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PHASE DIAGRAM IN THE Bi–Pb–Sr–Ca–Cu–O SYSTEM Buffer effect of non-superconducting phases on oxygen exchange of the superconducting ones

A. Sebaoun[1], *P. Satre*[1], *M. Mansori*[1,2] *and A. L'Honore*[1]

[1]Matériaux à Finalité Spécifique, Laboratoire de Physico-Chimie des Matériaux et du Milieu Marin, E. A. 1356, Université de Toulon-Var B. P. 132, 83957 La Garde cedex, France
[2]Laboratoire de Physico-Chimie des Matériaux, Université Chouaib Doukkali, B.P. 20, El Jadida, Maroc

Abstract

TG-DTA and X-ray diffraction measurements at different temperatures and under different oxygen partial pressures were carried out on the species $Bi_{1.6}Pb_{0.4}Sr_2CuO_{6\pm x}$, $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8\pm y}$ and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10\pm z}$ to analyse the influence of the oxygen chemical potential on the phase transformations. A new phase was found at isobaric invariant equilibrium for $0.5\leq P_{O_2}/P_{Tot}\leq 1$ at 884°C. This new phase presents a buffer effect towards oxygen exchange between superconducting oxides and the gas phase.

Keywords: Bi–Pb–Sr–Ca–Cu–O system, buffer effect, phase transformations

Introduction

This work comprises part of a large study on phase equilibria in the Bi–Pb–Sr–Ca–Cu–O system and more precisely on the isoplethic cut corresponding to the formula $Bi_{1.6}Pb_{0.4}Sr_2Ca_{n-1}Cu_nO_{2n+4\pm\delta}$ with $1\leq n\rightarrow\infty$ (Fig. 1) [1–4]. The well-defined and reproducible stoichiometry afforded by the soft method synthesis permitted the observation of reversible quantitative oxygen exchange between the condensed and gas phases both on heating and on cooling [5, 6]. We have also studied oxygen isothermal evaporation and condensation at different temperatures and under different oxygen chemical potentials of the gas phase. For the species Pb2212* and Pb2223** under different constraing oxygen partial pressures, DTA revealed an isobaric invariant for P_{Tot}=1013 hPa at 884°C for $0.5\leq P_{O_2}/P_{Tot}\leq 1$ [7].

In the present work, we have studied the temperature variations of the phase transformations as a function of constraint oxygen partial pressure. We have delimited monovariant fields and identified phases in equilibrium by means of X-ray diffraction. In the same way, we have characterized an additional new phase at the invariant equilibrium. The influence of this phase on the oxygen exchange between

* Pb2212=$Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8\pm y}$

**Pb2223=$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10\pm z}$

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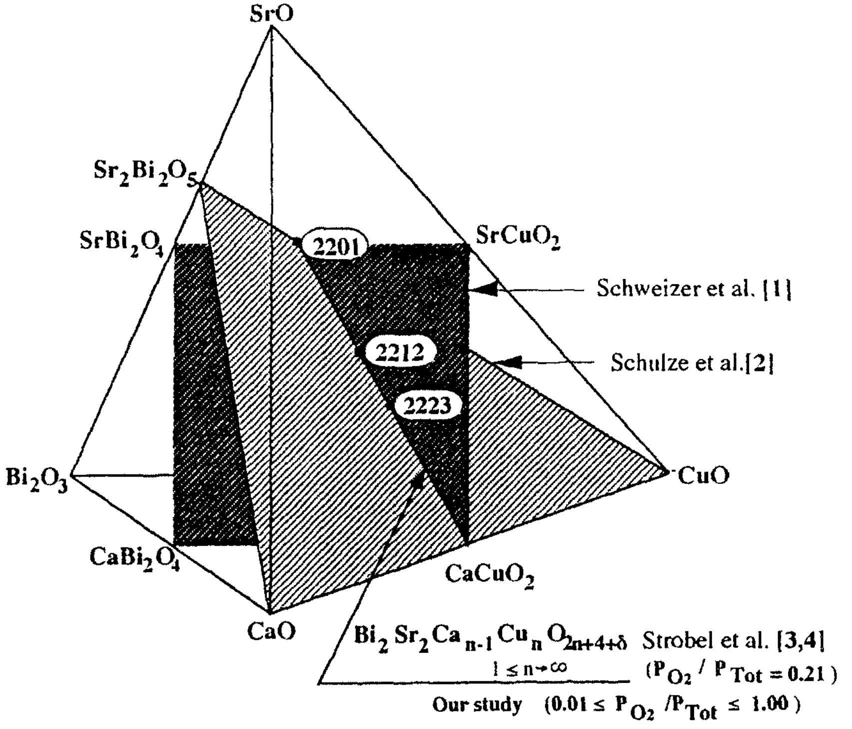


