

# High-pressure synthesis and superconducting properties of the oxychloride superconductor $(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-y}$

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Chlorine-containing  $(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-y}$  superconductors have been synthesized at 5.0 GPa and  $\sim 1000^\circ\text{C}$ . The double- $[\text{CuO}_2]$  layered compound crystallizes into  $(\text{La,Sr})_2\text{CaCu}_2\text{O}_6$  structure with Cl residing at the apical anion site relative to the  $[\text{CuO}_2]$  plane. The critical transition temperature  $T_c$  80 K has been achieved in these superconductors. The  $\text{Sr}_{2.3}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{1.3}$  superconductor was studied in terms of irreversibility field  $H_{\text{irr}}$  and intragrain critical current density  $I_c$ . It is found that the irreversibility field of the superconductor can be described by the power law dependence  $(1 - T/T_c)^n$ , with  $n \sim 2$ . The reduced  $H_{\text{irr}}(T/T_c)$  line is positioned between those of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  in the  $H$ - $T$  plane, close to  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ . The critical current density  $J_c(T)$  was extracted from the Bean critical-state model and showed a smooth temperature dependence. No significant difference was found for the general behavior of  $H_{\text{irr}}(T)$  and  $J_c(T)$  of  $(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-y}$  from those of oxide high- $T_c$  superconducting cuprates (HTSC). The off-plane space remains the important parameter to evaluate interlayer coupling of the oxyhalide HTSC, which is consistent with oxide HTSC. The results suggest the potential application capability of the oxyhalide superconductors even though the off-plane block is composed of oxyhalide instead of the routine oxides.

## I. INTRODUCTION

High-pressure synthesis paves a unique pathway to approach high- $T_c$  superconducting cuprates (HTSC). Since the historical discovery of high- $T_c$  superconductivity in the perovskitelike cuprate oxides in 1986 by Bednorz and Müller,<sup>1</sup> a large amount of oxide HTSC have been found. Actually halide can be the candidate anion besides oxygen in perovskite structures.<sup>2</sup> So far it is the consensus that the so-called  $[\text{CuO}_2]$  plane is indispensable to the superconductivity of HTSC. Leaving the  $[\text{CuO}_2]$  plane unchanged but replacing the anion of the off-plane block by, e.g., halide, would be an exciting quest for new HTSC. The oxyhalide cuprate superconductors<sup>3-5</sup> are appealing not only because of the fundamental values, but also the potential impact on the application implementation of HTSC.  $(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-y}$  is isostructural with  $(\text{La,Sr,Ca})_3\text{Cu}_2\text{O}_6$ ,<sup>6</sup> with  $(\text{La,Sr,Ca})$  being replaced by  $(\text{Sr,Ca})$ , and the apical oxygen by Cl. The stoichiometric parent compound  $(\text{Sr,Ca})_3\text{Cu}_2\text{O}_4\text{Cl}_2$ , with the average  $\text{Cu}^{2+}$  valence state is an antiferromagnetic insulator. To obtain superconductivity in HTSC, appropriate carrier

doping from the off-plane layers into the  $[\text{CuO}_2]$  layer is needed. Regarding the structure feature, the  $p$ -type doping mechanism has been proposed through a partial substitution of divalent  $\text{O}^{2-}$  for the monovalent  $\text{Cl}^{1-}$ , and thus to generate holelike carriers. Since all the Cl ions reside at the apex anion position, the doping mechanism is called "apical oxygen doping" to address the process that not only creates  $p$ -type carries, but also induces apical oxygen, which otherwise is absent in the parent structure. The structure is termed of "0212-Cl" in the nomenclature of "four-number nomination" of HTSC, referring to the "0212" structure but consisting of Cl-containing off-plane block. The "0212-Cl" crystal is built of double  $[\text{CuO}_2]$  planes and two layers of rock-salt type off-plane block as shown in the schematic view of Fig. 1.

