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Stability and doping of infinite-layer compound $(Ca_{1-x}Sr_x)\,CuO_2$ at ambient pressure

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The stability region of the infinite-layer compound $(Ca_{1-x}Sr_x)CuO_2$ has been investigated in detail along the composition line $CaCuO_2$–$SrCuO_2$ in the SrO–CaO–CuO system. The samples were prepared at 956 °C in air at ambient pressure. Single phase of the infinite-layer structure compound is found to lie at the intersection of two different phase regions and its stability region is extremely narrow near $x = 0.16$. Temperature also has pronounced effect on the stability of the infinite layer structure. A trial of doping into the infinite layer compound $(Ca_{1-x}Sr_x)CuO_2$ was performed by partial substituting (Ca, Sr) with lanthanum.

1. Introduction

The high temperature cuprate superconductors all contain CuO_2 layers which have been considered to be essential to the occurrence of high temperature superconductivity. The infinite-layer compound $ACuO_2$ (A = alkaline earth) consists of infinite stacking of CuO_2 layers with a minimum amount of metal-ion (A^{2+}) separator in between and represents the parent structure of the high temperature cuprate superconductors [1]. This compound has a tetragonal perovskite structure with the oxygen on the alkaline earth layers fully vacant (Fig. 1). This simplest structure of high temperature superconductors has attracted much attention, especially after superconductivity was induced in the structure by doping $SrCuO_2$ with trivalent ions such as Nd^{3+}, Pr^{3+} [2], La^{3+} [3] and Y^{3+} [4] or by introducing vacancies in the strontium site [5, 6]. However, superconductivity of the structure so far reported can be obtained only through high temperature–high pressure technique [2–6] or thin film preparation [7, 8]. These extreme preparation conditions have restricted extensive investigation of the compound to some extent.

At ambient pressure, $CaCuO_2$ is not stable in bulk form. The compound $Ca_{0.85}CuO_2$ can crystallize in an oxidizing atmosphere but as an orthorhombic phase [9]. At ambient pressure $SrCuO_2$ exists as an orthorhombic phase as well [10]. In the course of investigating the phase diagram of the SrO–CaO–CuO system, Roth *et al.* found that partial substitution of Ca in $CaCuO_2$ with Sr can stabilize the tetragonal infinite-layer structure and the infinite layer $(Ca_{1-x}Sr_x)CuO_2$ can stabilize only in a very limited composition range near $x = 0.15$ at 950 °C in air. However, Yamane *et al.* [13] reported that in the oxidizing atmosphere, the structure can stabilize only near $(Ca_{0.91}Sr_{0.09})CuO_2$.

The infinite layer compound $(Ca_{0.84}Sr_{0.16})CuO_2$ is an antiferromagnetic insulating phase with $T_N = 537$ K [12]. To induce its superconductivity, appropriate amount of charge carriers should be introduced into this structure. One way to realize the doping is to substitute the alkaline earth ions in the structure with aliovalent ions [13] and this will directly relate to its structure stability.

In this paper, we investigate the phase relation in detail along the composition line $CaCuO_2$–$SrCuO_2$ at 956 °C in air under ambient pressure. We found that the infinite layer structure lies in the intersection of two different phase regions. Though the infinite layer structure can coexist with other phases in a wide composition range, the single phase region is very limited and its stability is temperature-dependent. We also performed a trial of charge carrier doping into this structure by partial replacing (Ca, Sr) with lanthanum.

2. Experimental procedure

Samples were prepared by the conventional solid state reaction method using $SrCO_3$, $CaCO_3$, CuO and La_2O_3 as the starting materials. For $(Ca_{1-x}Sr_x)CuO_2$ samples, the appropriate amounts of starting materials were thoroughly mixed and calcined at 900 °C in air for 24 h. Then the calcined powders were pressed into pellets and sintered in air at 956 °C for 8–12 h. For the doping trial, lanthanum was introduced according to the composition $((Ca_{0.86}Sr_{0.14})_{1-x}La_x)CuO_2 (x = 0.00–0.10)$. The mixed powders were calcined at 900 °C in air for 24 h. Then the calcined powders were pressed into pellets and sintered in air at 950 °, 955 °, 960 °, 965 ° and 970 °C for 8 h each.