Fig. 1 $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4\pm\delta}$ (with $1 \leq n \to \infty$) isoplethic cut in the Bi_2O_3–SrO–CaO–CuO tetrahedron

the superconducting phases and the gas phase, both on heating and on cooling, has been studied.

Experiments

Setaram TG-DTA 92 equipment was used to determine phase transformation temperatures as a function of the oxygen chemical potential of the gas phase (by fixing different oxygen/helium ratios with ROSEMOUNT BROOKS 5850TR flow-regulators). The constant total pressure was 1013±15 hPa and the heating rate was 10°C min^{-1}. Phase characterization at the equilibrium temperature was performed by means of X-ray diffraction with the same oxygen chemical potential conditions in the gas phase, by using a PW 1050 Philips goniometer equipped with a high-temperature ANTON PAAR HTK10 camera. The temperature of this furnace was standardized by the method of Brown *et al.* [8]. The reproducibility thus obtained for the annealing temperatures was ±1°C. XRD was performed both for the powder resulting from the grinding of the pellets, and for the surface of the annealed pellets. The X-ray radiation used was CuK_α. The diffractograms were plotted from $2\theta = 3.5°$ to 40°.

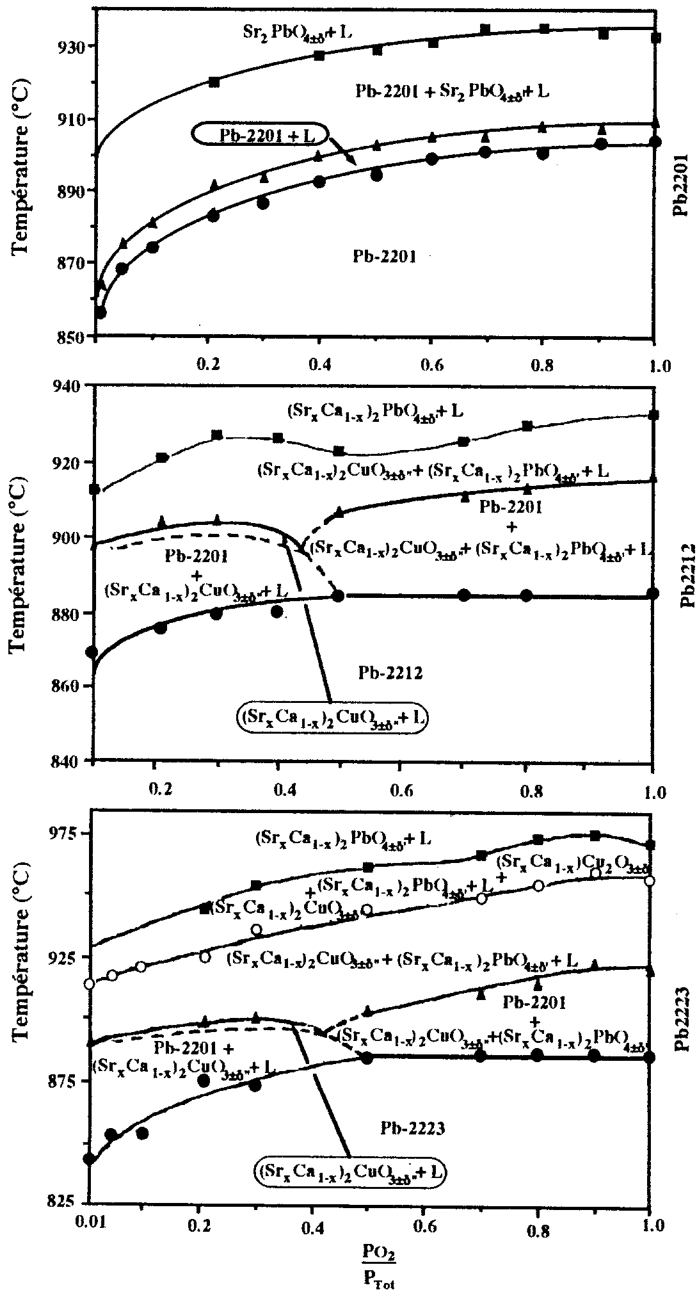


Fig. 2 T *vs.* P_{O_2}/P_{Tot} coordinate phase diagram of: a) Pb2201, b) Pb2212 and c) Pb2223. Here, the $[(Sr_xCa_{1-x})_2CuO_{3\pm\delta'}+L]$ field was not observed experimentally. Dotted lines are plotted with respect to the Palatnik and Landau rules [10]

Results

The diagrams established by using TG-DTA and X-ray results for Pb2201, Pb2212 and Pb2223 species under different constraint oxygen partial pressures ($0.01 \leq P_{O_2}/P_{Tot} \leq 1$) are presented in Fig. 2. Monovariant fields can be observed adjoining an isobaric invariant at 884°C and for $0.5 \leq P_{O_2}/P_{Tot} \leq 1$, for the superconducting species Pb2212 and Pb2223. For the species Pb2201, we have not observed such an invariant equilibrium. The main thermodynamic constraint is the conformity to the phase rule, which imposes a limit to the number of phases present in different parts of the diagram [9]. Note that the cut considered here is not a true quasi-binary diagram: the compositions of the stable phases are not expected, in general,

