Effects of simultaneous Pb/Bi and Y/Ca substitution on structural and superconducting properties of the 2212 BSCCO phase

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Abstract

By substituting Pb for Bi and Y for Ca in $Bi_2Sr_2CaCu_2O_8$, it is possible to prepare a $Bi_{2-x}Pb_xSr_2Y_{1-y}Ca_yCu_2O_z$ phase with a 2212–type structure that does not show structural modulation in a wide region of the phase diagram. In comparison with $Bi_2Sr_2CaCu_2O_8$ the non modulated phase exibits a larger orthorhombic distorsion and a different arrangements of the adjacent BiO layers. The vanishing of the structural modulation, which occurs in a similar way for any Ca/Y ratio by increasing the Pb content, involves changes in the modulation that are discussed in term of decrease of the oxygen content and adjustement of the structural mismatch which seem to play a role in different regions of the phase diagram. The non modulated $Bi_{2-x}Pb_xSr_2Y_{1-y}Ca_yCu_2O_z$ phase still shows superconductivity in the Ca–rich region with T_c decreasing with increasing the Y content, supplying a further example of superconductivity not related to structural modulation in BSCCO. The AF–SC transition in this system seems to be drived mostly by the Y/Ca ratio whereas the charge deriving from the Pb→Bi substitution seems to be accomodated mainly in the Bi(Pb)O layers through a partial oxydation of Pb^{2+} to Pb^{4+}. The existance of a similar mechanism has been confirmed by nitrogen annealing experiments showing a stabilizing effect of lead on the T_c.

1. Introduction

The origin of the modulation in the Bi–based high T_c superconductors (BSCCO) has been a subject of controversy for long time: for many authors it was due to the intercalation of extra oxygen within the BiO layers whereas others believed that it arises from the structural mismatch between the BiO layers and the perovskite blocks produced by the stereochemical requirements of bismuth, which in the idealized structure should have too long bond distances with the oxygen atoms. The presence of extra oxygen within the BiO layers, proposed [1,2] on the basis of high resolution electron microscopy (HREM) images, has been belived for long time to be the origin of the superconductivity in these systems. Several attempts, mostly based on single crystal X–ray diffraction data, to determine the real structure of the 2212 BSCCO phase were performed, utilizing both conventional three–dimensional approaches as well as the superspace symmetry formalism. The presence of extra oxygen was reported by some authors even if disagreement exists on the position and occupation of the extra oxygen atoms: in particular for the Y containing 2212 phase Torardi et al.[3] found extra oxygen in the BiO layer between adjacent BiO

ribbons whereas Tarascon et al.[4] found for $Bi_{10}Sr_{15}Fe_{10}O_{46}$, a compound with a fundamental structure similar to the 2212 BSCCO but with a different modulation symmetry, extra oxygen in the BiO ribbon (one for each modulation period) suggesting the presence of extra oxygen as origin of the modulation also in BSCCO. Petricek et al.[5] analyzed the 2212 BSCCO structure on the basis of the four–dimensional formalism and symmetry with results compatible with the existence of extra oxygen in a site similar to that found by Tarascon et al.[4]: whether the extra oxygen or the structural mismatch is the origin of the modulation remains however for the authors a subject for discussion. Other authors[6,7] found similar features of the displacive modulation without a clear evidence of extra oxygen in the BiO layers. The structural mismatch as origin of the modulation has been recently confirmed by the successful synthesis under argon of pure stoichiometric $Bi_2Sr_2CaCu_2O_8$ [8] which exhibits a T_c of 86K and shows an unidimensionally modulated structure with an almost commensurate period (p=4.91).

When Bi is partially replaced by Pb the 2212 structure is retained (the orthorhombic distorsion becomes larger)

but the structural modulation is strongly influenced: the modulation period increases (p>7), the symmetry of the modulation changes completely and the intensity of the satellite reflections decreases considerably indicating that the deviations of the local structure from the fundamental one become smaller [9–13]. In this optics the modulation is expected to vanish for larger Pb contents but unfortunately this cannot be proved since a limit in the substitution range (from 0.4 to 0.6 in the formula unit depending on authors) exists.

