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Growth of Na-Doped $Ca_2CuO_2Cl_2$ Single Crystals under High Pressures of Several GPa

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Abstract: Single crystals of Na-doped $Ca_2CuO_2Cl_2$ have been grown for the first time by a flux method under high pressures of up to 5.5 GPa. By changing the Na-solubility limit through the applied pressure, the Na content x was successfully controlled without introducing appreciable compositional inhomogeneity within the millimeter-sized crystals. Structural and chemical characterization indicated that the crystals span the phase diagram continuously from the parent antiferromagnetic insulator to an underdoped high-temperature superconductor. Because of the well-defined cleavage plane and resulting high surface quality, these oxychloride single crystals will provide a unique opportunity to explore the electronic evolution of the high-temperature superconductors, using spectroscopic techniques such as scanning tunneling microscopy/spectroscopy and angle-resolved photoemission spectroscopy.

1. Introduction

Although more than a decade has passed since its initial discovery, high-temperature superconductivity in copper oxides remains an unsolved problem. Without a doubt, one of the key questions in high-T_c physics is how the parent magnetic insulators evolve into the high-temperature *d*-wave superconductors. For instance, what is the relationship between the insulating (Mott) gap, caused by electronic correlations, and the superconducting gap or the pseudogap? In addition, is microscopic phase separation a phenomenon universal among all of the cuprates or merely a material-dependent phenomenon specific only to the $(La,Sr)_2CuO_4$ family?[1]

To address these fundamental questions, two spectroscopic techniques, scanning tunneling microscopy/spectroscopy (STM/STS) and angle-resolved photoemission spectroscopy (ARPES), have played a crucial role in studies of these materials, in that they can directly probe the electronic states either in real or in momentum space, respectively. These techniques, however, are highly surface sensitive, which places strong constraints on the materials which can be studied by these methods. Indeed, the vast majority of STM/STS and ARPES studies have been conducted on only two compounds, $Bi_2Sr_2CaCu_2O_y$ and $Bi_2Sr_2CuO_y$, because of their superior surface quality associated with their well-defined BiO cleavage planes. However, these Bi-based cuprates are known to be chemically unstable when synthesized in the heavily underdoped region of the phase diagram. Thus, the lack of heavily underdoped samples available to STM/STS or ARPES has been hindering our efforts to study the evolution of the parent insulator into the superconductor. In this sense, a compound which has a high surface quality and is also stable in the heavily underdoped region has long been desired.[2]

Among the known cuprates, Na-doped $Ca_2CuO_2Cl_2$ may be the only system that can satisfy the above requirements. As shown in Figure 1, the crystal structure of this system consists of alternate stacking of the $(Ca,Cl)_2$ layer and the single CuO_2 plane, which is closely related to the K_2NiF_4-type structure.[3] The parent compound, $Ca_2CuO_2Cl_2$, is an antiferromagnetic insulator with $T_N = 247 \pm 5$ K.[4] Single crystals of $Ca_2CuO_2Cl_2$ can be grown quite easily. They are cleaved easily along the *c*-axis like mica, possibly due to the weak ionic bonds within the $(Ca,Cl)_2$ layer. As a result of the high surface quality, an ARPES study on this magnetic insulator was recently conducted,[5] revealing a *d*-wave-like dispersion of the Mott gap suggesting a possible link between the Mott gap and the pseudogap.

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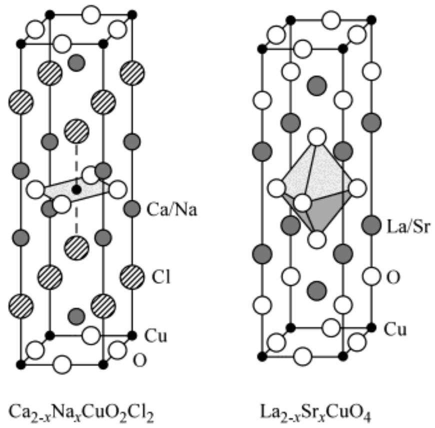

Figure 1. Crystal structures of $Ca_{2-x}Na_xCuO_2Cl_2$ and $La_{2-x}Sr_xCuO_4$ with the K_2NiF_4 structure. The crystal structures of these two systems are nearly identical. Chlorine atoms in $Ca_{2-x}Na_xCuO_2Cl_2$ replace the apical oxygens in $La_{2-x}Sr_xCuO_4$.