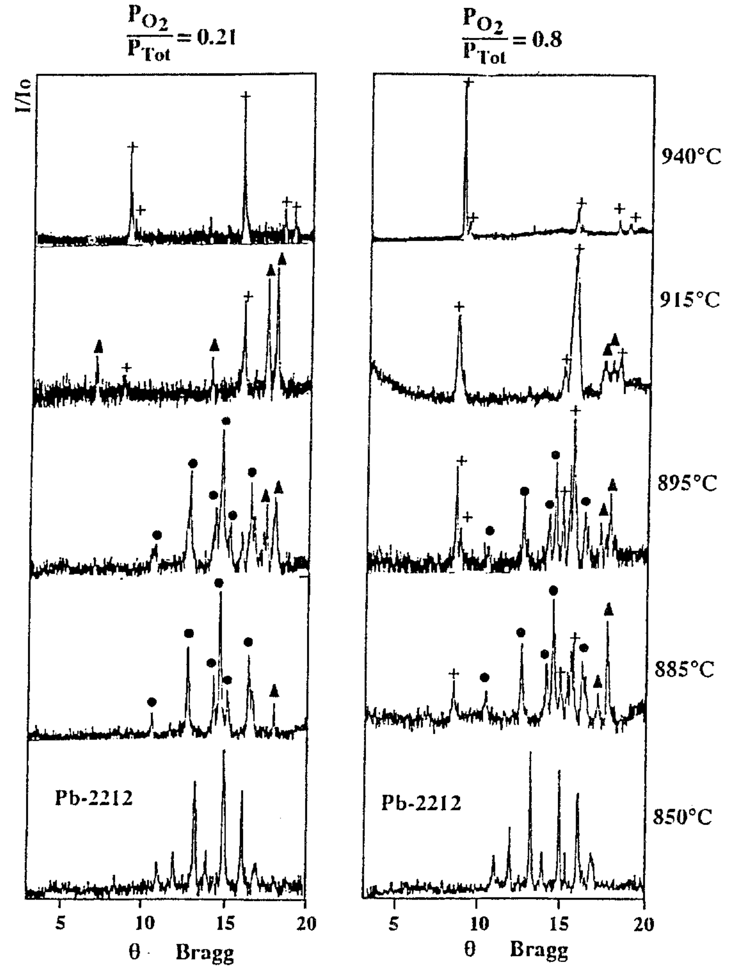


Fig. 3a Comparison of XRD results at different temperatures for the species Pb2212 for $P_{O_2}/P_{Tot}=0.21$ and 0.8; (•) Pb2201, (▲) $(Sr_xCa_{1-x})_2CuO_{3\pm\delta''}$ and (+) $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$

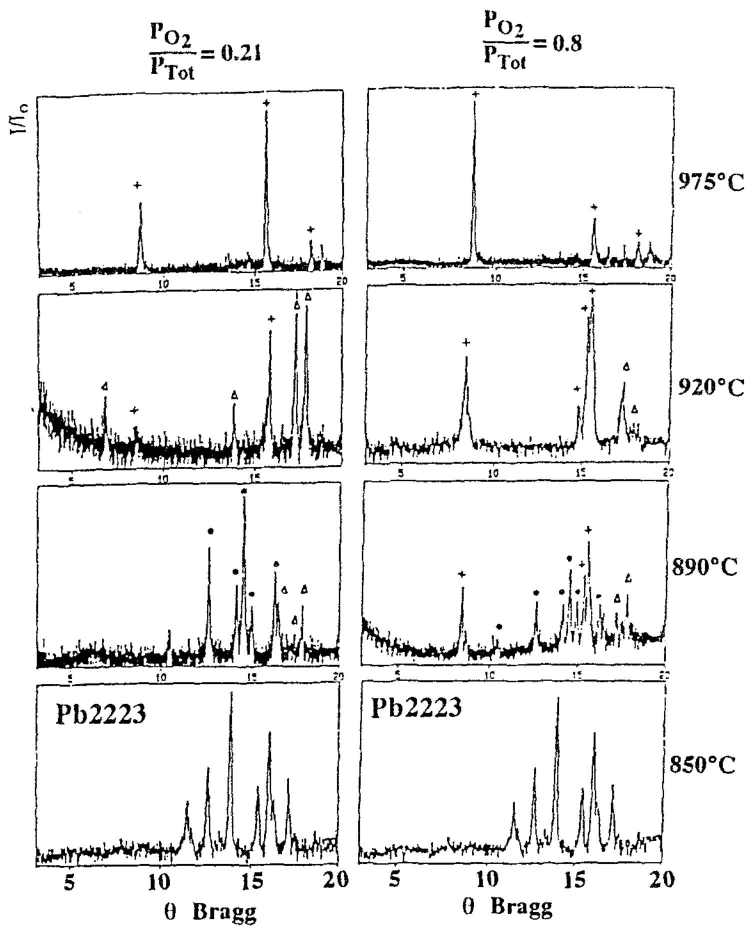


Fig. 3b Comparison of XRD results at different temperatures for the species Pb2223 for P_{O_2}/P_{Tot}=0.21 and 0.8; (•) Pb2201, (▵) $(Sr_xCa_{1-x})_2CuO_{3\pm\delta''}$ and (+) $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$

to be combinations of the nominal compositions of the two end-compounds, $Bi_{1.6}Pb_{0.4}Sr_2CuO_{6\pm x}$ and $CaCuO_2$. Isobaric invariant transformation implies an additional phase, which corresponds to the solid solution $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$ according to the characterization. The presence of solid solution $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$ shows that lead must be regarded as an independent component and not merely as an isomorphous bismuth-substituted constituent [4, 11–16].