## II. EXPERIMENT

The samples were synthesized in two steps. First is the ambient preparation of precursors, and second the high-pressure synthesis of the target compounds. Single phase

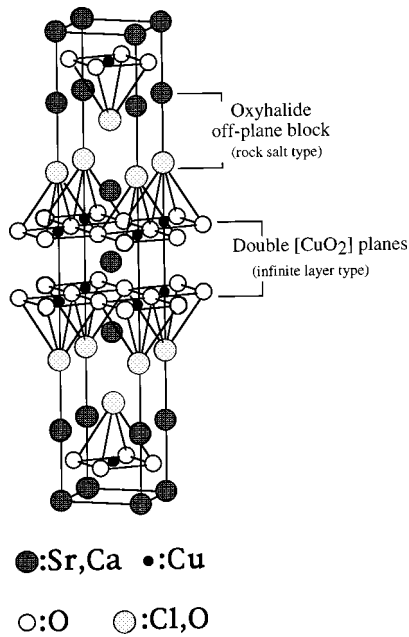


FIG. 1. The crystal structure of  $\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-y}$ , consisting of double  $[\text{CuO}_2]$  layers, and rock-salt-type off-plane block with chlorine residing at the apical anion site relative to the  $[\text{CuO}_2]$  plane.

precursor materials of  $\text{Sr}_2\text{CuO}_3$ ,  $\text{SrCuO}_2$ , and  $\text{Ca}_2\text{CuO}_3$ , as well as  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  or  $\text{Ca}_2\text{CuO}_2\text{Cl}_2$  (serving the chlorine source in the following high-pressure synthesis) were prepared by solid-state reaction at ambient. The precursors were thoroughly mixed in a flowing argon-filled glove box, with  $\text{SrO}_2$  and  $\text{CuO}$  powders according to the nominal compositions of  $\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{4.4+y/2}\text{Cl}_{2-y}$ . An excess amount of  $\text{CuO}$  (e.g., 10% in mole), which in most cases remained the impurity in the final yield, was found to enhance the formation of the “0212” phase. Besides being a chemical composition of the starting mixture, the  $\text{SrO}_2$  reagent also plays an oxidizer agency to generate oxygen atmosphere during high-pressure synthesis. The oxygen partial pressure was controlled by the  $\text{SrO}_2$  amount in the starting materials, e.g., 0.4 mole ration  $\text{SrO}_2$  was used in  $\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{4.4+y/2}\text{Cl}_{2-y}$ . The pressed pellets of the mixtures were loaded into an Au capsule and subjected to high-pressure synthesis. Graphitic sleeve has being the electric heater and phyrophyllite the pressure transmission medium in the high-pressure unit cell. The high-pressure synthesis has been carried out on a cubic-anvil-type high-pressure apparatus. Pressure scale was calibrated in advance according to the phase transition points of Bi, Tl, and Ba metals. The temperature value was read from a temperature vs electric power output curve calibrated using Pt-Pt(Rh) thermocouple in a previous separate experiment. A typical operation of the synthesis was performed under 5.0 GPa and at  $\sim 1000^\circ\text{C}$  for 30 min. Then the sample was rapidly cooled by turning off the electric power before the pressure was slowly released.

The structures were analyzed by means of x-ray powder diffraction with  $\text{Cu } K_\alpha$  radiation, high-resolution transmission electron microscopy, and the energy dispersive x-ray spectroscopy of a scanning electron microscopy (SEM-EDX). The superconducting properties of the samples were characterized by the dc electrical resistivity using a standard

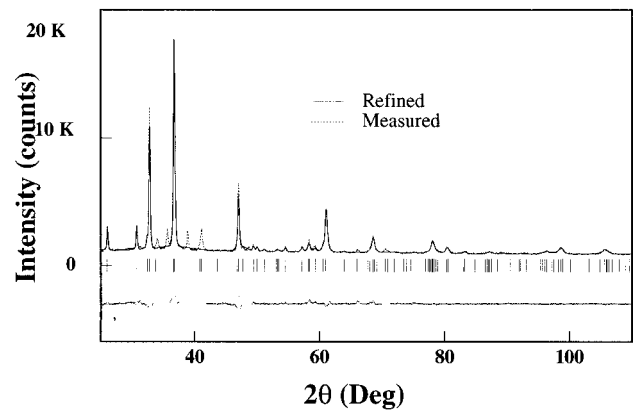


FIG. 2. The x-ray powder diffraction pattern for  $\text{Sr}_{2.3}\text{Ca}_{0.7}\text{Cu}_{2.0}\text{O}_{4.0+\delta}\text{Cl}_{1.3}$ . The dashed line is the measured one; solid line is the calculated from the Rietveld refinement based on a “0212-Cl” crystal-structure model. The difference curve (observed minus calculated) is plotted at the bottom.

four-probe method, and by dc susceptibility measurement using superconducting quantum interference device (SQUID) magnetometer. The accuracy of the magnetization resolution of the SQUID magnetometer was better than  $10^{-6}$  emu, which corresponds to the accuracy  $10 \text{ A/cm}^2$  in the resolution of critical-current density. The irreversibility line and intragrain critical-current density were obtained from isothermal magnetic hysteresis loop measurements performed on the sintered bulk sample with randomly oriented grain alignments. The magnetic field was changed in the “step-by-step” mode with 60 s interval before each magnetization measurement.