If the charge difference (Pb^{2+} substituted for Bi^{3+}) is responsible for the limit in the substitution range in BPSCCO, the substitution of Ca^{2+} with a trivalent cation is expected to increase the possible Pb content of the 2212 phase. Following this idea modulation–free 2212 BSCCO–type phases were recently produced [13–16] by simultaneous replacement of Bi by Pb and Ca by Y, but superconductivity was reported to be destroyed before the modulation. The structural properties of the non modulated semiconductor $BiPbSr_2YCu_2O_8$ were investigated by electron diffraction by Zandbergen et al.[15], which also investigated the variation of the structural modulation in the $Bi_{2-x}Pb_xSr_2YCu_2O_8$ samples. Tarascon et al. [17] reported the preparation of a series of 2201 compounds, $Bi_{2-x}Pb_xSr_{2-y}La_yCuO_z$, that do not show modulation for $x \approx y+0.2$ but still show superconductivity. The vanishing of the structural modulation was ascribed to the lack of extra oxygen within the Bi–O layers.

Very recently [18] we have investigated the Bi–Pb–Sr–Y–Ca–Cu–O system in order to establish the existence range of the 2212 phase and in particular to determine the variations produced by the simultaneous substitutions (Pb for Bi and Y for Ca) on its structure and superconducting properties. In this study the existence of a modulation free 2212 phase with a wide range of composition ($Bi_{2-x}Pb_xSr_2Y_{1-y}Ca_yCu_2O_z$, $0 \leq y \leq 0.8$ and $x=(1-y/2)\pm 0.2$) was pointed out by electron diffraction. The non modulated phase still shows superconductivity in the Ca–rich region, supplying a further example of superconductivity not related to structural modulation in BSCCO. We report here a detailed study of the effects of the substitutions on the structural and superconducting properties of in air prepared $Bi_{2-x}Pb_xSr_2Y_{1-y}Ca_yCu_2O_z$ phases. Moreover preliminary results on the effects of the annealing conditions on samples of the Ca rich region are presented and discussed.

2. Experimental

The samples have been prepared by solid state reactions starting from Bi_2O_3, PbO, Y_2O_3, CuO, $SrCO_3$ and $CaCO_3$ in the appropriate ratios required for an overall 2212 stoichiometry. The preparation of the samples was performed in air; a serie of compounds was subjected, after a preliminary resistivity measurement, to a post annealing in nitrogen in order to verify the effects of thermal tratments in a reducing atmosphere on the electrical properties.

The intimate mixtures were prereacted at 780–820°C depending on the composition (higher temperatures for higher Y contents) for 8 hours and then annealed (with intermediate grinding) at 860–920°C (depending on the composition) for periods ranging from 24 to 120 hours until the formation of a single 2212 phase or the coexistence of different phases was evidenced by X–ray powder diffraction. The highest temperatures and the longest heating periods were required by the Pb–free Y–containig samples owing to the inhomogeneity (Y and Ca rich regions) produced in the initial stage of the reaction. The annealing was prolonged in these cases until the linewidth of the 00l diffraction peaks (typically broadened for inhomogeneous samples) became comparable with that of the other reflections at similar diffraction angles.

The sample were characterized by X–ray powder diffraction by using an automatized Philips PW1050 powder diffractometer (CuKα radiation) after any step of the preparation procedure and of the successive thermal treatments in controlled atmosphere. The electron diffraction (ED) study was performed by using a Philips CM30 TEM operating at 300 KV. Powders were ground in an agate mortar, suspended in alcohol and deposited on holey carbon coated grids. For checking the homogeneity of the samples [001] patterns were recorded from about twenty crystals of each sample. Electrical resistivity measurements were performed by the DC four probe technique in the range 10–300K.

3. Results and discussion

3.1 Structural properties

It has been shown [18] that in a pseudoquaternary phase diagram involving $Bi_2Sr_2CaCu_2O_x$, $Bi_2Sr_2YCu_2O_x$

and the two phases resulting from a hypothetical complete replacement of Bi with Pb ($Pb_2Sr_2CaCu_2O_x$ and $Pb_2Sr_2YCu_2O_x$), the 2212 phase exists in a wide region characterized by high Bi contents (Fig. 1a). The Pb–rich region results on the contrary to be polyphasic at least in the studied temperature range.