Phase characterization demonstrates that the species Pb2212 and Pb2223 undergo incongruent melting. In addition, not all the phases in equilibrium have a constraint ratio Bi/Sr=1 and Bi/Pb=4. Some X-ray data at different temperatures for P_{O_2}/P_{Tot}=0.21 (through the monovariant boundary) and P_{O_2}/P_{Tot}=0.8 (through the invariant boundary) are presented in Figs 3a and 3b for Pb2212 and Pb2223, respectively. It is seen that solid solution $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$ appears at the invariant temperature equilibrium and above, and becomes the main phase at temperatures higher than 915°C. The phase diagram appears to involve a six-component system with fixed external conditions: constant total pressure and oxygen chemical potential (μ_{O_2}). The stabilities of the different phases were studied in their different equilibrium fields after annealing by X-ray diffraction directly in the HTK camera. From this, we observed that Pb2223 is stable during more than one month in the interval from 835°C to ambient temperature. This is exemplified in Fig. 4, where XRD shows the stability of the Pb2223 phase at 800°C and for P_{O_2}/P_{Tot} =0.21.

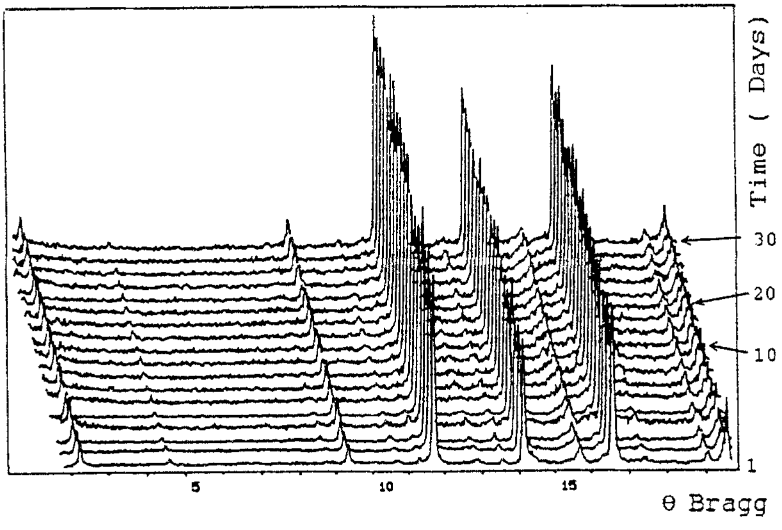


Fig. 4 X-ray diffraction at 800°C and P_{O_2}/P_{Tot}=0.21 for different annealing times for the species Pb2223

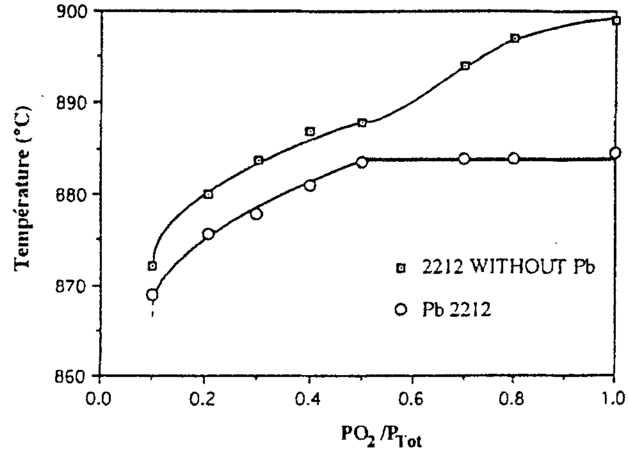


Fig. 5 Influence of constraint oxygen pressure on the first phase transformation observed on heating for Pb2212 and 2212 (without Pb)

Buffer effect of solid solution $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$