### III. RESULTS AND DISCUSSION

Figure 2 shows the powder x-ray diffraction pattern of the sample  $\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-y}$  with  $x=0.7$  and  $y=0.7$ , together with the results of Rietveld refinement. The sample is nearly single phase of “0212-Cl” with minor impurities ( $\text{CuO}$  and an unidentified phase). The SEM-EDX analysis on the random grains revealed that the detected composition for the separate grain is close to the formal composition. The average Sr:Ca:Cu:Cl atomic ratio over tens of well-grown grains is approximately 2.1:0.9:2.0:1.3, in general agreement with the proposed structure formula, suggesting that the chlorine has been significantly incorporated into the crystal. Further structure refinements based on “0212-Cl” model give a reasonable  $R_{\text{wp}}$  factor of 5.69%, as shown in Table I. Resulting from the larger Cl ion size, the  $22.16 \text{ \AA}$   $c$ -axis length of “0212-Cl” is substantially longer than that of  $20.6 \text{ \AA}$  for the oxide 0212 compound  $(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{6+\delta}$  (Ref. 7) and  $21 \text{ \AA}$  for  $\text{Sr}_3\text{Cu}_2\text{O}_{6+\delta}$ .<sup>8</sup> Figure 3(a) shows the data of dc magnetic susceptibility measurements performed in both zero-field cooling (ZFC) and field cooling (FC) modes using SQUID magnetometer at a 10 Oe applied field. The superconducting volume fraction is estimated to be 39% at 5 K from the FC signals without demagnetization correction. The demagnetization field correction reduces the measured susceptibility by about 25% for our sample geometry of a rectangular-like bulk shape. Therefore, we believe that the measured field cooling diamagnetic response is above 50% of the

TABLE I. Refined atomic parameters for  $\text{Sr}_{2.3}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{4.7}\text{Cl}_{1.3}$ . Space group  $I4/mmm$ ,  $a=b=3.8679(2)$  Å,  $c=22.161(1)$  Å.  $\rho^{\text{calc}}=4.78$  g/cm<sup>3</sup>, weighted profile  $R_{\text{wp}}=5.69\%$ ; expected  $R_e=2.78\%$ . Values in the parentheses are the standard deviation in the last digit.

| Atom       | Site | $x$ | $y$ | $z$       | Occupancy  | $B_{\text{ISO}}$ (Å <sup>2</sup> ) |
|------------|------|-----|-----|-----------|------------|------------------------------------|
| (Sr/Ca)(1) | 2a   | 0   | 0   | 0         | 0.5/0.5(3) | 3.0/1.0                            |
| (Sr/Ca)(2) | 4e   | 0   | 0   | 0.1507(8) | 0.9/0.1(2) | 2.0/1.0                            |
| Cu         | 4e   | 0   | 0   | 0.428(1)  | 1.0        | 1.0                                |
| O(1)       | 8g   | 0.5 | 0   | 0.428(1)  | 1.0        | 3.0                                |
| O(2)       | 4e   | 0   | 0   | 0.31(2)   | 0.38(18)   | 2.0                                |
| Cl         | 4e   | 0   | 0   | 0.298(8)  | 0.62(18)   | 3.0                                |

full Meissner signal. Caution should be made to identify the responsible phase for the discussed physical property such as the superconductivity in the text in a multiphase sample. This has been particularly addressed by Scott *et al.*<sup>9</sup> to the high-pressure synthesized Sr-Cu-O yields with chlorine containing oxidizer. The yields showed low superconducting volume fraction, which was assigned to  $\text{Sr}_3\text{Cu}_2\text{O}_5\text{Cl}$ , a phase detected using a very special combination of scanning SQUID petrology. The large superconducting volume fraction in our sample ensures the bulk superconducting transition in nature, supporting the concept that the superconductivity comes from the major phase “0212-Cl.” Figure 3(b) shows the curve of resistivity vs temperature of the sample.