Differential thermal analysis (DTA) was carried out at a heating rate of 10 °C min^{-1} with Al_2O_3 as

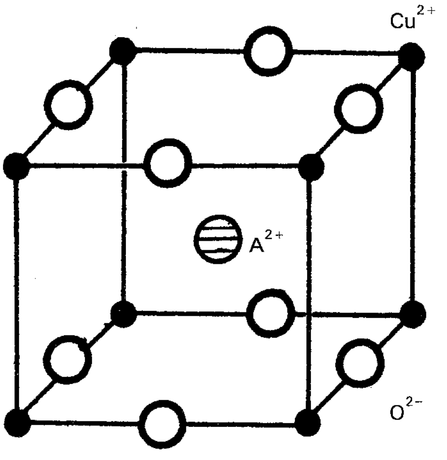

Figure 1 Unit cell of the ideal infinite layer structure.

standard. The samples were characterized by X-ray diffraction using a 18 Kw self-rotating anode X-ray diffractometer (M18XHF type) and CuK_α radiation. Its accuracy was calibrated by the silicon standard. The lattice constant was calculated by the least squares method of the selected peaks. The resistance of the sample was measured by the standard four-terminal method.

3. Results and discussion

3.1. Stability of the infinite layer structure

Fig. 2 shows the X-ray diffraction patterns of the samples with the composition $(Ca_{1-x}Sr_x)CuO_2$ ($x = 0.07$–0.31) prepared at 956 °C in air for 12 h. It can be seen that the sample with $x = 0.16$ consists nearly of pure single phase which can be indexed to a tetragonal infinite-layer structure (the infinite-layer phase is abbreviated as IL hereafter). On the one hand, when the Sr content is larger than $x = 0.16$, another phase appears which is due to the orthorhombic (Sr, Ca)CuO_2. With the increasing of the Sr content, the amount of the orthorhombic phase (Sr, Ca)CuO_2 increases while the infinite-layer phase (Ca, Sr)CuO_2 decreases. The orthorhombic phase has become the main phase for the sample with $x = 0.28$ and the

