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Relation between the upper critical magnetic field and La content for the $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ system

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Abstract. The behaviour of the electrical resistance, AC susceptibility, x-ray powder diffraction and upper critical field H_{c2} were investigated for the $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ system. It was found that the transition temperature and the upper critical field are closely related to the lattice constant c of the 2:2:1:2 phase. From the x-ray diffraction analysis we found that lanthanum first substitutes for calcium and then for strontium as the concentration of La is increased.

1. Introduction

The recent discovery of high-T_c superconductors [1, 2] has generated great interest in the mechanism which causes the high transition temperature in these materials. The upper critical magnetic field H_{c2} is one of the important parameters for revealing the nature of high-temperature superconductivity, because H_{c2} reflects the electron state of the superconducting materials [3–7]. The behaviour of the upper critical field H_{c2} in the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2+x}O_y$ and $Bi_{1.9-x}Pb_xSb_{0.1}Sr_2Ca_2Cu_3O_y$ systems was studied in our early work [6, 7]. The experimental results indicated that H_{c2} changed dramatically for different compositions in these systems. Here we report the effect of La doping on the superconducting properties of $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ system. It is suggested that the superconductivity of this oxide superconductor is closely related to the lattice constant c.

2. Experimental details

Samples with the nominal composition $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ ($x = 0$, 0.05, 0.10, 0.15, 0.2, 0.3 and 0.4) were prepared by solid state reaction in air. The starting materials are high-purity Bi_2O_3, Pb_2O_4, $SrCO_3$, $CaCO_3$, La_2O_3 and CuO powders. These powders were mixed, ground and calcined at 800 °C for 12 h. After being ground and pressed into

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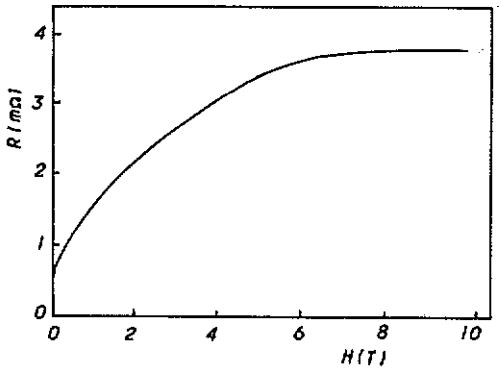

Figure 1. The variation in the electrical resistance with the pulsed magnetic field for $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ at 108 K.

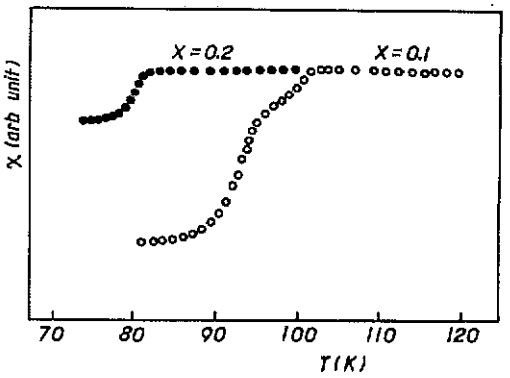

Figure 2. AC susceptibility as a function of temperature for $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ with $x = 0.1$ and 0.2.

pellets (diameter, 13 mm; thickness, 1.5 mm) at a pressure of 120 kgf cm^{-2}, they were sintered at 850 °C for 120 h and then quenched to room temperature in air.

The x-ray powder diffraction measurements were carried out with D/max-rA using Cu Kα radiation. A standard four-probe technique was used for the measurements of the electrical resistance, and the AC susceptibility was measured at 100 Hz. The H_{c2} measurements were obtained under a pulsed magnetic field [6, 7] whose pulsing time is about 32 ms. The AC for the measurements with a frequency of 100 kHz was 0.05 A cm^{-2}. The magnetic field and the voltage signals were recorded simultaneously with a transient converter model TCCJ-2000. The variation in resistance with the magnetic field is shown in figure 1. As shown in this figure, the resistance appears as soon as the pulsed field is applied, which is due to the existence of the Josephson junction between the grains. When the field is high enough, the resistance tends to saturate. Welch *et al* [8] pointed out that the upper critical field H_{c2} was the field at which the resistance returns to half its normal state value, but we noted that the sample was still in a superconducting state using this criterion. We found that, when the oxide superconductor was in normal state, its resistance was almost unchanged with magnetic field. Therefore, we regard the value of the upper critical field H_{c2} as the field above which the resistance becomes field independent.