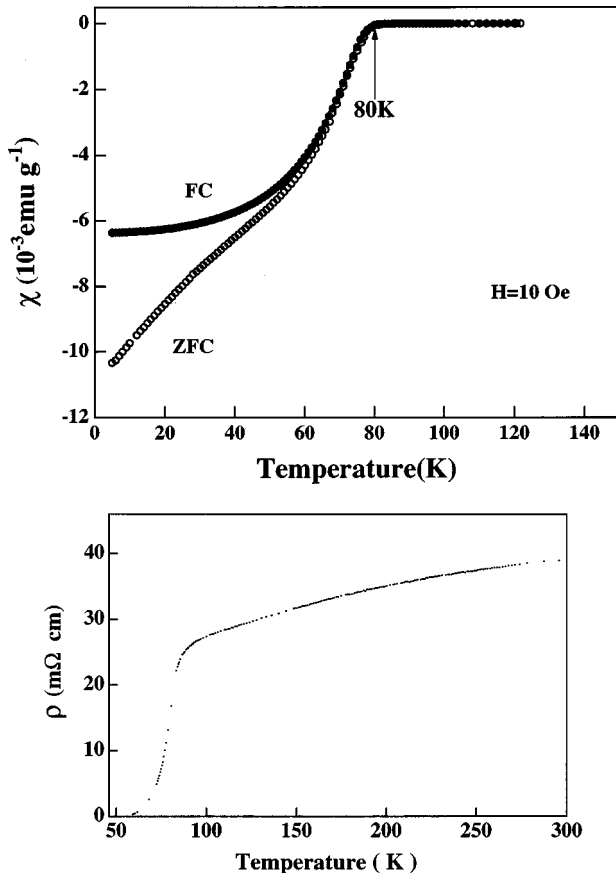


FIG. 3. (a) The temperature dependence of dc magnetic susceptibility of  $\text{Sr}_{2.3}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{4.0+\delta}\text{Cl}_{1.3}$  at both zero field cooling (ZFC) and field cooling (FC) modes; (b) the curve of resistivity vs temperature of the sample.

Both magnetic and resistivity measurements showed the superconducting transition occurred around 80 K.

The irreversibility field  $H_{\text{irr}}$  and the reduced  $H_{\text{irr}}(T/T_c)$  line are among the top concerns of the flux dynamics research of HTSC for both the theory and applications. In particular the  $H_{\text{irr}}(T/T_c)$  line location in  $H$ - $T$  plane gives the direct information on the capabilities of the superconductors to be practically running at high-temperature regions close to  $T_c$ .  $\text{YBa}_2\text{Cu}_3\text{O}_7$  keeps the high position of  $H_{\text{irr}}(T/T_c)$  line almost in the entire temperature range below  $T_c$ , showing the best comprehensive superconducting properties hitherto. The  $H_{\text{irr}}(T)$  above which an obvious energy dispersion takes place was chosen as a field of the appearance/disappearance of the undetectable difference between the magnetization for decreasing and increasing magnetic field. It is noted that the  $H_{\text{irr}}(T)$  increases with increasing the angle between the  $c$  axis and applied field.<sup>10</sup> Since the sample is polycrystalline, in order to compare the measurements with those of literature reports on single crystals ( $H//c$ ) of the oxide HTSC, a criterion of 0.2 G was chosen to make a preliminary estimation of the  $H_{\text{irr}}(T)$  of “0212-Cl.” The criterion was found to meet with the general conditions employed for single crystals or  $c$ -axis aligned powder samples.<sup>11</sup> Using the criterion will not overestimate the irreversibility field of the polycrystal, meanwhile the criterion is also of technological interest (corresponding to  $10^4$  A/cm<sup>2</sup> via Bean model—the threshold value for general applications). Figure 4 shows the  $H_{\text{irr}}(T)$  data of “0212-Cl” plotted with the reduced temperature scale  $(1 - T/T_c)$ , together with those of routine oxide HTSC for comparison.

The irreversibility field  $H_{\text{irr}}(T)$  obtained near  $T_c$  is often described by the power law dependence  $H_{\text{irr}}(T) = H_{\text{irr}}(0)(1 - T/T_c)^n$ , where the exponent  $n$  is a model-dependent parameter. Value  $n = 3/2$  is predicted in the framework of “giant-flux creep” description,<sup>12,13</sup> while  $n = 2$  in the flux melting model.<sup>14,15</sup> It is noted that the estimated irreversibility fields of “0212-Cl” basically take the similar shape to those of oxide HTSC. The experimental data of “0212-Cl” can be approximated to the power-law temperature dependence with  $n \sim 2$ , suggesting that the  $H_{\text{irr}}(T)$  of “0212-Cl” may be controlled by the vortex lattice melting process.