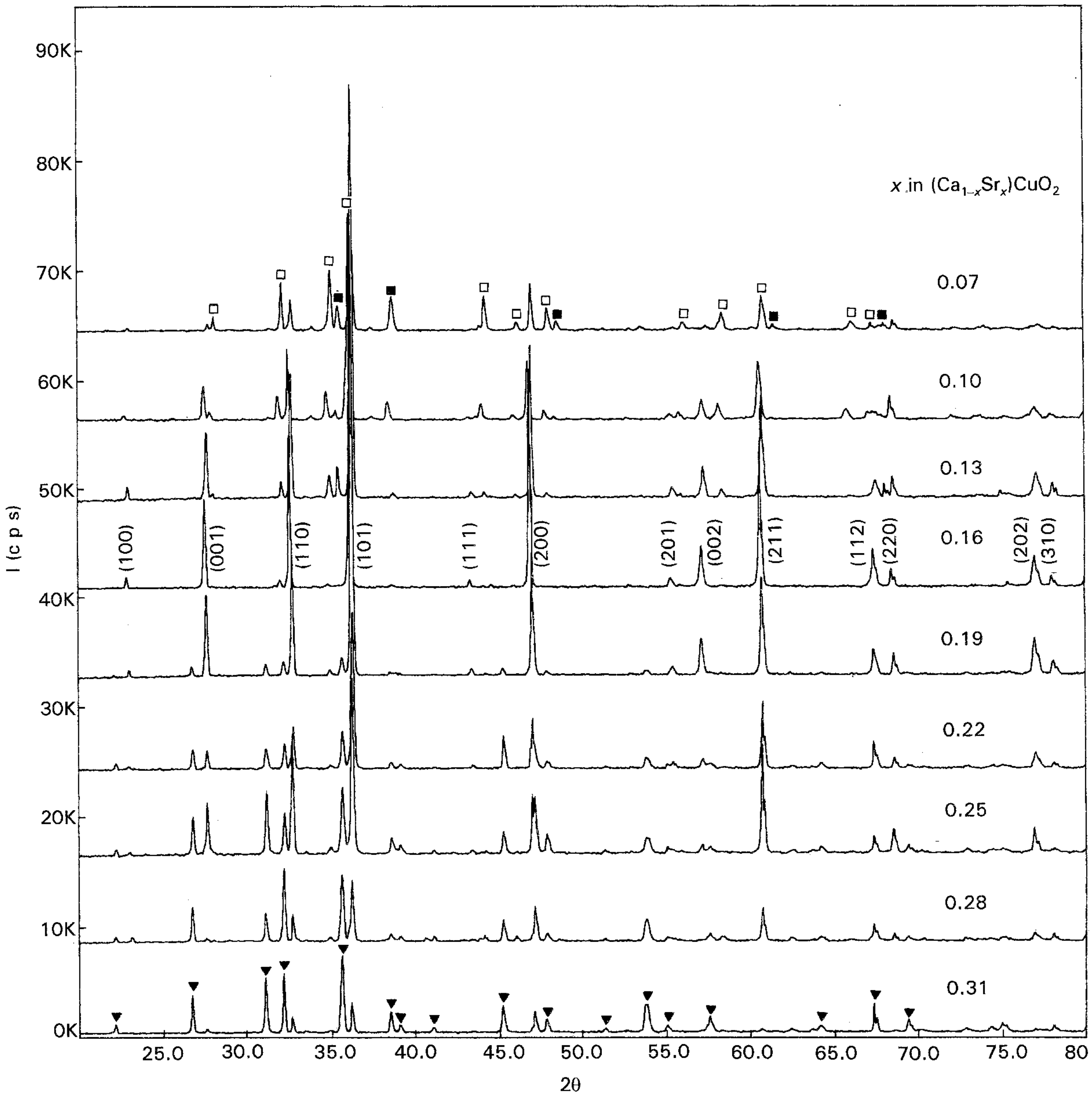

Figure 2 X-ray diffraction patterns for the $(Ca_{1-x}Sr_x)CuO_2$ samples ($x = 0.07$–0.31) sintered at 956 °C in air. Peaks of the infinite layer phase are indexed. (□) $(Ca, Sr)_2CuO_3$; (■) CuO; (▼) orthorhombic (Sr, Ca) CuO_2.

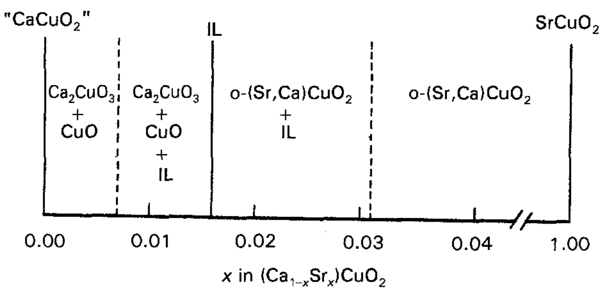

Figure 3 Phases present in the $(Ca_{1-x}Sr_x)CuO_2$ samples at 956 °C in air.

infinite-layer phase almost disappears for the sample with $x = 0.31$. On the other hand, when the Sr content is lower than $x = 0.16$, in addition to the infinite-layer phase, different impurity phases appear including $(Ca, Sr)_2CuO_3$ and CuO. With the decreasing of Sr content in $(Ca_{1-x}Sr_x)CuO_2$, the amount of the infinite-layer phase decreases abruptly and for the sample with $x = 0.07$ its amount has become very small.

The above phase change with the composition of $(Ca_{1-x}Sr_x)CuO_2$ is shown in Fig. 3. The sample with $x < 0.07$ consists of $(Ca, Sr)_2CuO_3$ and CuO. The sample with $x > 0.31$ contains a single orthorhombic solid solution $(Sr_{1-x}Ca_x)CuO_2$ (abbreviated as o-$(Sr, Ca)CuO_2$ hereafter) [11]. It can be seen that along the composition line $CaCuO_2$–$SrCuO_2$, the infinite-layer compound lies at the intersection of the two different phase regions, i.e., $(Ca, Sr)_2CuO_3$ + CuO + IL and IL + o-$(Sr, Ca)CuO_2$. The infinite-layer phase can coexist with other impurity phases in a wide composition range of $x = 0.07$–0.31 but the single phase region is extremely narrow near $x = 0.16$. When the Sr content is lower than 0.16, the infinite-layer phase decomposes into $(Ca, Sr)_2CuO_3$ and CuO. When the Sr content is higher than 0.16, the infinite-layer tetragonal structure (IL) transforms into the orthorhombic $(Sr, Ca)CuO_2$.

