Doping of Bi–Sr–Ca–Cu–O superconductors with Pb, Sn and Ag

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Abstract. Basic and substituted superconductors in the homologous series $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$, $\text{Bi}_{2-x/2}\text{Sr}_{2-x/2}\text{L}_x\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ and $\text{Bi}_2\text{Sr}_{2-x}\text{L}_x\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ ($\text{L} = \text{Sn}, \text{Pb}$ or Ag , $x = 0 - 0.4$, $n = 2, 3$ or 4) have been synthesized. All the prepared ceramic samples show superconducting behaviour with zero resistance at $T_c = 70$ to 85 K. The compounds with $n = 3$ or 4 showed onset temperature around 115 K indicating involvement of a disproportionate solid-state reaction and formation of a two-phase system. The phase involving tin or lead oxides showed similar superconducting properties. Final rapid quenching of samples contributed to preservation of the high temperature equilibria with higher solubility of tin oxide in the quaternary system Bi–Sr–Ca–Cu–O. Silver was not soluble but precipitated in a colloidal form at interfaces between the crystalline grains.

Keywords. Superconductors; Bi–Sr–Ca–Cu–O; doping.

1. Introduction

A typical structural feature of the high- T_c superconductors of the type $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$, $\text{Bi}_{2-x/2}\text{Sr}_{2-x/2}\text{L}_x\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ as well as $\text{Bi}_2\text{Sr}_{2-x}\text{L}_x\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ ($\text{L} = \text{Sn}$ or Pb , $x = 0 - 0.4$, $n = 2, 3$ or 4) is the layered arrangement, in which the lamella $\text{BiO-SrO-CuO}_z\text{-(Ca-CuO}_z\text{)}_{n-1}\text{-SrO-BiO}$ represents, in the first approximation, a stacking unit. In the sandwich arrangement, the double layers BiO-BiO close in n -parallel superconducting layers $\text{-CuO}_z\text{-}$. The $\text{-SrO-CuO}_z\text{-(Ca-CuO}_z\text{)}_{n-1}\text{-SrO-}$ slabs form a close packed perovskite-like sequence (Maeda *et al* 1988; Tarascon *et al* 1988; Gao *et al* 1988; Subramanian *et al* 1988). The bond strength between the two adjacent $(\text{BiO})_2$ layers is rather weak. The coordination of the Bi ion in the $(\text{BiO})_2$ double rocksalt type layer is 6. The actual structures in the homologous series $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ are incommensurate long-period modulated superstructures presumably induced by the extra oxygen atom in the BiO layers and by the misfit between the $(\text{BiO})_2$ rocksalt-like layers and the perovskite-like slabs. Modulation was found to consist of an almost sinusoidal displacement of the Bi and Sr atoms in the a and c directions of the unit cell and a similar displacement of the Cu atoms in the c direction only (Zandbergen *et al* 1988).

The superconducting transition temperature T_c increases with increasing number of $\text{-CuO}_z\text{-}$ layers in the sandwich stacking unit of the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ homologue, i.e. with increasing n value. Partial substitution performed with lead oxide in the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ homologue was found to support formation of the high- T_c phase (Takano *et al* 1988).

Since Sn ions show similar double valence fluctuation of the type $M^{n+} + 2\text{O}^{2-} \leftrightarrow M^{(n-2)+} + \text{O}_2^{2-}$, such as typical lead valence states, Pb^0 , Pb^{2+} and Pb^{4+} show (the stable valence states differ by two electrons), we tried to prove the partial substitution of the type $\text{Bi}_2\text{Sr}_{2-x}\text{Sn}_x\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ and $\text{Bi}_{2-x}\text{Sr}_{2-x}\text{Sn}_x\text{Ca}_{n-1}$

$\text{Cu}_n\text{O}_{2n+4+y}$ and its influence on the superconductive properties of the solid solutions. This work also aims at a comparison of the superconducting properties of the corresponding lead and tin solid solutions. We also tried to prove the role of the Ag ions in the system Bi-Sr-Sn(Pb)-Ca-Cu-O.

2. Experimental

The samples of nominal compositions of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$, $\text{Bi}_2\text{Sr}_{2-x}\text{L}_x\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ and $\text{Bi}_{2-x/2}\text{Sr}_{2-x/2}\text{L}_x\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ where $\text{L} = \text{Sn}$ or Pb , $n = 2, 3$ or 4 , $x = 0.4$, were prepared by solid-state reaction of the equivalent amounts of corresponding oxides (Bi_2O_3 , CuO , PbO_2 , SnO_2) and carbonates (CaCO_3 , SrCO_3). First, the homogenized mixture of oxides (without SnO_2 or PbO_2) and carbonates was decarbonated at $830\text{--}840^\circ\text{C}$ for 4 h. The product was then homogenized with equivalent amounts of SnO_2 or PbO_2 , compressed into pellets, sintered for 1 h at 880°C and finally annealed at 850°C for 4 h in air by quenching or slow cooling ($100^\circ\text{C}/1\text{ h}$). In some experiments, in which the influence of annealing temperature on the structure, phase composition and superconducting properties of the homologues was tested, sintering temperatures of 917 , 894 and 880°C were used for 20 min, followed by quenching of samples.

All prepared samples were characterized by measuring the $R(T)$ dependence, for which the d.c. four-point resistance method was used. X-ray diffraction patterns were taken on a Philips powder diffractometer using CuK_α radiation.