The selected HTSC in Fig. 4 are all double-[CuO<sub>2</sub>] layered.<sup>16</sup> The compounds were reasonably doped giving the optimum transition temperatures of 91.4 K for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , 89 K for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ , and 120 K for  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ . Figure 4 shows that the reduced

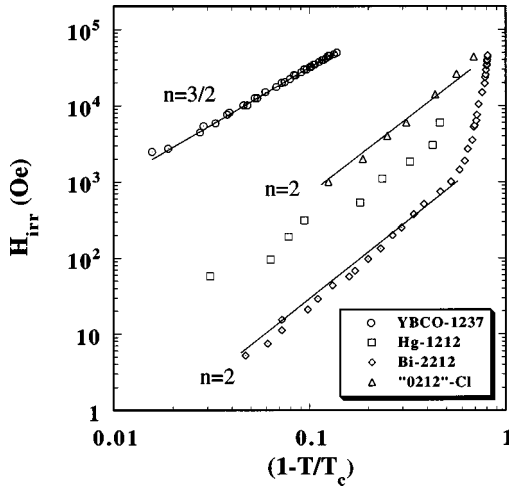


FIG. 4. The irreversibility field vs temperature of “0212-Cl” superconductor  $\text{Sr}_{2.3}\text{Ca}_{0.7}\text{Cu}_{2.0}\text{O}_{4.0+\delta}\text{Cl}_{1.3}$  in the reduced log-log scales ( $\Delta$ ). The experimental data could be described by a power law behavior of  $H_{\text{irr}}(T) = H_{\text{irr}}(0)(1 - T/T_c)^n$  with  $n \sim 2$  (the solid line). Also included are those for the double  $[\text{CuO}_2]$  layered oxide HTSC:  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c$  91 K);  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  ( $T_c$  120 K), and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  ( $T_c$  89 K).

$H_{\text{irr}}(T/T_c)$  line of “0212-Cl” is located intermediate between those of YBCO-1237 and Bi-2212, close to Hg-1212. This is an encouraging fact to develop application-oriented multilayered oxyhalide superconductors.

The irreversibility fields are complex in nature but are basically flux pinning behaviors closely related to the interlayer coupling between  $[\text{CuO}_2]$  conducting planes across the off-plane block. Intrinsically the interlayer coupling depends on the thickness of the off-plane block as well as the structure details of the block such as composition, chemical bonding, and conductivity, etc. Among the well-known HTSC the double BiO layers lead Bi-22( $n-1$ ) $n$  to the extremely longer interlayer distance, resulting in much weak interlayer coupling, which severely suppresses the  $H_{\text{irr}}(T)$  at high-temperature region. On the other hand, the metallic  $[\text{CuO}_{2-\delta}]$  layer intervening the off-plane block may short-circuit the  $c$ -axis tunneling in YBCO-1237. Therefore the effective interlayer distance for YBCO-1237 can be halved from the full off-plane space  $\sim 8.6$  Å to  $\sim 4.3$  Å, giving rising to a unique strong coupling strength and much improved pinning properties, which ensure the very high reduced  $H_{\text{irr}}(T/T_c)$  line at almost entire  $H$ - $T$  plane.<sup>17-19</sup> The effective interlayer space for HTSC thus analyzed is  $\sim (8.6/2)$  Å for YBCO-1237,<sup>20</sup>  $\sim 7.8$  Å for “0212-Cl” (calculated from the data in Table I),  $\sim 9.5$  Å for Hg-1212,<sup>21</sup> and  $\sim 12$  Å for Bi-2212.<sup>22</sup> Focusing on the off-plane constructions, “0212-Cl” is composed of oxyhalide and rock-salt (RS) type  $(\text{Sr,Ca})(\text{Cl,O})/(\text{Sr,Ca})(\text{Cl,O})$  sheets, while YBCO-1237, Bi-2212, and Hg-1212 are all of oxides, but with perovskite-type  $\text{BaO}[\text{CuO}_{2-\delta}]/\text{BaO}$ , RS-type  $\text{SrO}/\text{BiO}/\text{BiO}/\text{SrO}$ , and RS-type  $\text{BaO}/\text{HgO}_{1-\delta}/\text{BaO}$  sheets, respectively. Therefore it suggests that the thickness instead of the composition of the off-plane block plays a dominant role in the interlayer coupling and consequently the flux dynamics to the HTSC. This is supported with the fact in Fig. 4 that the reduced  $H_{\text{irr}}(T/T_c)$  line systematically shifts to high fields with decreasing the off-plane space.

