting phases Pb2212 and Pb2223 is a reversible phenomenon on heating and cooling. The mass losses of Pb2212 and Pb2223 mixtures at the 980°C isotherm are due to the oxygen stoichiometry variations and to PbO evaporation (this latter phenomenon being irreversible).

For the Pb2223 mixture, we observed that a very small oxygen pressure variation induces a large mass variation.

At the 905°C isotherm, X-ray diffraction revealed the occurrence of the phases $(Sr_xCa_{1-x})_2CuO_{3\pm\varepsilon}$ and $(Sr_xCa_{1-x})_2PbO_{4\pm\delta}$, but at 980°C only $(Sr_xCa_{1-x})_2PbO_{4\pm\delta}$ was observed.

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