By substituting Ca^{2+} with Na^+, mobile holes can be introduced into the CuO_2 plane in $Ca_{2-x}Na_xCuO_2Cl_2$. Upon doping, superconductivity emerges at a carrier concentration of $x \approx 0.07$. A maximum T_c of 28 K was reported for $x \approx 0.2$.[6,7] In contrast to the parent insulator, however, Na-doped $Ca_2CuO_2Cl_2$ can only be synthesized under pressures of several GPa. Because of the difficulties associated with crystal growth under high pressures, large single crystals doped with an appreciable amount of Na have never been available.

This paper reports the first single-crystal growth of Na-doped $Ca_2CuO_2Cl_2$ under pressures of several GPa. A novel pressure control of the Na content was developed, and we were able to control the composition from $x = 0$ (a magnetic insulator) to 0.12 (an underdoped superconductor) without introducing any appreciable compositional inhomogeneity.

2. Experimental Section

Single crystals of $Ca_{2-x}Na_xCuO_2Cl_2$ were grown by a flux method using a specially designed cubic-anvil-type high-pressure apparatus with a large sample space of ~1 cm^3. Note that the large space for the crystal growth was key in obtaining sizable single crystals. Pt cylindrical capsules were charged with powder mixtures of $Ca_2CuO_2Cl_2$, $NaClO_4$ (flux, Na source, and oxidizer), and NaCl (flux and Na source). $Ca_2CuO_2Cl_2$ powder was prepared by a solid-state reaction of Ca_2CuO_3, CuO, and $CaCl_2$ at 750 °C in a nitrogen flow for 2 days with intermediate grindings. All of the processes were carried out in an argon-filled drybox to avoid reactions of $CaCl_2$ and $Ca_2CuO_2Cl_2$ with moisture.

The Pt capsules were placed at the center of the high-pressure cells and compressed in the high-pressure apparatus. The temperature was increased to 1170−1250 °C in 10 min, kept stable for 2 h, then slowly (−5 to −10 °C/h) decreased to 970−1050 °C, crossing the melting point for pressures of 2−5.5 GPa. The high pressure was maintained throughout the growth and was removed only after the cell was cooled to room temperature. The melting points of the samples were determined by means of a powder X-ray diffraction (XRD) study performed under high pressures at beamline BL14B1 of SPring-8, Japan Synchrotron Radiation Research Institute. Details of the XRD study have been reported elsewhere.[8]

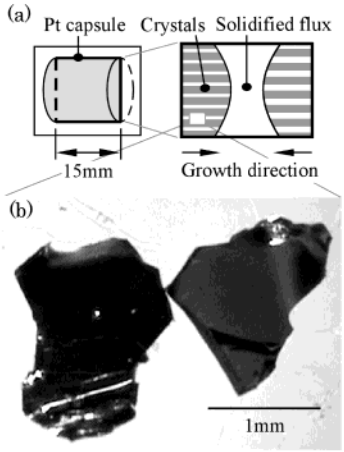

Figure 2. (a) A schematic of the solidified melt inside the capsule: crystal growth initiated from the ends of the platinum capsule and moved toward the center. As a result, the products inside the capsule were separated into two regions: single crystals at the ends and the solidified flux at the center. (b) A photograph of a $Ca_{2-x}Na_xCuO_2Cl_2$ single crystal grown under high pressure.

The compositions of the obtained single crystals were analyzed by electron-probe-microanalysis (EPMA) using a JEOL JXA-8200. The powder XRD data were collected using a Rigaku RINT 2500 diffractometer (Cu Kα radiation) equipped with a monochromator. The lattice constants were refined by Rietveld analyses using Rietan-2000.[9] The magnetization was measured using a SQUID magnetometer (Quantum Design MPMS) in an external field of 10 Oe.

3. Results and Discussion

3.1. Crystal Growth. The first single-crystal growth was composed of a powder mixture of $Ca_2CuO_2Cl_2$, $NaClO_4$, and NaCl in a molar ratio of 1:0.2:0.2 at a pressure of 4 GPa. After soaking at 1230 °C for 2 h, the melt was slowly cooled to 1050 °C over 30 h. The pressure was kept at 4 GPa during the heat treatment. It was found that single crystals of $Ca_{2-x}Na_xCuO_2Cl_2$ were successfully synthesized inside the Pt capsule. As shown schematically in Figure 2a, the products inside the capsule were separated into two regions: one at the ends, where single crystals were formed, and the other at the center, where the flux had solidified, clearly indicating a temperature gradient inside the capsule with the ends being cooler. It is highly likely that the crystal growth originated at both ends and that the remaining flux eventually condensed at the center of the capsule.