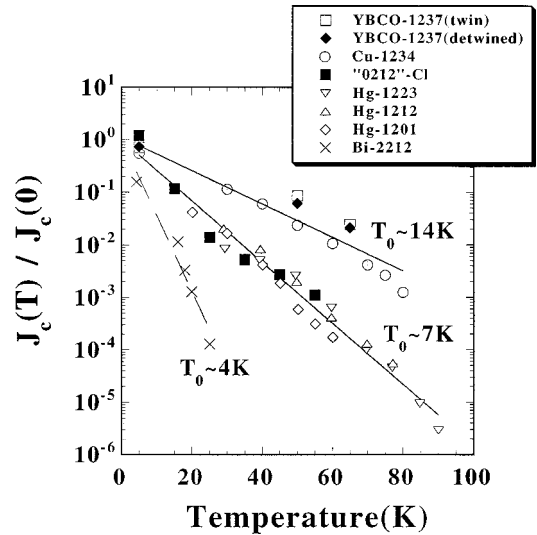


FIG. 5. The normalized critical current density  $J_c(T)/J_c(0)$  to the Arrhenius function  $J_c(T) = J_c(0) \exp(-T/T_0)$  for  $\text{Sr}_{2.3}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{1.3}$  superconductor ( $\blacksquare$ ) in 1 T external field. Also included are those of  $J_c(T)/J_c(0)$  for a group of oxide HTSC:  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c$  93 K);  $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$  ( $T_c$  117 K);  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  ( $T_c$  85 K, 128 K, and 135 K for  $n=1, 2$ , and 3, respectively); and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  ( $T_c$  85 K). The data can be roughly viewed into three groups: YBCO-1237 and Cu-1234 with an average  $T_0 \sim 14$  K; “0212”-Cl and Hg-12( $n-1$ ) $n$  with an average  $T_0 \sim 7$  K; and Bi-2212 with  $T_0 \sim 4$  K.

It is shown that in the temperature range close to  $T_c$ , e.g., for  $(1 - T/T_c) < 0.5$ , curve fitting to the power law relation gives the exponent  $n$  approximately between 1.5 and 2. Value  $n=1.5$  corresponds to the strongly coupled YBCO-1237 with low degree of anisotropy, while  $n=2$  to the weakly coupled Bi-22( $n-1$ ) $n$  with high degree of anisotropy, which is one of the keys to the  $H_{\text{irr}}(T)$  location near  $T_c$ .<sup>15</sup> Figure 4 suggests that the “0212”-Cl may have the moderate interlayer coupling with an anisotropy degree intermediate between those of YBCO-1237 and Bi-2212. Based on the magnetization hysteresis loop measurements below the reversible field, the intragrain critical current density  $J_c$  was estimated according to the Bean critical-state model.<sup>23</sup> Assuming the spherical shapes of the grains, then  $J_c$  ( $\text{A}/\text{cm}^2$ ) =  $30\Delta M/d$ , where  $\Delta M$  (Gauss) is the difference of magnetic moment during increasing and decreasing field, and  $d$  (cm) is the average dimension of the crystal grains, which was taken  $5 \mu\text{m}$  according to the SEM observation. For certain HTSC, the magnetic hysteresis  $\Delta M$  were found to decrease substantially with increasing temperature. The  $\Delta M$  can be generally described by the Arrhenius-type temperature dependence, which is an indication of the thermally activated flux motion. In turn the intragranular critical current density  $J_c$  can be approximated to the temperature relation  $J_c(T) = J_c(0) \exp(-T/T_0)$ ,<sup>24</sup> where  $T_0$  is a fitting parameter and provides a rough measure to the decaying speed of  $J_c$  with increasing temperature. Applying the Arrhenius function to the “0212-Cl” data gives a fitted  $T_0$  value of about 7 K. Figure 5 presents the normalized  $J_c(T)$  over  $J_c(0)$  for the “0212-Cl” at 1 T applied field, as well as the reported results on oxide HTSC for reference. Again the “0212-Cl” shows no obvious difference in the general trend

from those of oxide HTSC. Here we point out that the samples are just as prepared and are not subjected to specified post-treatment, e.g., by neutron irradiation, which can substantially enhance  $J_c$  in orders of magnitude by inducing strong extrinsic pinning sites.