Figure 5 shows the influence of the constraint oxygen partial pressure on the first 'onset' temperature phase transformation of Pb2212 and 2212 (without lead) on heating. For Pb2212 the invariant reaction appears at 884°C for $0.5 \leq P_{O_2}/P_{Tot} \leq 1$, while without lead, only a monovariant transformation is observed. Figure 6 corresponds to TG-DTG-DTA under the partial constraint oxygen pressure $P_{O_2}/P_{Tot}=0.8$ for Pb2212 and 2212 (without lead). In Figure 6a, the DTG curve (dotted line corresponding to matter flow) for Pb2212 reveals the existence of two small mass losses ($\Delta m'$ and $\Delta m''$, quantified in Fig. 7), associated with the same endothermic heat flow peak and with an interruption of the mass loss, while for 2212 without lead (Fig. 6b), we do not observe the buffer effect toward oxygen exchange, and the mass loss becomes more important. This result is in good agreement with the appearance, above 884°C, of the solid solution $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$, observed by XRD (Figs 3a and 3b).

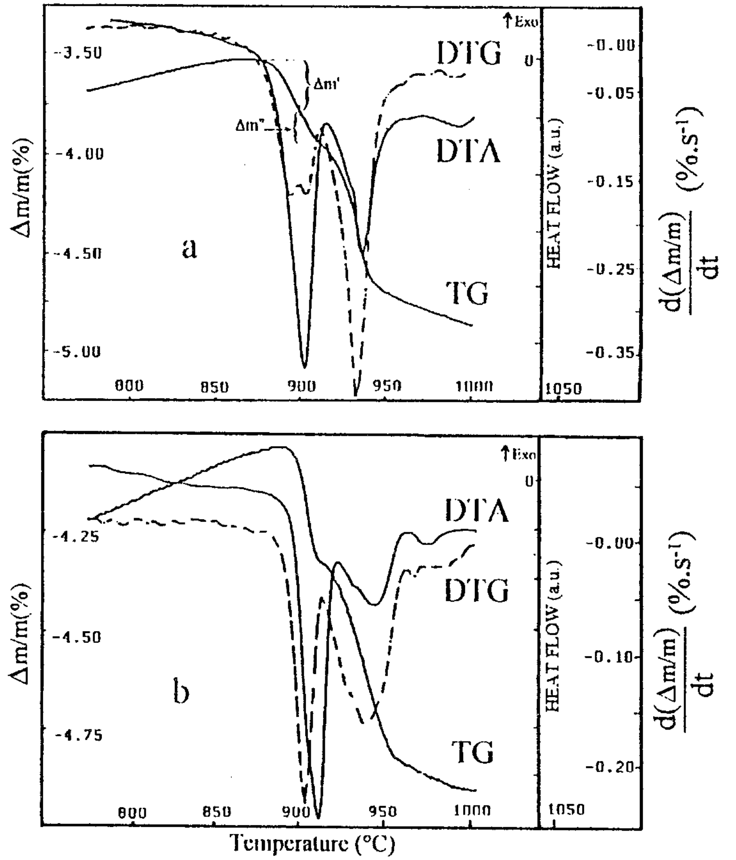


Fig. 6 Comparison of TG–DTG–DTA curves under $P_{O_2}/P_{Tot}=0.8$ for Pb2212 (a) and 2212 without Pb (b)

Figure 7 shows the buffer effect associated with the additional phase at the invariant equilibrium temperature. When $0.01 \le P_{O_2}/P_{Tot} \le 0.5$, the solid solution