Typical dimensions of the obtained crystals were $1 \times 1 \times 0.05$ mm^3. Similar to the stoichiometric $Ca_2CuO_2Cl_2$ crystals, these doped crystals were very easily cleaved, leaving a flat and shiny *ab*-plane surface, as shown in Figure 2b. The color of these crystals was black, distinctly different from the golden color of the Na-free crystals, implying that Na was successfully introduced in these crystals. To confirm that a substantial amount of carriers were doped into the crystals, superconductivity was measured by temperature-dependent magnetometry. Figure 3a shows temperature-dependent magnetization curves for crystals removed from the end of the capsule and the center parts, respectively, clearly indicating the occurrence of bulk superconductivity at 15 K. According to the T_c versus x curve previously obtained on powder samples,[7] $T_c = 15$ K corresponds to a Na content of $x \approx 0.1$. We note that the transition temperatures for crystals originating from different parts of the

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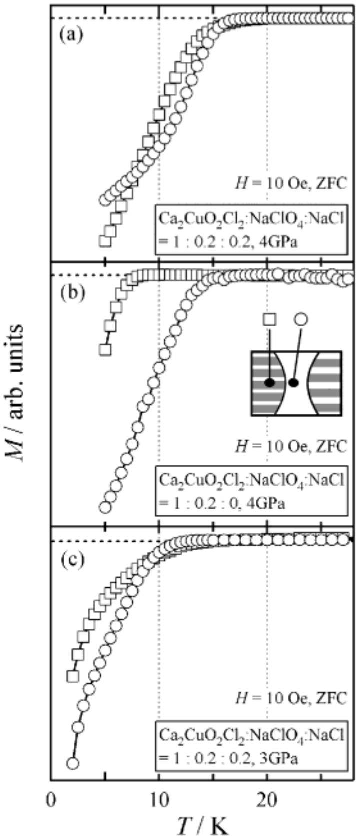

Figure 3. Temperature-dependent magnetizations for $Ca_{2-x}Na_xCuO_2Cl_2$ crystals grown under different conditions. (a) $Ca_2CuO_2Cl_2$:$NaClO_4$:NaCl = 1:0.2:0.2 at 4 GPa. (b) $Ca_2CuO_2Cl_2$:$NaClO_4$:NaCl = 1:0.2:0 at 4 GPa. (c) $Ca_2CuO_2Cl_2$:$NaClO_4$:NaCl = 1:0.2:0.2 at 3 GPa. Squares and circles represent the data obtained from crystals taken from the capsule ends and center, respectively.

capsule were almost identical, indicating that the concentration did not depend crucially on the position inside the capsule.

After establishing that the Na-doped single crystals can be obtained by a high-pressure flux growth, we have then explored ways to control the Na content, to grow the crystals ranging from a magnetic insulator to a high-temperature superconductor. We found that controlling the Na content by means of pressure is essential to ensure the homogeneity of the Na distribution within the crystals, whereas the compositional control worked rather poorly, because a substantial compositional inhomogeneity is inevitably introduced. To demonstrate, we show in Figure 3b the temperature-dependent magnetization of crystals grown from a mixture of $Ca_2CuO_2Cl_2$, $NaClO_4$, and NaCl in a molar ratio of 1:0.2:0.0, which contains substantially less Na than the mixture used for the crystals shown in Figure 3a. The single crystal taken from the capsule end in Figure 3b shows a distinctly lower T_c than those in Figure 3a, indicating a lower Na content x. In contrast, the crystals taken from the capsule center show substantially higher T_c's than those from the capsule end and are comparable to those of the crystals shown in Figure 3a. This remarkable difference clearly indicates that the Na content of crystals grown from the Na-poor melt varies appreciably from piece to piece within the same batch.

