Mendeleev Commun., 2004, 14(4), 181–182

Internal oxidation in $Bi_{2.1-x}Pb_xSr_{2-y}Ca_{1-z}Y_{y+z}Cu_2O_{8+d}$ solid solutions

Alexander V. Knotko,*[a] Alexey V. Garshev,[b] Maksim N. Pulkin,[b] Denis I. Kirdyankin,[b] Andrei V. Geyer,[a] Valery I. Putlayev[a] and Ru-Shi Liu[c]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation.*
Fax: +7 095 939 0998; e-mail: knotko@inorg.chem.msu.ru
[b] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation*
[c] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan*

DOI: 10.1070/MC2004v014n04ABEH001977

The $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+d}$ solid solutions with the replacement of Sr or Ca by Y were prepared at 760–790 °C in a flow of nitrogen, oxidised in air under isothermal conditions and tested using XRD, TGA, chemical analysis, TEM and XANES.

The internal oxidation of $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) solid solutions coupled with the formation of fine precipitates in the bulk is a promising way to prepare nanocomposite materials (superconductive matrix – nonconductive inclusion) with improved critical current density. To control the oxidation process, one can carry out certain substitution in the cation sites of Bi-2212, *e.g.*, the replacement of Bi by Pb and of Ca (or Sr) by rare-earth elements (RE).

Samples of $Bi_{2.1-x}Pb_xSr_{2-q}Ca_{1-y}Y_yCu_2O_{8+d}$ solid solutions were prepared by a conventional nitrate route, *i.e.*, a nitrate mixture after evaporation of acidic solutions with adequate stoichiometry was calcined at 700 °C for 15–20 min in air followed by annealing at 760 °C in a nitrogen flow for 24–48 h or at 850 °C in air depending on RE content. Phase composition was examined by X-ray diffraction (DRON-3M, Russia) using $CuK_{\alpha m}$ radiation.

Oxidation kinetics was studied by thermogravimetrical analysis (TGA) (MOM Q-1500D, Hungary) under isothermal annealing in air at 650–750 °C up to 24 h long. The microstructure of the oxidised solutions was examined by transmission electron microscopy (TEM) (JEM-2000FXII, JEOL, Japan, operated at 200 kV). The fine structure of near-edge area of X-ray absorption band (XANES) was revealed using the facilities of a synchrotron source at Taiwan National Center of Synchrotron Research. The amount of an excessive oxidant (assuming O^{2-}, Cu^{2+}, Bi^{3+} and Pb^{2+} formal charges) was assessed by iodometric titration.[1] Briefly, a sample (*ca*. 50 mg) was placed in an aqueous KI solution and dissolved by adding several drops of concentrated HCl. The I_3^- ions were liberated in the reactions

$$2Cu^{2+} + 5I^- = 2CuI + I_3^-,$$
$$Cu^{3+} + 4I^- = CuI + I_3^-,$$
$$Bi^{5+} + 3I^- = Bi^{3+} + I_3^-,$$
$$Pb^{4+} + 3I^- = Pb^{2+} + I_3^-,$$

The solution was treated with a standard $Na_2S_2O_3$ solution to determine the total equivalent of $Cu^{3+} + Cu^{2+} + Bi^{5+} + Pb^{4+}$. To determine the total amount of Cu^{2+} about 50 mg of a sample was dissolved in 2–3 ml of concentrated HCl and 10 ml of water. Thus prepared stock solution was boiled for 10 min for elimination of an excessive oxidant:

$$2Cu^{3+} + 2Cl^- = 2Cu^{2+} + Cl_2.$$

After cooling the stock solution to room temperature, a volume of an aqueous KI solution was added to the stock solution. Finally, the total amount of Cu was determined by iodometric titration.

According to the results of iodometric titration, the amount of an excessive oxidant in the as-synthesised solid solutions (*i.e.*, the overall amount of Cu^{3+}, Bi^{5+}, Pb^{4+} and O^-) increased with Pb content. At the same time, the content of oxygen drops with increasing Pb fraction in the solution. Note that the replacement of Ca by Y caused an opposite effect: the oxygen content increased with decreasing excessive oxidant amount (Figure 1). It is widely accepted to treat the amount of over-stoichiometric oxygen in such materials as a concentration of holes. Sometimes, the term 'hole' is loaded by the same meaning as charge carrier in the case of semiconductors. This is not strictly correct in our case since the conductivity of Bi-2212 has a metallic character; here, the term 'hole' should be regarded as an imperfection of the electronic structure of a certain ion. The situation described above is, in fact, a picture of the localization of holes leading to an increase in the formal charge of a corresponding ion. The concentration of such 'defects' is to be related to the position of the Fermi level in the zone structure of Bi-2212.