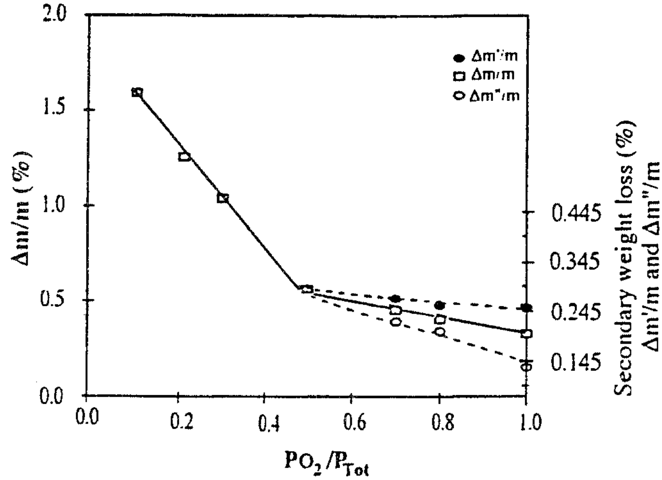


Fig. 7 Mass loss observed in TG curves under different P_{O_2}/P_{Tot} for the first phase transformation ($\Delta m/m = \Delta m'/m + \Delta m''/m$ for $0.5 \le P_{O_2}/P_{Tot} \le 1$)

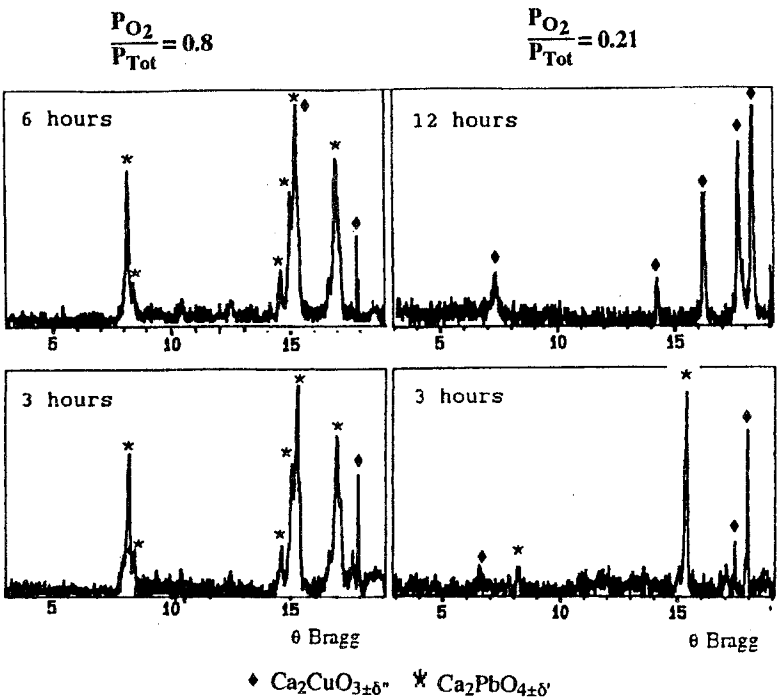
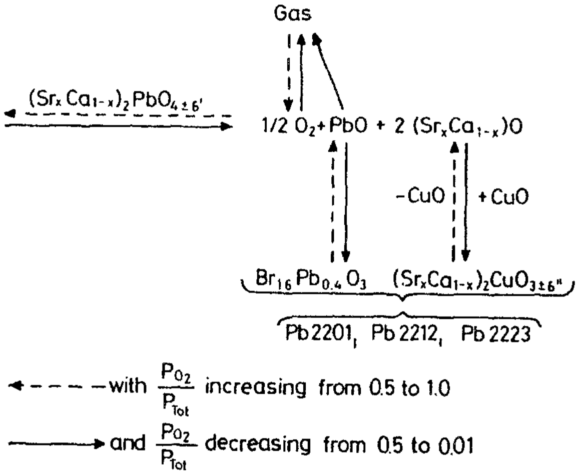