As a comparison, Figure 5 also shows the  $J_c(T)/J_c(0)$  data for a group of oxide HTSC (Ref. 25) including the twin and detwined  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (both  $T_c$  93 K),  $\text{HgBa}_2\text{CuO}_{4+\delta}$  ( $T_c$  85 K),  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  ( $T_c$  128 K),  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  ( $T_c$  135 K),  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  ( $T_c$  85 K), and  $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$  ( $T_c$  117 K). Among the compounds ‘‘0212-Cl’’ shows a temperature dependence of  $J_c$  relative smooth to that of Bi-2212 and comparable to Hg-12( $n-1$ ) $n$ . Regarding the evolution trend,  $J_c$  behavior presented in Fig. 5 can be roughly viewed into three groups. YBCO-1237 and Cu-1234 rank in the most steady ones characterized by an average  $T_0$  of  $\sim 14$  K, followed by Hg-12( $n-1$ ) $n$  and ‘‘0212-Cl’’ with an average  $T_0$  of  $\sim 7$  K, and then the Bi-system with  $T_0$  of  $\sim 4$  K.

The critical-current density of type-II superconductor is governed by the flux-pinning states. A few factors contribute to the flux-pinning process such as (1) intrinsically the thermodynamic critical field  $H_c$  and the coherence length  $\xi$ , which is of the order of lattice parameter for HTSC, (2) the size and density of defects, which can be the possible effective extrinsic pinning sites once the size becomes comparable to the coherence length or to the lattice parameter. To keep the rigid three-dimensional flux lines from breaking down, consequently maintain higher critical current density, one certainly needs to improve the interlayer coupling of the adjacent  $[\text{CuO}_2]$  planes. Crystallographically, Cu-12( $n-1$ ) $n$  contains the very similar off-plane block to YBCO-123 (Ref. 26) (note, Cu-1212 is isostructural with YBCO-123). Therefore the evolution trend of  $J_c(T)/J_c(0)$  with temperature in Fig. 5 corroborates that a shorter effective interlayer space (hence stronger interlayer coupling strength) shall be crucial to build up an alternative HTSC of rigid flux pinning and improved  $J_c$  properties.

So far both the data on  $H_{\text{irr}}(T)$  and  $J_c(T)$  revealed that the oxyhalide HTSC can behave in a comparable way to those of oxide HTSC. This would give some insight into the systematic treatment of the oxide and oxyhalide HTSC. The results should be inspiring in line with developing new multilayered oxyhalide superconductors aiming at high  $T_c$  and good performance in conjunction with the oxide counterparts.

In summary, chlorine containing high- $T_c$  superconductor  $(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-y}$  or ‘‘0212-Cl’’ has been synthesized under 5.0 GPa and at  $\sim 1000$  °C. Bulk superconducting transition with temperature up to 80 K has been achieved. Superconducting properties of irreversibility field and intra-grain critical current density of the as-prepared ‘‘0212-Cl’’ were investigated and compared with the related oxide HTSC. The irreversibility fields of ‘‘0212-Cl’’ can be described by the power law relation  $(1-T/T_c)^n$  with  $n \sim 2$ . The reduced  $H_{\text{irr}}(T/T_c)$  line is positioned intermediate between those of YBCO-1237 and Hg-1212 in the  $H$ - $T$  plane. It is shown that ‘‘0212-Cl’’ has a relative smooth temperature dependence of critical-current density to that of Bi-2212 and comparable to Hg-12( $n-1$ ) $n$ . The results indicate that with the oxyhalide containing off-plane block, the present ‘‘0212-Cl’’ superconductor shows no systematic differences in the general manner from those of oxide HTSC. This implies that the interlayer coupling behavior seems more sensitive to the off-plane space than to the concrete composition. Inducing one more anion into HTSC would open an alternative access to new HTSC, while the possible joint usage of oxide and oxyhalide HTSC certainly offers more opportunities and flexibility to the fundamental research and industrial applications.

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