We have found that the stability of the infinite-layer phase is also sensitive to the sintering temperature. Fig. 4 shows the X-ray diffraction patterns of the $(Ca_{0.86}Sr_{0.14})CuO_2$ samples sintered at five different temperatures. It can be seen that for the sample sintered at 960 °C, it contains a pure single phase of the infinite-layer structure with $a = b = 3.858$ Å and $c = 3.210$ Å. When the sintering temperature deviates from 960 °C, the same impurity phases $(Ca, Sr)_2CuO_3$ and CuO appear for both higher and lower sintering temperatures. This is consistent with the phase relation shown in Fig. 2 and indicates that the composition $(Ca_{0.86}Sr_{0.14})CuO_2$ lies in the $(Ca, Sr)_2CuO_3$ + CuO + IL phase region. When the sintering temperature reaches 970 °C, the sample melts partially and the infinite-layer phase decomposes into $(Ca, Sr)_2CuO_3$ and CuO.

Fig. 5 shows a typical differential thermal analysis (DTA) result of the mixed starting materials with the composition $(Ca_{0.84}Sr_{0.16})CuO_2$. The peaks at 840 °C and 936 °C represent the decomposition temperatures of $CaCO_3$ and $SrCO_3$ respectively. The peak at 958 °C represents the formation of the infinite-layer compound which is identical to the sintering temperature we have used. When the temperature reaches 974–993 °C, the sample becomes partially melted