The temperature was measured with a copper–constantan thermal couple which was calibrated with a Pt resistance thermometer. The measuring end of the thermal couple contacts the samples directly. The error in the temperature measurement is estimated to be less than 0.1 K. Since the time of the pulsed magnetic field is very short and the measuring current is very small, the temperature of the sample did not change during the measuring process.

3. Results and discussion

The temperature dependences of AC susceptibility for the samples of $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ with $x = 0.1$ and 0.2 are shown in figure 2. There are two transition steps on the susceptibility curves in the range $0 \leqslant x \leqslant 0.1$ and only one step for the samples with $0.15 \leqslant x \leqslant 0.3$, which may imply that the former has two

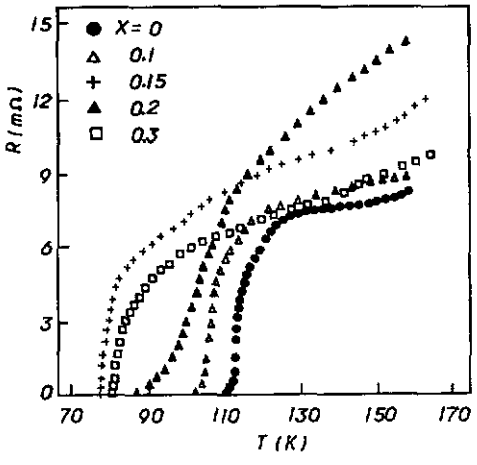

Figure 3. The temperature dependence of the resistance for $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ with $x = 0, 0.1, 0.15, 0.2$ and 0.3.

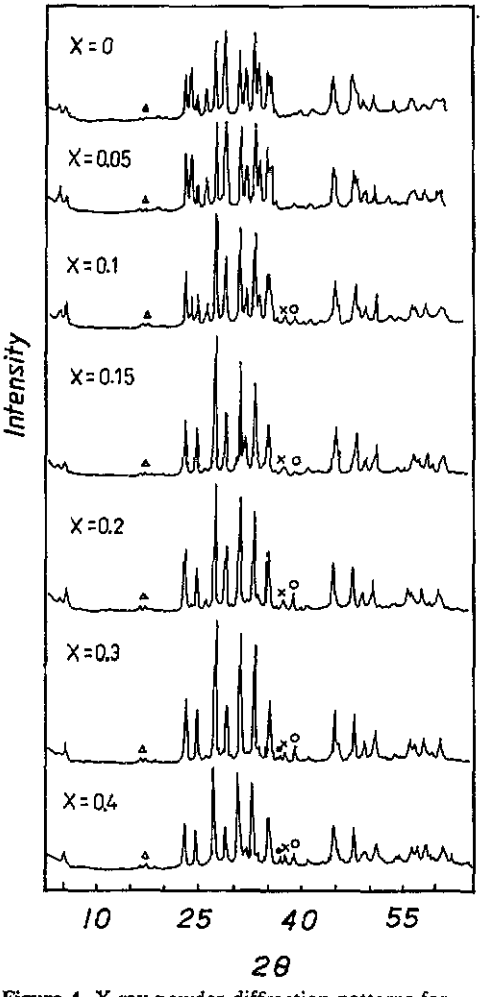

Figure 4. X-ray powder diffraction patterns for $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ with $x = 0, 0.05, 0.1, 0.15, 0.2, 0.3$ and 0.4: △, Ca_2PbO_4; ×, Ca_2CuO_3; ○, CuO; ●, SrO.

superconducting phases and the latter almost only one. Figure 3 shows the variation in the resistance with temperature for $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ with $x = 0$, 0.1, 0.15, 0.2 and 0.3. It is interesting that the resistance of the sample with $x = 0.2$ drops apparently at about 110 K, but the R–T curves for $x = 0.15$ and $x = 0.3$ scarcely show such a phenomenon. The transition temperature T_c measured from AC susceptibility and zero-resistance temperature T_{c0} for all the samples are listed in table 1.