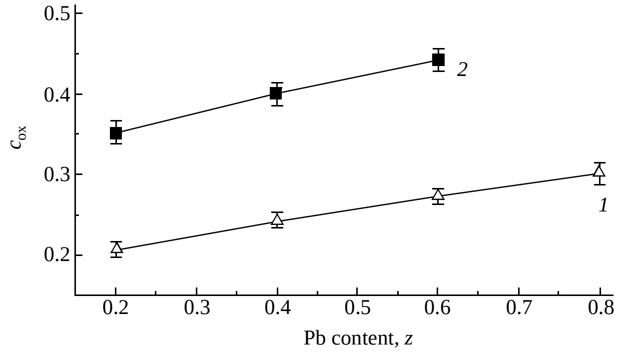

Figure 1 The amount of an excessive oxidant in $Bi_{2.1-x}Pb_xSr_2Ca_{1-y}Y_yCu_2O_{8+d}$, C_{ox}; (*1*) $y = 0.2$ and (*2*) $y = 0$.

Information on possible localization of holes in B-2212 was extracted from the fine structure of the O–K edge of absorption band (Figure 2; the pre-peak at 528 eV was attributed to the $3d^9L \rightarrow 1s3d^9$ transition, where L is the hole in the O $2p_{x,y}$ orbital.[2] It was found that the replacement of Bi by Pb did not cause an increase in the hole concentration in a $[CuO_2]$ layer, which is responsible for the superconducting properties of the material. The contradiction between the results of chemical analysis and XANES can be resolved taking into account the possibility of electron exchange between $[CuO_2]$ and $[Bi_2O_2]$ layers in the structure of Bi-2212. From the viewpoint of changing the formal charge of an atom, there is no preference in the localization of holes within the $[Bi_2O_2]$ layer, one can select both Bi and Pb, and also O atoms as special sites for it. However, bearing in mind the tendency of the Pb-doped solutions to oxidation in coupling with the precipitation of $Pb_3Sr_5CuO_{12}$ containing Pb^{4+} and a decrease in oxygen content per formula unit in Pb-doped samples, the formal charge of the Pb atom in the as-synthesised solid solutions is likely to be regarded as 2+. Thus, lead was excluded as a probable trap for holes.

TGA experiments on the oxidation of solid solutions with a low level of Pb doping (less than 0.4 Pb per formula unit) stated the presence of an incubation period in oxidation kinetics, as it was found earlier[3] for $Bi_2Sr_{2-x}Ca_{1-y}Pr_{x+y}Cu_2O_{8+d}$. The oxidation can be described as follows:

$$\begin{aligned} &Pb_xBi_{2-x}(Sr,Ca,Y)_3Cu_2O_8 + 0.5xO_2 \rightarrow \\ &[1 - 2x/(3-y)]Bi_2(Sr,Ca,Y)_3Cu_2O_8 + 0.5x/(3-y)Bi_2(Sr,Ca,Y)_3CuO_6 + \\ &\qquad x/(3-y)Pb_{3-y}Bi_y(Sr,Ca,Y)_5CuO_{10.5} + 2.5x/(3-y)CuO \end{aligned}$$