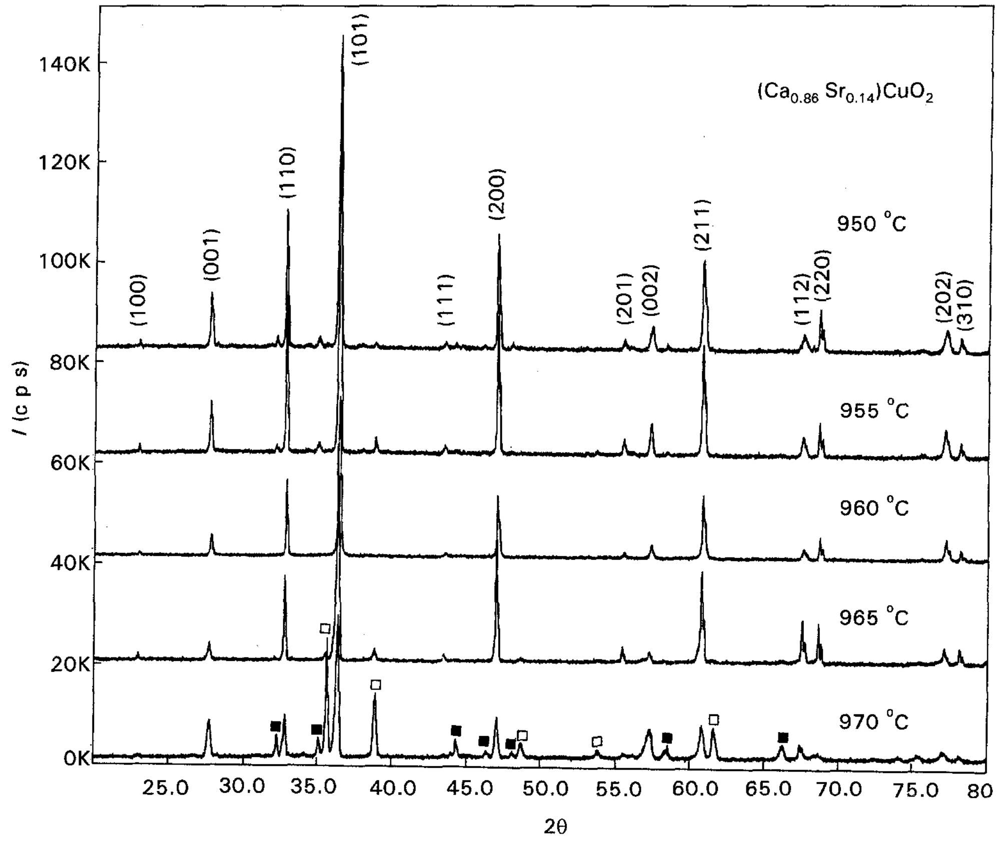

Figure 4 X-ray diffraction patterns for $(Ca_{0.86}Sr_{0.14})CuO_2$ samples sintered at different temperatures. Peaks of the infinite-layer phase are indexed. (■) $(Ca, Sr)_2CuO_3$; (□) CuO.

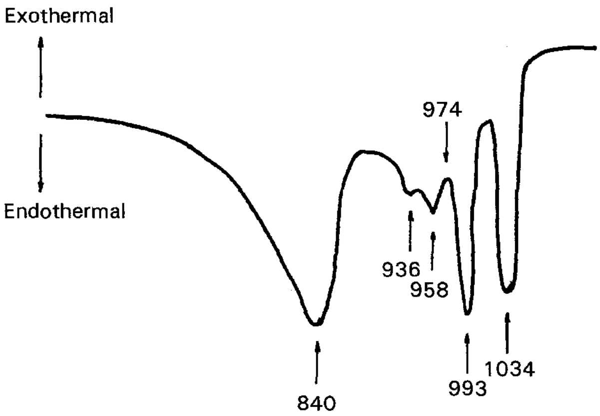

Figure 5 DTA curve for $(Ca_{0.84}Sr_{0.16})CuO_2$.

and the infinite layer structure decomposes into $(Ca,Sr)_2CuO_3$ and CuO, in agreement with the result shown in Fig. 4. With the temperature increasing further to 1034 °C, the sample becomes completely molten.

From Fig. 4, it is clear that, before partial melting occurs, the sintering temperature does not change the phase region of the composition but can adjust the amount of the impurity phase. For a sintering temperature of 960 °C, we have found that the sample $(Ca_{0.86}Sr_{0.14})CuO_2$ consists of a pure single phase of the infinite-layer structure. However, at this temperature, the sample $(Ca_{0.84}Sr_{0.16})CuO_2$ contains apparent amount of the impurity phase $(Ca,Sr)_2CuO_3$ and CuO. On the contrary, for the sintering temperature 956 °C, the sample $(Ca_{0.84}Sr_{0.16})CuO_2$ consists of a single infinite layer phase as shown in Fig. 2 while the sample $(Ca_{0.86}Sr_{0.14})CuO_2$ contains apparent amounts of $(Ca,Sr)_2CuO_3$ and CuO as seen from Fig. 4. It seems that the stability of the infinite-layer structure is the result of a delicate balance between the composition and the sintering temperature. The composition $(Ca_{0.84}Sr_{0.16})CuO_2$ and $(Ca_{0.86}Sr_{0.14})CuO_2$ all belong to the phase region of $(Ca,Sr)_2CuO_3 +$ CuO + IL while the composition $(Ca_{0.19}S_{0.81})CuO_2$ belongs to the IL + o-(Sr, Ca)CuO_2 phase region. So from the phase relation in Fig. 3, the "ideal" single phase composition is expected to lie within 0.16–0.19. For a given sintering temperature, the stability region of the pure single infinite-layer phase is rather limited. Though we can adjust the sintering temperature to get pure single infinite-layer phase $(Ca_{1-x}Sr_x)CuO_2$ in the vicinity of $x = 0.16$, the available composition range is still rather limited: $x = 0.13$–0.19.