The variation of the lattice parameters (choosen so that the a axis coincides with the principal modulational direction) makes however possible to divide the existence range of the 2212 phase in three structural regions characterized by a/b ratios lower than, close to and greater than one (O_1, O_2 and O_3 respectively). The O_1 structure is typical of $Bi_2Sr_2YCu_2O_x$ and characterizes the Y–rich region for low Pb content. O_3 is, in contrast, observed for the higher possible Pb content of 2212 phase independently from the Y/Ca ratio. The pseudotetragonal O_2 cell, similar to those of $Bi_2Sr_2CaCu_2O_x$, characterizes the central region of the 2212 existence range in the phase diagram. In reality this cell is orthorhombic but the difference between a and b is too small to be resolved by powder x–ray diffraction. Contrary to $Bi_{2-x}Pb_xSr_{2-y}La_yCuO_z$, for which the structural transition between the pseudotetragonal and the O_3 ($a<b$) phases seem to be discontinuous [17] in a relatively wide range of x ($\approx$0.3), in this case, all the structural transitions involved seems to be continuous or at least to show a narrow discontinuity range which could also be related to some sample inhomogeneity. The c lattice parameter decreases, as expected, with increasing Y content. However, for a fixed Y/Ca, ratio it remains almost independent from the Pb content, with the exception of the pure Y compounds for which c shows an initial progressive increase, on substituting Bi with Pb, up to $\approx$30.35A and than remains almost constant up to the upper limits of the Pb substitution.

Four different type of structural modulation have been found in this system by electron diffraction and are schematically represented in Fig. 2. $Bi_2Sr_2CaCu_2O_8$ shows a typical unidimensional modulated structure (type II in Fig. 2). The description of the diffraction spots requires four indexes according to the four–integer indexation scheme: all the reflections can be assigned on the basis of four integers and four vectors as $H=ha^*+kb^*+lc^*+mk=G+mk$ in wich G is any basic reciprocal lattice vector, a^*,b^*,c^* are the reciprocal
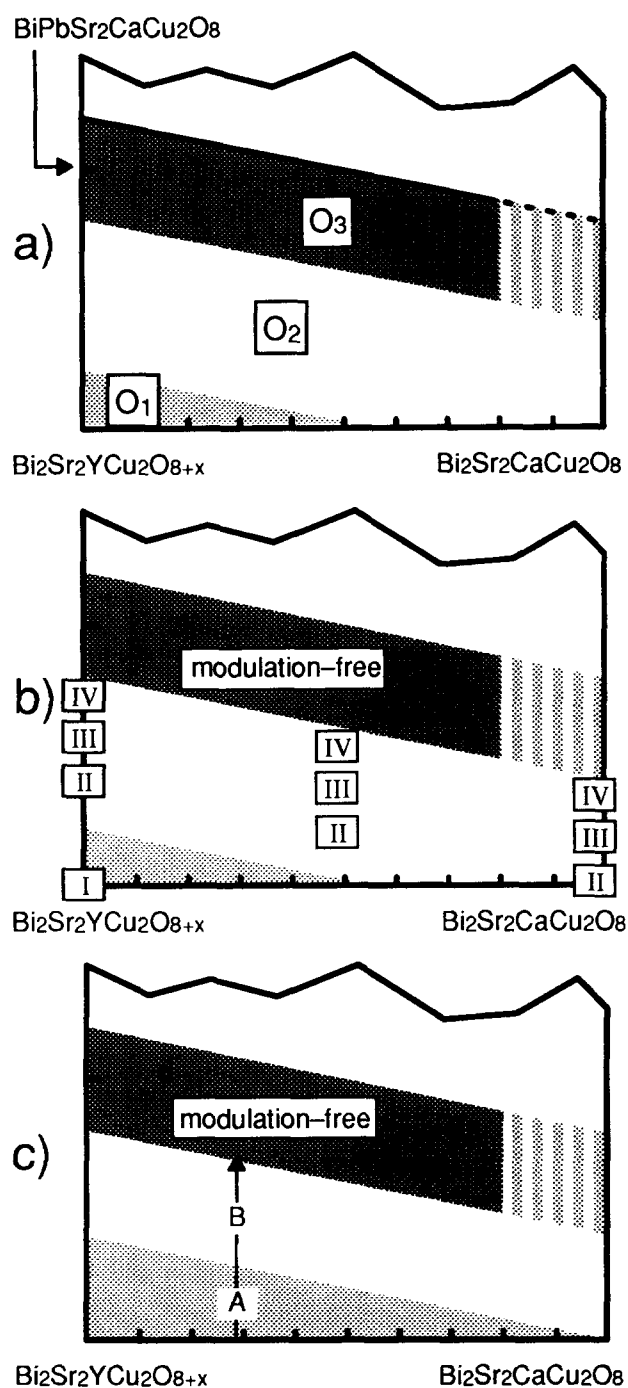

Figure 1: The 2212 phase in the $(Bi,Pb)Sr_2(Y,Ca)Cu_2O_z$ system: a) structural domains; b) evolution of the modulation c) regions A and B in which the evolution of the structural modulation seems to be determined by different effects (see text).

lattice unit vectors and k the modulation wave vector which can be expressed in this case as $k=(1/p)a^*$ with p, the modulation period, close to 5 (4.91 for pure stoichiometric $Bi_2Sr_2CaCu_2O_8$ [8]).