The x-ray powder diffraction patterns of $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ indicated that the dominant phases are a mixture of both 2:2:2:3 and 2:2:1:2 phases within $0 \leqslant x \leqslant 0.1$, and the 2:2:1:2 phase within $0.15 \leqslant x \leqslant 0.4$, as shown in figure 4. Some peaks of the Ca_2PbO_4 phase always existed and are indicated as open triangles in this figure, and those of CuO were also observed in all samples except for those with $x = 0$ and 0.05. In addition, very weak peaks of Ca_2CuO_3 appeared when $x = 0.1$. This suggests that

Table 1. The values of the lattice constant c of the 2:2:1:2 phase and the critical parameters in the $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ system. T_c is the transition temperature determined from the AC susceptibility measurements. T_{c0} is the zero-resistance temperature. T_c^* is extrapolated from the H_{c2} versus temperature curve. $H_{c2}(0)$ is deduced from the WHH theory.

x	c (Å)	T_c (K)	T_{c0} (K)	T_c^* (K)	$\left.\frac{dH_{c2}}{dT}\right\|_{T=T_c^*}$	$H_{c2}(0)$ (T)
0	30.930	108	107	112	−2.36	182
0.05	30.875	107	106	107	−2.71	200
0.1	30.733	101	103	102	−2.53	179
0.15	30.834	78	77	87	−0.85	51
0.2	30.931	86	85	109	−1.16	87
0.3	30.738	81	80	94	−1.93	125
0.4	30.633	73	66	90	−1.18	73

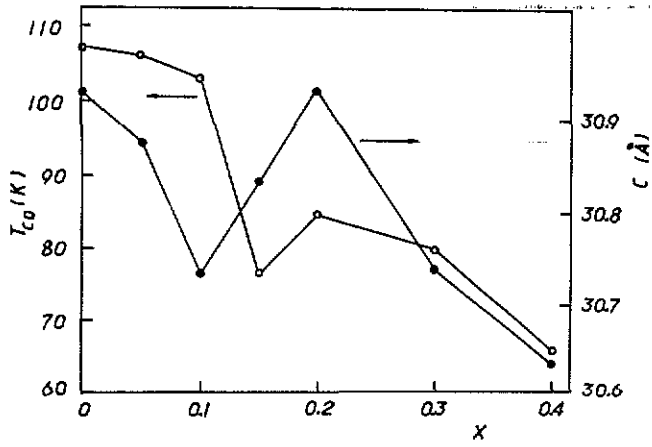

Figure 5. The dependence of the lattice constant c of the 2:2:1:2 phase and T_{c0} on x.

lanthanum first substitutes for calcium. Furthermore, tiny and small SrO phases were observed for the samples with $x = 0.2$ and 0.3. This may imply that La will substitute for Sr as the La concentration increases further. When $x = 0.4$, a small fraction of the insulating phase $Bi_2LaCaCuO_y$ [9] appeared.

The variation of the lattice constant c of the 2:2:1:2 phase with x (La content) is shown in figure 5 and table 1. For very low La content, $0 \leq x \leq 0.1$, the calcium due to the substitution of La for Ca in the 2:2:2:3 phase may enter the 2:2:1:2 phase, and this process makes the 2:2:1:2 phase Ca rich, i.e. $Bi_2Sr_{2-z}Ca_{1+z}Cu_2O_y$ ($z > 0$). Therefore, the length of the c axis of 2:2:1:2 phase becomes gradually smaller for the primarily substitutional processes. When $0.1 < x \leq 0.2$, the substitution of La for Ca causes the value of c to be larger because $r(La^{3+}) > r(Ca^{2+})$ and, if $0.2 < x \leq 0.4$, then some Sr was substituted by La, which makes c become smaller owing to $r(La^{3+}) < r(Sr^{2+})$.