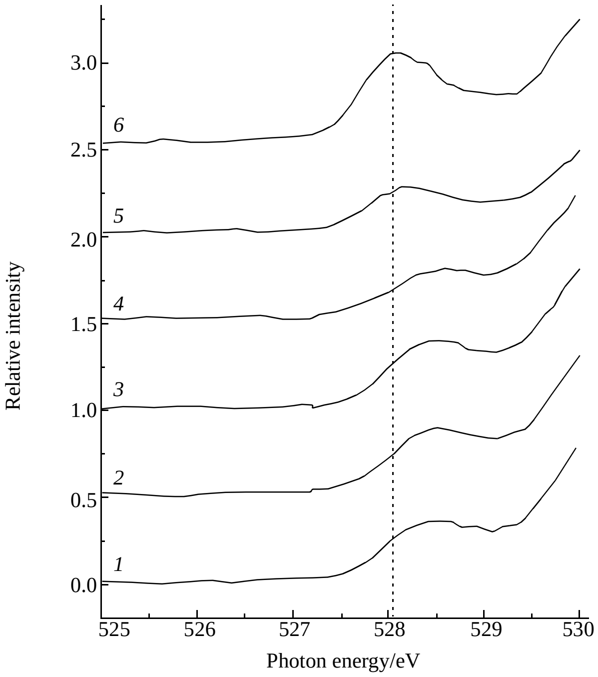

Figure 2 Fine structure of O–K edge in $Bi_{2.1-x}Pb_xSr_2Ca_{1-y}Y_yCu_2O_{8+d}$ solid solutions: (*1*) $x = y = 0$; (*2*) $x = 0.4$, $y = 0$; (*3*) $x = 0.8$, $y = 0.4$; (*4*) $x = 0.6$, $y = 0.4$; (*5*) $x = y = 0.4$ and (*6*) $x = 0.2$, $y = 0.4$.

The TEM examination of the samples revealed that the oxidation was accompanied by the precipitation of non-uniform inclusions in the bulk with the sizes up to 20 nm during the incubation period. The formation of the precipitates in the bulk without noticeable oxidation of the materials (according to TGA curves, Figure 3) is likely to be related to a cation rearrangement in the solid solutions followed by oxidation of a small fraction of Pb. Such a behaviour significantly differs from the oxidation of solutions with a high level of Pb doping described earlier,[4] where the oxidation proceeded in an internal mode due to fast oxygen diffusion. The features of the above oxidation can be deduced from difference in the chemical potentials of oxygen in the solid solutions and in air. This difference is larger for the solid solutions with the high level of Pb doping (they were prepared at $p_{O_2} = 10^{-3}$ atm, and the preparation temperature exceeded the temperature of oxidation by less than 100 °C) compared to the solutions with low Pb contents ($p_{O_2} = 0.21$ atm and fabrication temperature exceeded the oxidation one by more than 100 °C). Thus, oxidation (treated here as the incorporation of oxygen from a vapour phase into the lattice of the solutions) is resolved only after decreasing of oxygen potential in the bulk due to demixing of the solid solution (probably, through the development of fluctuations) leading to the formation of inhomogeneities with a high oxygen content. The inhomogeneities accumulate a significant part of oxygen from the bulk. Therefore, the oxidation of such materials is described by a mechanism alternative to the mechanism of the internal reaction, which becomes possible after a sufficient increase in the oxygen pressure.

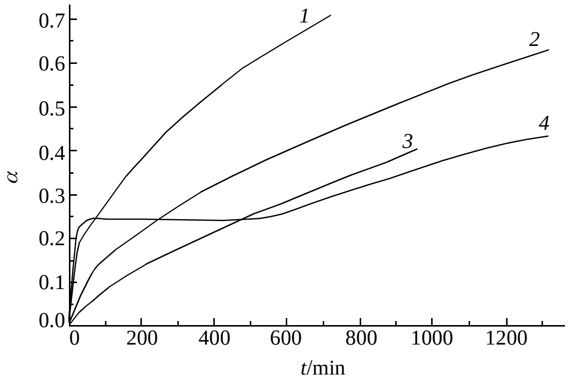

Figure 3 The kinetics of oxidation of $Bi_{2-x}Pb_xSr_2Ca_{1-y}Y_yCu_2O_{8+d}$ solid solutions at various temperatures (α is the transformation degree calculated assuming full oxidation $Pb^{2+} \rightarrow Pb^{4+}$): (*1*) $Pb_{0.6}Bi_{1.5}Sr_2CaCu_2O_z$ at 700 °C;[4] (*2*) $Pb_{0.8}Bi_{1.3}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_z$ at 700 °C; (*3*) $Pb_{0.8}Bi_{1.3}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_z$ at 650 °C and (*4*) $Pb_{0.6}Bi_{1.5}Sr_2CaCu_2O_z$ at 650 °C.[4]

This work was supported in part by the Russian Foundation for Basic Research (grant no. 02-03-33270a).

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Received: 4th June 2004; Com. 04/2302