When Ca is substituted by Y the modulation period decreases progressively from 5 to 4 and a second wave vector, parallel to the b^* direction, appears for high Y

contents. The modulation become therefore bidimensional (type I in Fig. 2) and the description of the diffraction spots requires five indexes according to the five–integer indexation scheme: $H=ha^*+kb^*+lc^*+m_1k_1+m_2k_2$. The modulation wave vectors k_1 e k_2 can be expressed in this case as $k_1=(1/p_1)a^*$ and $k_2=(1/p_2)b^*$. For $Bi_2Sr_2YCu_2O_z$ p_1 and p_2 are close to 4 and 8.5 respectively.
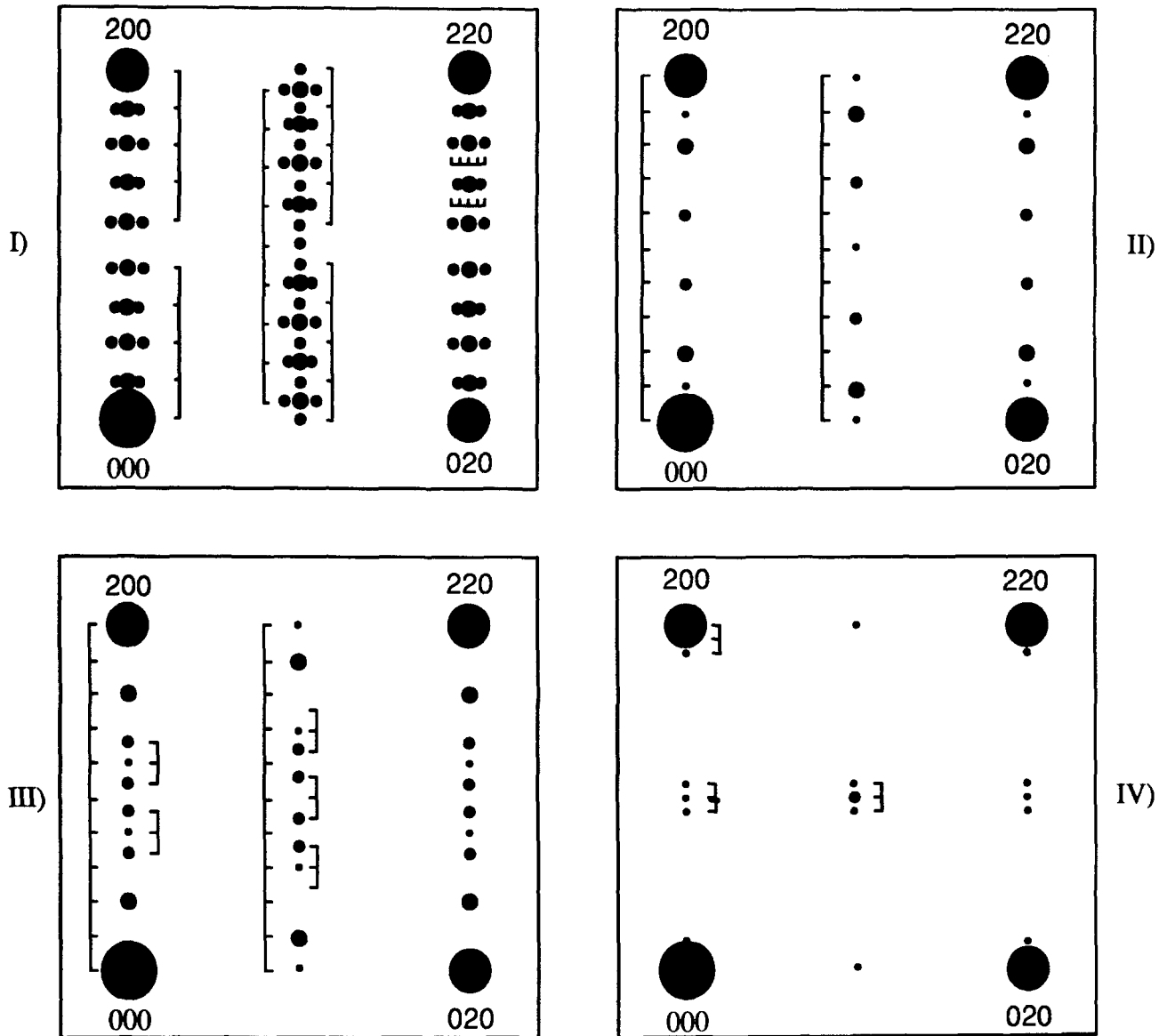