The single infinite-layer phase region of our investigation corresponds to that reported by Roth *et al.* [11]. Kijima *et al.* studied the stability field of the infinite-layer phase by preparing the sample at 1000 °C in flowing oxygen [13]. They reported that the stability region of the infinite layer lies at $x = 0.09$–0.15. This result together with that of Yamane *et al.* [12] seems to indicate that the oxidizing atmosphere shifts the stability field of the infinite layer structure to a lower Sr content. These results further confirm that the stability of the infinite layer structure is dependent on the preparation condition. Kijima *et al.* reported that for samples $(Ca_{1-x}Sr_x)CuO_2$ with lower Sr content, the sample consists of Ca_2CuO_3 and

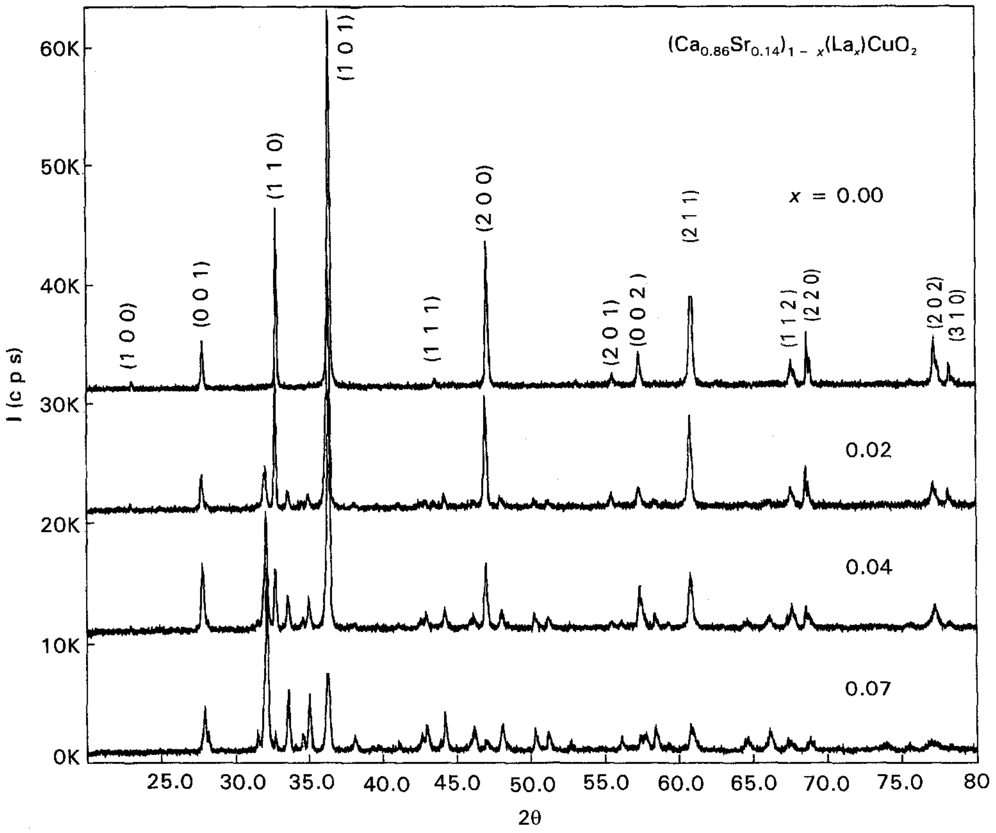

Figure 6 Typical X-ray diffraction patterns for the samples $((Ca_{0.86}Sr_{0.14})_{1-x}La_x)CuO_2$ sintered at 950–970 °C in air.

$CaCu_2O_3$, while the samples with greater Sr content contain Sr_2CuO_3, Ca_2CuO_3 and $CaCu_2O_3$ [13]. This phase variation with the Sr content is different from our result in Fig. 3 and it seems inadequate for Sr_2CuO_3 and Ca_2CuO_3 to coexist because they can form a complete solid solution $(Ca,Sr)_2CuO_3$ [11]. Roth *et al.* [11] reported that the solid solution orthorhombic $(Sr_{1-x}Ca_x)CuO_2$ can extend from $x = 0$ to nearly $x = 0.25$ at 950 °C. Our result indicates that the solid solution region lies in the range of $x = 0$–0.31 at 956 °C.