In flux growth, the chemical composition of the flux inevitably changes during the growth process. In the case of the crystals shown in Figure 3b, Na tended to remain in the flux, resulting in an increase of the Na concentration in the flux during the growth process. Because of the constant partition coefficient between the crystals and the flux, the Na content in the crystals will also increase along the growth direction, consistent with the observed increase of T_c toward the center of the capsule. This result, in turn, raises a question regarding the first result: why was the Na uniformly introduced into the $x \approx 0.1$ crystals shown in Figure 3a? We propose the following hypothesis as a plausible explanation for this behavior: because the $x \approx 0.1$ crystals were grown from the heavily Na-rich melt, the Na content in these crystals may likely have already reached its Na-solubility limit from the beginning of the growth. In this case, the solubility limit, and not the partition coefficient, in the $Ca_{2-x}Na_xCuO_2Cl_2$ solid solution ($x \approx 0.1$) dominated the Na content in these crystals, resulting in the constant Na content from the beginning to the end of the growth.

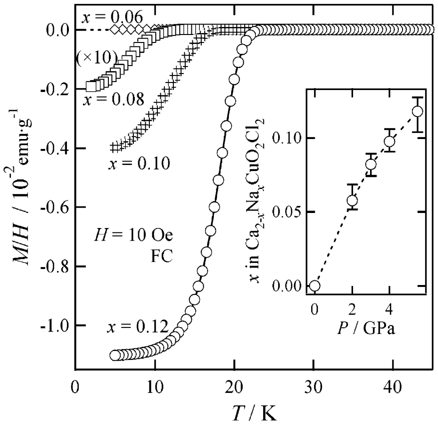

Figure 4. Temperature-dependent magnetization of $Ca_{2-x}Na_xCuO_2Cl_2$ single crystals. The measurements were performed with a field cooling under H = 10 Oe. Inset: Pressure dependence of the Na content, x, in $Ca_{2-x}Na_xCuO_2Cl_2$ single crystals. Na content was determined by the EPMA analysis. The open circles are the mean values of x averaging over the data from several points on each crystal surface, while the error bars correspond to its maximum and minimum values.

As is evident from the fact that Na cannot be introduced into $Ca_2CuO_2Cl_2$ without the application of pressure, the Na-solubility limit crucially depends on pressure and, therefore, can be controlled very easily by varying the external pressure. To demonstrate this, we have attempted to grow crystals with $x <$ 0.1 by decreasing the Na-solubility limit through the reduction of pressure, which should result in homogeneous crystals. Using the same powder mixture and same temperature profile as was used for $x \approx 0.1$ samples shown in Figure 3a, we then grew crystals at a pressure of 3 GPa. In contrast to the composition-controlled crystals in Figure 3b, the lightly doped pressure-controlled crystals in Figure 3c do not show any appreciable variation of T_c within the same batch, providing further evidence for the solubility-limited growth scenario. Therefore, we can conclude that the pressure control of the Na content is effective in eliminating the compositional inhomogeneity.

3.2. Characterization. Using this strategy, we finally obtained $Ca_{2-x}Na_xCuO_2Cl_2$ single crystals with various Na content x by growing crystals at 0, 2, 3, 4, and 5.5 GPa. It was confirmed by the EPMA analysis that x is a function of the applied pressure shown in the inset of Figure 4. Na content systematically increases from x = 0 to 0.12 with increasing pressure from 0 to 5.5 GPa. The error bars are almost comparable to our instrumental resolution, demonstrating the homogeneous Na distribution over the crystals. The main panel of Figure 4 shows

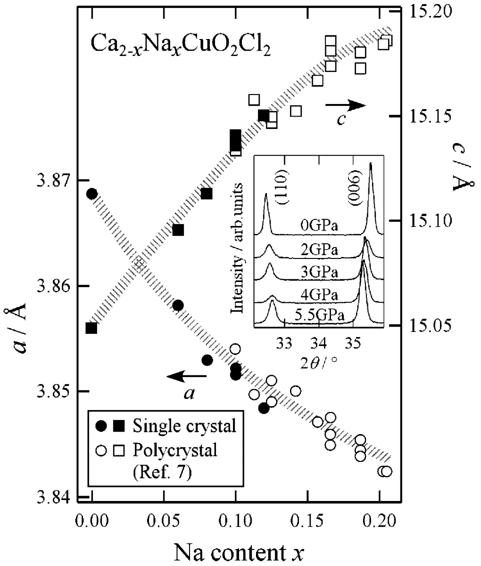

Figure 5. Lattice constants versus the Na content, *x*, in $Ca_{2-x}Na_xCuO_2Cl_2$. Polycrystalline results are taken from ref 7 for comparison. The curves are guides to the eye. (inset) Powder XRD patterns of the $Ca_{2-x}Na_xCuO_2Cl_2$ crystals grown under various pressures, indicating tetragonal (110) and (006) peaks. Note that the preferred orientation changes the intensity ratio of the two peaks.