Figure 2: Schematic representation of the four principal type of modulation in the $(Bi,Pb)Sr_2(Y,Ca)Cu_2O_z$ system: I) bidimensional, $k_1=(1/p_1)a^*$ and $k_2=(1/p_2)b^*$, $p_1\approx4$–4.5, $p_2\approx8$–18; II) unidimensional, $k_1=(1/p)a^*$, $p\approx4.5$–5; III) bidimensional, $k_1=(1/p_1)a^*$ and $k_2=(1/p_2)a^*$, $p_1\approx5$, $p_2\approx7.5$; IV) unidimensional, $k_1=(1/p)a^*$, $p\approx7.5$->11.

The structural variation related to the Y→Ca substitution in the 2212 phase seems to be connected mostly with a progressive intercalation of extra oxygen in the BiO layers. In fact, whereas the difference in the Y and Ca atomic radii results in an almost linear decrease of c with increasing the Y content, the increase of the oxygen content can explaine both the decrease of p_1 as well as the appearing of a new modulation wave vector along b^*. In particular this last feature could be produced by the ordering along b of the extra oxygen located in the BiO plane by Torardi et al. [3] between adjacent Bi–O chains. This oxygen should be responsible also for the increasig of b in the Y–substituted phase.

The substitution of Pb for Bi in $Bi_{2-x}Pb_xSr_2YCu_2O_z$ produces an evolution of the structural modulation, which is connected with a progressive increase of the main modulation period and leads to the vanishing of the modulation. At $x=0.2$ both k_1 and k_2 show an increased modulation period ($p_1≈4.5$ and $p_2≈19.5$) but the modulation can be still classified as type I. By increasing x to 0.4, the modulation along b disappeares and only the type II modulation, with the typical $k_1≈(1/5)a^*$ wave vector of $Bi_2Sr_2CaCu_2O_8$, is observed. With respect to $Bi_2Sr_2CaCu_2O_z$, for which an A–centered foundamental lattice is generally accepted, the solid solution $Bi_{1.6}Pb_{0.4}Sr_2YCu_2O_z$ shows extra reflections indicating a lower symmetry with a primitive foundamental lattice. However, the presence of weak reflections indicating a lowering of the symmetry was also reported for $Bi_2Sr_2CaCu_2O_z$ [6,7].

For $x=0.6$ the modulation become complicated and requires two modulation wave vectors, this time both along the a^* direction; k_1 and k_2 are close to $(1/5)a^*$ and $(1/7.5)a^*$ respectively. However, the complicated systematic absences show that the diffraction pattern does not consist of superimposition of satellites related to two independent modulations, but that a new superstructure is formed (type III in Fig. 2). For $x>0.7$ the structure becomes unidimensionally modulated and the period increases quickly from 7.5 to 11 by increasung x (type IV). The intensity of the satellites becomes weaker and weaker and only few of them are visible in overexposed diffraction pattern whereas the intensity of the foundamental reflections $hk00$ with h and/or k odd becomes stronger. For $x>0.8$ and up to the 2212 stability limit the structure can be considered modulation–free.

The structure of the modulation–free phase has been determined by single crystal X–ray diffraction[18]. It is

essentially that found for $Bi_2Sr_2CaCu_2O_8$: in both structures the presence of the lone pair on Bi(Pb) atoms gives rise to an arrangement of short and long Bi–O bonds, which distorts the ideal stacking and forms ribbons along a. However, with respect to the foundamental structure of the 2212 BSCCO phase, the vanishing of the structural modulation involves a change of the symmetry: the skeletons of the –Bi–O– chains in adjacent BiO layers are in this case almost superimposed (with a small shift due to the different polarity of the ribbons) whereas in BSCCO they are mutually shifted by $a/2$. This structural variation seems to be connected with the changement of structural symmetry related to the transition to the type IV modulation.