3.2. Doping trial of the infinite-layer compound

The pure single phase $(Ca_{0.86}Sr_{0.14})CuO_2$ of the infinite-layer structure can be obtained at 960 °C in air as seen from Fig. 5. Previously a trial has been attempted to replace Ca^{2+} with Y^{3+} to induce its superconductivity but was unsuccessful [14]. For the average radius of $(Ca_{0.86}Sr_{0.14})$ (1.14 Å), we chose La^{3+} ions to partially substitute the $(Ca_{0.86}Sr_{0.14})$ unit because it is expected that the similarity of the La^{3+} radius, 1.18–1.14 Å might enhance the solubility of La^{3+} in the infinite-layer structure. Fig. 6 shows the typical X-ray diffraction patterns of the samples $((Ca_{0.86}Sr_{0.14})_{1-x}La_x)CuO_2$ ($x = 0.00$–0.07) prepared at 950–970 °C in air. From the intensity variation of the (1 1 0) and (2 0 0) peaks it is obvious that the introduction of La^{3+} destroyed the stability of the infinite layer structure remarkably. For the sample with $x = 0.02$, Ca_2CuO_3 and other impurity phases appear for all the samples sintered at different temperatures. This indicates that the solubility of La^{3+} in the infinite-layer structure is less than 0.02 at ambient pressure. With increasing La^{3+} content, the amount of the impurity phase also increases rapidly and the infinite-layer phase almost disappears for the sample with $x = 0.07$.

Fig. 7 shows the temperature dependence of the resistivity for the samples $((Ca_{0.86}Sr_{0.14})_{1-x}La_x)CuO_2$ ($x = 0.00$, 0.02 and 0.04). All samples show semiconductor-like behaviour. The introduction of La^{3+} by 2% decreases the resistivity of $(Ca_{0.86}Sr_{0.14})CuO_2$ by nearly two orders of magnitude and the temperature dependence of the resistivity also becomes smoother. This indicates that charge carriers are doped into the infinite-layer structure, though the amount of them is rather small. The increase of resistivity for the sample with $x = 0.04$ may be due to the impurity phases. Superconductivity was not observed in these samples since the concentration of the charge carriers is too low.

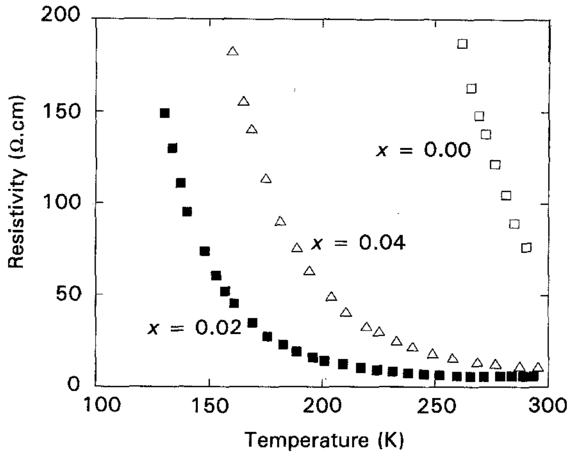

Figure 7 Temperature dependence of the resistivity for the $((Ca_{0.86}Sr_{0.14})_{1-x}La_x)CuO_2$ samples.

In summary, we have studied the phase relations along the $CaCuO_2$–$SrCuO_2$ composition line at 956 °C in air. The infinite-layer phase lies at the intersection of two different phase regions, i.e., $(Ca,Sr)_2CuO_3 + CuO + IL$ and o-$(Sr,Ca)CuO_2 + IL$. The infinite-layer phase can coexist with other phases in a wide composition range $(Ca_{1-x}Sr_x)CuO_2$ with $x = 0.07$–0.31 but the pure single phase region is rather limited and temperature-dependent. We found that the single phase region of the infinite layer structure $(Ca_{1-x}Sr_x)CuO_2$ lies in $x = 0.13$–0.19, in agreement with the results of Roth *et al.* [11]. Doping of the infinite layer $(Ca_{0.86}Sr_{0.14})CuO_2$ with La^{3+} has been tried at ambient pressure, but the solubility of La^{3+} is too small (less than 0.02) to induce the superconductivity.

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