3. Results, discussion and conclusions

The resistance $R(T)$ measurements showed that all prepared homologue compounds $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$, $\text{Bi}_2\text{Sr}_{1.6}\text{L}_{0.4}\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ and $\text{Bi}_{1.8}\text{Sr}_{1.8}\text{L}_{0.4}\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ ($\text{L} = \text{Sn}$ or Pb , $n = 2, 3$ or 4) were superconducting with zero resistance at $T_c = 70$ to 85 K . However, the phases with $n = 3$ or 4 showed the onset temperature around 115 K indicating involvement of a disproportionate solid-state reaction with formation of a two-phase system. A typical $R(T)$ record is shown in figure 1 for the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ homologue sintered at 880°C for 1 h and annealed at 850°C for 4 h, followed by quenching of sample.

Figure 1. $R(T)$ dependence for $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ sintered at 880°C for 1 h and annealed at 850°C for 4 h in air, followed by quenching of sample.

Figure 2. $R(T)$ dependence for $\text{Bi}_{1.8}\text{Sr}_{1.8}\text{Pb}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ sintered at 880°C for 1 h and annealed at 850°C for 4 h in air, followed by quenching of sample.

Figure 3. $R(T)$ dependence for $\text{Bi}_{1.8}\text{Sr}_{1.8}\text{Sn}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ sintered at 870°C for 1 h and annealed at 850°C for 4 h in air, followed by quenching (full line) or by slow cooling (dotted line).

The $R(T)$ behaviour of the Sn and Pb homologues $\text{Bi}_{1.8}\text{Sr}_{1.8}\text{L}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ is compared in figures 2 and 3. The Pb homologue in figure 2 was sintered at 880°C , the Sn homologue in figure 3 at 870°C for 1 h followed by annealing at 850°C for 4 h in both cases. The Pb sample was quenched after annealing, while the Sn sample was either quenched (full line in figure 3) or slowly cooled (dotted line in figure 3). The $R(T)$ characteristics of quenched Pb and Sn samples are approximately similar to the lower zero resistance temperature value of the Pb homologue ($T_c = 75\text{ K}$) in comparison with the Sn homologue ($T_c = 80\text{ K}$). However, the slow cooling of the Sn sample changed its $R(T)$ characteristics unfavourably, the T_c being 71 K . This is due to precipitation of a non-superconducting SnO phase, as demonstrated by the X-ray powder diffraction record in figure 4 (the upper part of the picture).

Figure 4. Part of the X-ray powder diffraction records of the $\text{Bi}_{1.8}\text{Sr}_{1.8}\text{Sn}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ samples characterized in figure 3: upper part, quenched sample; lower part, slowly cooled sample.

The influence of the sintering temperature on the $R(T)$ characteristics is shown in figure 5. Annealing at 917, 894 and 880°C (lines 1, 2 and 3) of the homologue $\text{Bi}_{1.8}\text{Sr}_{1.8}\text{Pb}_{0.4}\text{CaCu}_2\text{O}_{8+y}$ for 20 min gave the best results for the lowest temperature with the onset temperature of 85 K with $T_c = 50$ K, while sintering at 917 K resulted in the onset temperature of 80 K with $T_c = 30$ K.

The importance of sintering at higher temperatures is demonstrated for instance on the $\text{Bi}_{1.8}\text{Sr}_{1.8}\text{Pb}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ phase. When the homologue was sintered at 850°C for 10 h, it showed a semiconducting character (figure 6, line 2) and an onset temperature value of 90 K, with the zero resistance temperature value $T_c = 76$ K. The sintering of the sample at 880°C followed by annealing at 850°C for 4 h changed the semiconducting character into metallic one (figure 6, line 1) with the onset temperature of 80 K and $T_c = 72$ K.

The additions of Ag_2O (0.016, 0.16, 1.6 and 10.0 at.% Ag) did not change unit cell parameters of the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ phase thus confirming that the Ag component did not enter the structure. However, the presence of silver precipitated at interfaces between the crystalline grains of the superconductor, influenced significantly the texturing of the ceramic bulk.

Figure 5. $R(T)$ dependence for samples $\text{Bi}_{1.8}\text{Sr}_{1.8}\text{Pb}_{0.4}\text{CaCu}_2\text{O}_{8+y}$ sintered at 917°C (line 1), 894°C (line 2) and 880°C (line 3) for 20 min in air and then quenched.

Figure 6. $R(T)$ dependence for $\text{Bi}_{1.8}\text{Sr}_{1.8}\text{Pb}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ sintered at 880°C for 1 h followed by annealing at 850°C for 4 h in air (line 1) or annealed only at 850°C for 10 h in air (line 2)

In conclusion, we may say the substitution of Sn for Bi and Sr in the homologous series $\text{Bi}_{2-x}\text{Sr}_{2-x}\text{Sn}_{2x}\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ or $\text{Bi}_2\text{Sr}_{2-x}\text{Sn}_x\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$ results in similar superconducting behaviour of the phases, as observed in Pb substitution. Substitution of Sn does not change the unit cell volume; however, relative changes of the a , b , c parameters take place.

References

- Gao Y, Lee P, Coppens P, Subramanian M A and Sleight A W 1988 *Science* **241** 954
- Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 *Jpn J. Appl. Phys. Lett.* **27** L209
- Subramanian M A, Torardi C C, Calabrese J C, Gopalakrishnan J, Morrissey K J, Askew T R, Flippen R B, Chowdhry U and Sleight A W 1988 *Science* **239** 1015
- Takano M, Takada J, Oda K, Kitaguchi H, Miura Y, Ikeda Y, Tomii Y and Mazaki H 1988 *Jpn J. Appl. Phys.* (Preprint)
- Tarascon J M, Page Y, Barboux P, Bagley B G, Green L H, McKinnon W R, Hull G W, Giroud M and Hwang D M 1988 *Phys. Rev.* **B37** 9382
- Zandbergen H W, Groen W A, Mijhoff F C, van Tendeloo G and Amelinckx S 1988 *Physica* **C156** 325