The evolution of the structural modulation with increasing Pb content, that leads to the disappearing of the structural modulation, remains the same for any Y/Ca ratio in the system. The O_1 region is characterized by the two–dimensional type I modulation while in the O_2 region the type II modulation is progressively substituted, by increasing Pb content, by the type III and IV. The O_3 region seems on the contrary to be free from structural modulation at least for high Y contents.

The slope, which delimits in the phase diagram the modulation–free domain, seems to be a constant of the diagram; in fact it determines, beside the $O_2→O_3$ phase transition, the $O_1→O_2$ transition as well as the change, in period and symmetry, of the modulation in the O_2 region. The similarity of the structural evolution in the O_2 region suggests to divide the modulated region of the phase diagram in two zone (Fig. 1c): A extends from the binary $Bi_2Sr_2YCu_2O_x$–$Bi_2Sr_2CaCu_2O_8$ edge to the modulation of type II whit p close to 5; B ranges between A and the modulation–free region. The variation of the modulation in A seems to be mostly connected with the removal, by increasing Pb content, of the extra oxygen introduced by the Y→Ca substitution. The situation in the zone B is more complicated. Starting from the hypothesis that a type II modulation with a period close to 5 should correspond to 2212 phase with an oxygen stoichiometry close to eight, the further variation of the modulation could be produced either by a simple adjustement of the structural mismatch or by a further decrease of the oxygen content. It is however hardly credible, on the basis of stereochemical consideration, that the oxygen content of a 2212 phase could decrease much belove eight, as required in this hypothesis by high Pb contents. In fact in the modulation free phase Pb and Bi show only three short mutual

perpendicular bonds with oxygen and the decrease of the oxygen content implies necessarily a further reduction of their mean coordination number.

3.2 Superconducting properties

In the pseudobinary $Bi_2Sr_2Y_{1-y}Ca_yCu_2O_z$ system, which shows the AF↔SC transition at y≈0.4, the T_c shows an increase, with respect to BSCCO, at low Y content; the maximum of T_c, which should correspond to the optimun value of the carrier concentration in the CuO_2 planes, is observed for y≈0.8 [18–20]. Any modification of the Y/Ca ratio produces a variation of the carrier concentration, decreasing consequently the T_c; the Pb→Bi substitution in $Bi_2Sr_2Y_{0.2}Ca_{0.8}Cu_2O_z$ is therefore expected to produce a decrease of T_c. However, the T_c of air annealed $Bi_{2-x}Pb_xSr_2Y_{0.2}Ca_{0.8}Cu_2O_z$ samples are comparable for 0<x<0.6 and only at x=0.8 a small decrease of T_c has been reported [18]. Fig. 3 shows a comparison of the normalized resistivity curves for the x=0.0, 0.2 and 0.4 series.
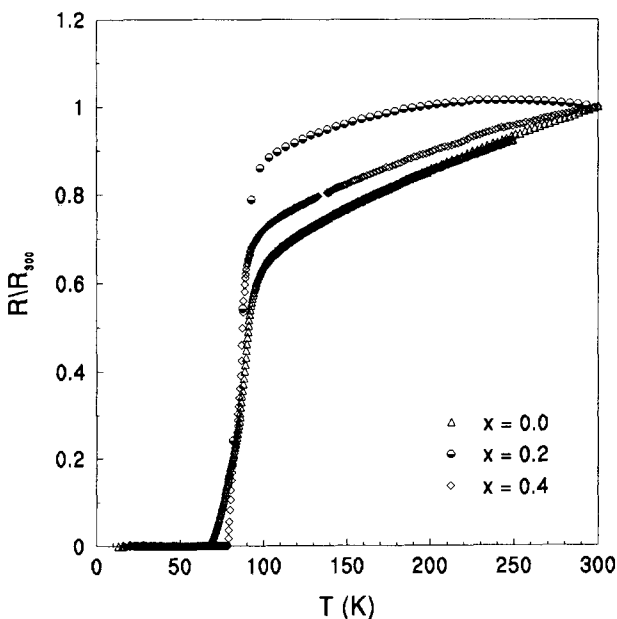

Figure 3: Normalized resistivity vs. temperature curves for as prepared $Bi_{2-x}Pb_xSr_2Y_{0.2}Ca_{0.8}Cu_2O_z$ samples

The behaviour of the superconducting properties with incresing the Pb content is similar in all the $Bi_{2-x}Pb_xSr_2Y_{1-y}Ca_yCu_2O_z$ system, where the AF–SC transition seems to be drived mostly by the Y→Ca substitution. In fact for the same Y/Ca ratio the T_c values of lead containing samples are comparable with those of

the corresponding Pb–free samples and decrease in a similar way with increasing the Y content. On the basis of these results the introduction of Pb in the Bi_2O_2 block seems to be not very effective in determining variation of the superconducting properties leading to the conclusion that the charge deriving from the Pb→Bi substitution seems to be accomodate mainly in the Bi(Pb)O layers.