temperature-dependent magnetization data where superconductivity was observed in the crystals above $x = 0.06$ (pressures above 2 GPa). As the pressure is further increased up to 5.5 GPa ($x \approx 0.12$), T_c increases monotonically up to 21 K. These results indicate that, by changing the applied pressure alone, the Na content and, hence, the hole carrier concentration can be varied substantially.

The XRD data are consistent with the EPMA results. The inset of Figure 5 shows (110) and (006) powder XRD peaks for the crystals grown under various pressures. First of all, we did not find any noticeable changes in the peak width, which strongly indicates that Na was uniformly doped throughout the crystals. By increasing the synthesis pressure, the (110) peaks shift toward higher angles, while the (006) peaks shift toward lower angles. These shifts represent the increase (decrease) in the *a*-axis (*c*-axis) lattice constant with increasing pressure and, hence, the Na content, in agreement with the polycrystalline results.[7] In the main panel of Figure 5, the refined lattice constants are plotted against the Na content *x* estimated from the EPMA analysis. Previous polycrystalline results[7] are also shown for comparison. The excellent agreement between the single crystal and the polycrystalline results further supports the present estimate of the Na content in our crystals.

By combining the T_c as determined from the magnetization measurements (Figure 4) and the above estimate of Na content, we are now able to summarize our single-crystal results in a T_c versus *x* curve in Figure 6. Polycrystalline results[7] are also shown for comparison. It is clear that the T_c curve for the single crystals agrees well with the polycrystalline results. Superconductivity appeared around $x \approx 0.07$ and, with a maximum growth pressure of 5.5 GPa, reached to $x = 0.12$, with a T_c of 21 K. We were unable to attain the highest possible T_c for this family, because to prepare the optimally and overdoped concentrations, pressures up to 10 GPa are likely required,[10] but they will hopefully be reached soon.

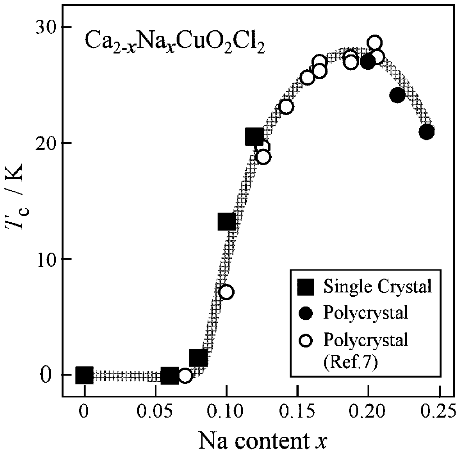

Figure 6. The phase diagram, T_c versus *x*, of $Ca_{2-x}Na_xCuO_2Cl_2$ single crystals grown under various pressures. Previous polycrystalline results (ref 7) were also shown for comparison. The curve is a guide to the eye.

4. Conclusion

We have succeeded in synthesizing single crystals of Na-doped $Ca_2CuO_2Cl_2$ for the first time by a flux method under high pressures of several GPa. To eliminate the compositional inhomogeneity inherent to the flux growth process, a novel pressure control of the Na content was employed, whereby the solubility limit was the dominant factor in determining the Na content inside the crystals. The resulting single crystals span a wide range of doping and evolve from a parent insulator to an underdoped superconductor. The Na-doped $Ca_2CuO_2Cl_2$ crystals are easily cleaved like the parent insulator, and the high surface quality has the potential for some of the first explorations of the heavily underdoped region of the cuprate phase diagram using surface sensitive techniques. Indeed, our first attempts at imaging the electronic states both in real space (STM/STS)[11] and in momentum space (ARPES)[12] proved quite successful, and the electronic evolution from magnetic insulator to superconductor is finally being elucidated.

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(10) We found the reduction of T_c in powder samples prepared at 8 and 9 GPa, suggesting that the samples were overdoped. These polycrystalline data are also plotted in Figure 6, on the basis of *x* values estimated roughly from the comparison of the lattice constants with the reported polycrystalline data (ref 7).

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