Fig. 8 XRD of oxide mixture CaO–PbO–CuO under P_{O_2}/P_{Tot}=0.21 and 0.8

$(Sr_xCa_{1-x})2PbO_{4\pm\delta'}$ does not exist, and there is no buffer effect. When $0.5\leq P_{O_2}/P_{Tot}\leq 1$, a buffer effect and a solid solution $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$ are observed. To confirm that the species $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$ has a buffer effect toward oxygen exchange, we synthesized an oxide mixture CaO–PbO–CuO and studied the influence of oxygen partial pressure P_{O_2} on this mixture at 884°C. Figure 8 shows that the X-ray peak intensities of the species $Ca_2PbO_{4\pm\delta'}$ decrease as P_{O_2}/P_{Tot} decreases and increase as P_{O_2}/P_{Tot} increases. For the species $Ca_2CuO_{3\pm\delta''}$ an opposite effect is observed.

Conclusions

The incongruent melting of the species Pb2212 and Pb2223 produces liquid and crystalline phases. The number and nature of these phases depend on the oxygen chemical potential of the gas phase. When the oxygen partial pressure $P_{O_2}/P_{Tot}<0.5$, the liquid is in equilibrium with Pb2201 and $(Sr_xCa_{1-x})_2CuO_{3\pm\delta''}$. The oxygen and $PbO_{(g)}$ mass losses are buffered by $(Sr_xCa_{1-x})_2PbO_{4\pm\delta'}$ formation. This additional phase appears in the invariant reaction and seems to fix the oxygen excess when $0.5\leq P_{O_2}/P_{Tot}\leq 1$, and to give oxygen and PbO when $P_{O_2}/P_{Tot}<0.5$. This buffering mechanism could be schematized by the following hypothetical overall reaction:



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References

1 T. Schweizer, R. Müller, P. Bohac and L. J. Gaukler, Proc. 2nd International Céram. Sci. and Technology Congress, Orlando, FL., 12–15, Novembre 1990.
2 K. Schulze, P. Majewski, B. Hettich and G. Petzow, Z. Metallk., 81 (1990) 836.

3 P. Strobel and T. Fournier, J. Less-Common Met., 164 –165 (1990) 519.
4 P. Strobel, J. C. Toledano, D. Morin, J.Schneck, G. Vacquier, O. Nonnereau, J. Primot and T. Fournier, Physica C, 201 (1992) 27.
5 M. Mansori, P. Satre, C. Breandon, M. Roubin and A. Sebaoun, Ann. Chim. Fr., 18 (1993) 537.
6 P. Satre and A. Sebaoun, J. Thermal Anal., 41 (1994) 211 (in French).
7 P. Satre, A. Sebaoun, O. Monnereau and G. Vacquier, J. Phys. III Fr., 4 (1994) 261.
8 N. E. Brown, S. M. Swapp, C. L. Bennett and A. Navrotsky, J. Appl. Cryst., 26 (1993) 77.
9 J. W. Gibbs, on the Equilibrium of Heterogeneous Substances. Transactions of the Connecticut Academy, III, (May 1877–July 1878) 343–524.
10 L. S. Palatnik and A. I. Landau, Phase Equilibria in Multicomponent System, publishe by Holt, Rinehart and Winston, New York 1964, p. 342.
11 S. Bansal, T. K. Bansal, A. K. Jha and R. G. Mendiratta, Physica C, 173 (1991) 260.
12 G. Gritzner and K. Bernhard, Physica C, 181 (1991) 201.
13 M. Takano, J. Takada, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda, Y. Tomii and H. Mazaki, Jpn. J. Appl. Phys., 27 (1988) L1041.
14 S. Kuyama, U. Endo and T. Kawai, Jpn. J. Appl. Phys., 27 (1988) L1861.
15 J. Schneck, J. C. Toledano, L. Pierre, A. Lizler, D. Morin, J. Primot, H. Savary and C. Daguet, J. Less. Comm. Metals, 164–165 (1990) 545.
16 G. Jakob, M. Huth, T. Becherer, M. Schmitt, H. Spille and H Adrian, Physica B, 165–166 (1990) 1677.