The substitution of Bi^{3+} with Pb^{2+} is expected to decrease, if the oxygen content is retained, the charge in the block and consequently to increase the number of carriers into the CuO_2 planes. Consequently a first hypothesis that could explaine the superconducting behaviour of this system is the decrease of the oxygen content, which would compensate the charge difference introduced in the $(Bi,Pb)_2O_2$ blocks by the substitution. However, as discussed in the previous subsection concerning the structural properties, this hypothesis seems not to be acceptable in the whole exixtence range of the 2212 phase.

The oxygen non–stoichiometry is not the unic way in which the double (Bi, Pb)O layer could play a competitive role (with respect to the CuO_2 plane) in accomodating the extra charge deriving from the Pb→Bi substitution. An alternative mechanism could be represented by a partial oxydation of Pb^{2+} to Pb^{4+} which would compensate the nominal excess of oxygen in the structure deriving from the $Pb^{2+}→Bi^{3+}$ substitution. This mechanism, which does not involve a large deviation from eight in the oxygen content, could be the most influent factor in determining the structural and superconducting properties in the zone B of the phase diagram.

In order to better understand the particular behaviour of $Bi_{2-x}Pb_xSr_2Y_{0.2}Ca_{0.8}Cu_2O_z$, the samples with x=0.0, 0.2 and 0.4 were subjected to different thermal treatments. After the T_c measurement reported in Fig. 3, the samples were treated in flowing nitrogen at 500°C for 2 hours. In spite of the powder XRD analysis, which showed no significative variation in the diffraction pattern after the annealing, the electrical properties (Fig. 4) changed dramatically in some case. Whereas for x=0.4 the resistance curve shows (within 2K at the transition) the same behaviour, the other two samples are semiconductor in the normal state. For x=0.2 the superconducting transition becomes very wide, mantaining the same onset but showing zero resistance below 20K; for x=0.0 the transition is only hinted at very low temperature. The reversibility of the pheneomena was checked by a further heating of the pelletes for two hours in air at the same temperature. As previously no appreciable structural

changement was pointed out by XRD. The results of the resistivity measurements (Fig. 5) showed however unambiguously the reversibility of the process even if, for the previously most damaged sample, the kinetics seems to be slower.
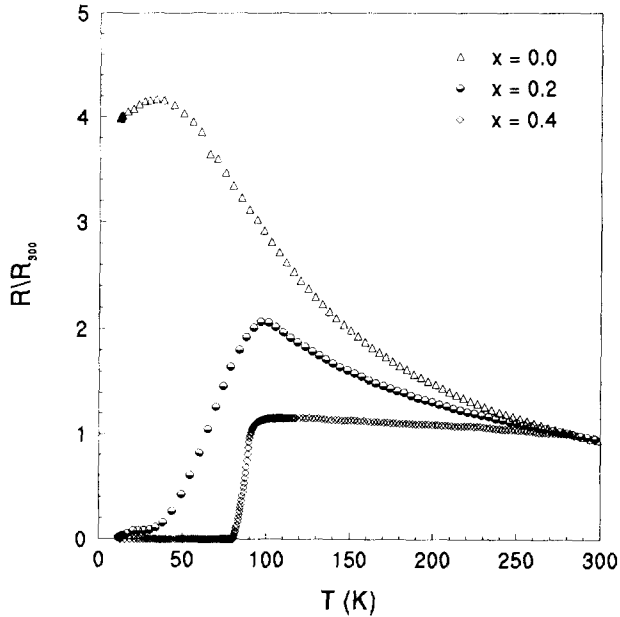