Figure 6 shows the variation in the upper critical field H_{c2} with temperature T in the $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ system. It can be seen that there is a linear relationship between H_{c2} and T except for the compound with $x = 0.1$. This curve for $x = 0.1$ shows

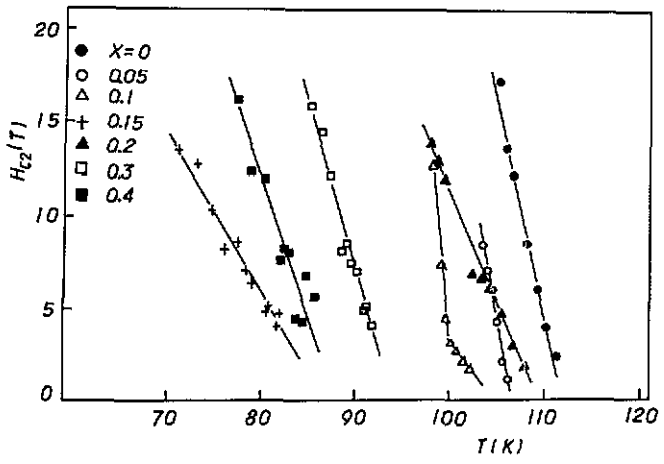

Figure 6. The upper critical field $H_{c2}(T)$ as a function of temperature: the full lines are guides for the eyes.

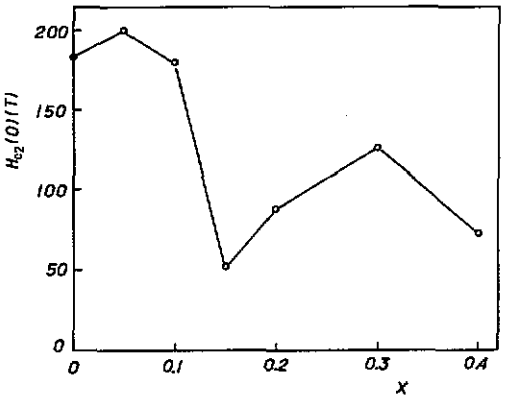

Figure 7. Plot of $H_{c2}(0)(T)$ versus x.

a bend at about 100 K, which is obviously due to the existence of the two superconducting phases (2:2:1:2 and 2:2:2:3 phases) in this sample (see figure 2). Using the Werthamer–Helfand–Hohenburg (WHH) [10] theory, the upper critical field at zero temperature can be deduced from the equation $H_{c2}(0) = -0.69T_c^*\,(\mathrm{d}H_{c2}/\mathrm{d}T)|_{T=T_c^*}$, as shown in figure 7. The T_c^* is extrapolated from the H_{c2} versus temperature curve data, which is listed in table 1. It can be seen that the changing trends of $H_{c2}(0)$ are similar to those of the lattice constant c of the 2:2:1:2 phase, and we believe that the upper critical field is associated with c. A point to note is that the value of T_c^* for the sample with $x = 0.2$ is higher than those for the samples with $x = 0.15$ or $x = 0.3$. This could be attributed to the fact that there is still a small fraction of the 2:2:2:3 phase for the sample with $x = 0.2$. This phenomenon coincides with the resistance measurements (see table 1).

From the above experimental results, one can see that the changes in the lattice constant c of the 2:2:1:2 phase are consistent with those of the zero resistance temperature of the superconducting system. When x changes from 0.15 to 0.3, the variations in T_{c0} and c show a maximal value at $x = 0.2$. It seems that, the larger the c of the 2:2:1:2

phase is, the higher the critical temperature would be. As we know, the Ca–O plane is near the Cu–O planes which was considered as essential for high-temperature superconductivity; therefore, T_{c0} decreases promptly with the substitution of La for Ca (see figure 5). However, the samples with $x = 0.15$, 0.2 and 0.3 have almost the same x-ray diffraction patterns and the dominant phase is the 2:2:1:2 phase; so the values of T_{c0} of these samples change relatively little. This implies that the substitution of La for Sr or Ca at a certain content does not obviously influence T_{c0} for the 2:2:1:2 phase. When $x = 0.4$, the appearance of the insulating phase $Bi_2LaCaCuO_y$ causes the superconductivity of the sample itself to become poor and, as a result, the zero-resistance temperature for the sample with $x = 0.4$ is lower.

In summary, we have studied the structure and superconductivity of $Bi_{1.7}Pb_{0.3}Sr_{2-x}La_xCa_2Cu_3O_y$ system. It was found that the 110 K superconducting phase itself is very sensitive to the concentration of lanthanum, and the fraction of the 2:2:2:3 phase decreases rapidly with the increasing x value and degenerates basically into the 2:2:1:2 phase when $0.15 \leqslant x \leqslant 0.3$. The experimental data indicated that the transition temperature and the upper critical field are closely related to the lattice constant c of the 2:2:1:2 phase when it is the dominant phase in this system.

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