Figure 4: Normalized resistivity vs. temperature curves for $Bi_{2-x}Pb_xSr_2Y_{0.2}Ca_{0.8}Cu_2O_z$ samples post annealed for 2 hous in flowing nitrogen at 500°C.
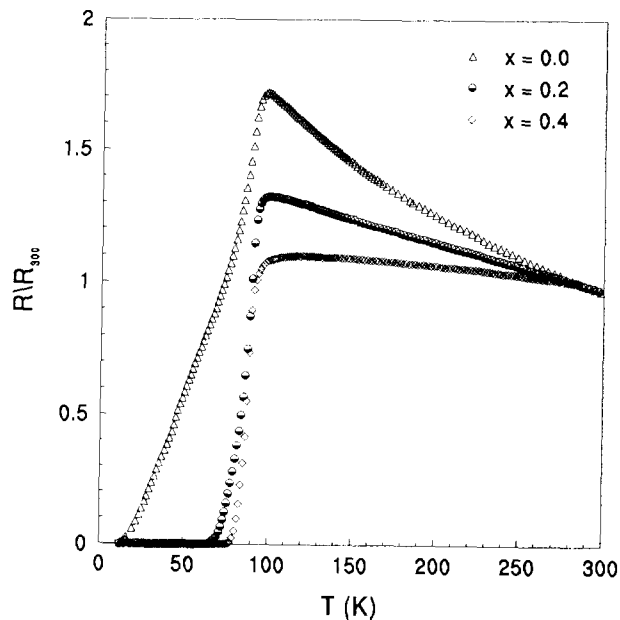
Figure 5: Normalized resistivity vs. temperature curves for $Bi_{2-x}Pb_xSr_2Y_{0.2}Ca_{0.8}Cu_2O_z$ samples after a further 2 hours annealing in air at 500°C.

This behaviour should be related to disintercalation of oxygen. In fact the cationic mobility at the utilized annealing temperature (500°C) is sufficiently low for preventing solid state rections or changes of the cationic distribution in the different sites; only oxygen shows at this temperature a sufficient mobility and consequently only a change in the oxygen stoichiometry could be expected from similar treatments. In the lead–free sample the expected decrease of the oxygen content produces a variation of the carrier density in the CuO_2 layers which acts dramatically on the T_c. On the other hand the addition of lead stabilizes the T_c. This clearly indicates either that the Pb→Bi substitution makes more difficult the oxygen depleeting or that the $Pb^{2+}\leftrightarrow Pb^{4+}$ equilibrium, previously hypotesized for justifying the similar electrical properties of sample with the same Y/Ca but different Pb/Bi ratios, is influenced by variations of the oxygen stoichiometry in a preferential way with respect to the charge transfer in the CuO_2 layers. This second hypothesis, which is based on a mechanism able to explaine the variation of both structural and superconducting properties in this system, seems to be more appropriate. A detailed study of the variation of the oxygen stoichiometry with the nitrogen annealing, which can provide a definitive confirmation, is in progress.

4. Conclusions

By substituting Pb for Bi and Y for Ca in $Bi_2Sr_2CaCu_2O_8$, it is possible to prepare a $Bi_{2-x}Pb_xSr_2Y_{1-y}Ca_yCu_2O_z$ phase with a 2212–type structure that does not show structural modulation in a wide region of the phase diagram. In comparison with $Bi_2Sr_2CaCu_2O_8$ the non modulated phase exibits a larger orthorhombic distorsion and a different arrangements of the Bi–O ribbons in adjacent BiO layers. A detailed analysis showed that the vanishing of the structural modulation occurs in a similar way for any Ca/Y ratio by increasing the Pb content and involves changes in the modulation that can be attributed at the beginning mostly to the removal of the extra oxygen introduced by the Y substitution and than mostly to the adjustement of the structural mismatch. The non modulated $Bi_{2-x}Pb_xSr_2Y_{1-y}Ca_yCu_2O_z$ phase still shows superconductivity in the Ca–rich region with T_c decreasing with increasing the Y content, supplying a further example of superconductivity not related to structural modulation in BSCCO. The AF–SC transition in

this system seems to be drived mostly by the Y/Ca ratio whereas the charge deriving from the Pb→Bi substitution seems to be accomodated mainly in the Bi(Pb)O layers through a partial oxydation of Pb^{2+} to Pb^{4+} as observed in lead cuprates. This seems to be confirmed by nitrogen annealing at relatively low temperature (500°C) showing a stabilizing effect of lead on the T_c. In lead free samples small variations of the oxygen content result in large, in some case dramatic, changes of T_c, whereas the addition of lead reduces progressively the T_c shift. This indicates that the previously hypotesized $Pb^{2+} \leftrightarrow Pb^{4+}$ equilibrium is influenced by variations of the oxygen stoichiometry in a preferential way with respect to the charge transfer in the CuO_2 layers. A detailed study of the variation of the oxygen stoichiometry with the annealing is necessary for a definitive description of the phenomenon.

5. Acknowledgments

5. References

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