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Halooxocuprate Superconductors and Related Compounds with the 02(n − 1)n and 0222 Structures

S. Adachi,* T. Tatsuki, T. Tamura, and K. Tanabe

SRL-ISTEC, 1-10-13 Shinonome, Koto-ku, Tokyo 135-0062, Japan

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Halooxocuprates with the so-called 02(n − 1)n (n = 1−5) and the 0222 structures, containing F, Cl, and Br, are reviewed. These compounds are prepared by conventional solid-state reaction: low-temperature fluorination or high-pressure synthesis. Their structural properties and superconductivity are focused on in this review. Bulk superconductivity has been observed in various samples prepared using high-pressure techniques. On the other hand, the reported halooxocuprate superconductors prepared at ambient pressure need more data for verification of superconducting behavior. The carrier-doping routes for the halooxocuprates are discussed. It is confirmed that p-type superconductivity occurs in oxychlorides in which the apical sites are completely occupied by chlorine. This indicates that the existence of the apical oxygen is not a must for high-T_c superconductivity with p-type carriers.

Contents

1. Introduction

Since the discovery of high-T_c superconductivity, a huge number of superconducting cuprates have been found. All of them have a layered structure containing two-dimensional CuO_2 sheets. It is well-established that the CuO_2 sheet in the structure is responsible for the high-T_c superconductivity. When a moderate level of hole or electron carriers are doped into the sheets, superconductivity with p-type or n-type carriers is induced, respectively. From the viewpoint of crystal structure, the former cuprate superconductor contains copper ions which are pyramidally or octahedrally coordinated with oxygen, while the latter contains copper in a planar coordination. This picture is currently widely accepted for cuprate superconductors.

It is known that there are halogen-containing cuprates, or halooxocuprates, in which copper ions are coordinated with four oxygen ions, forming the CuO_2 sheet, and the halogen ion occupies a so-called apical site.[1] For example, the crystal structure of $Sr_2CuO_2Cl_2$ is illustrated in Figure 1(b). That of $La_{1.85}Sr_{0.15}CuO_4$, which is a 40 K class p-type superconductor is also drawn in Figure 1a, for comparison. The Sr_2Cl_2 rock-salt block is considerably puckered, though these two structures are very similar. It is expected that a proper carrier doping would induce superconductivity in $Sr_2CuO_2Cl_2$ and other halooxocuprates. Many researchers have attempted carrier doping into the halooxocuprates. However, for about 7 years after the discovery of high-T_c cuprates, no one had succeeded in preparing a superconducting halooxocuprate. In 1994, the first halooxocuprate superconductor, $Sr_2CuO_2F_{2.6}$ (T_c = 46 K), was reported by Al-Mamouri et al.[2] This report stimulated further research on these halooxocuprates. Since then, various halooxocuprates have been synthesized and some of them have exhibited superconductivity.

In this review, we make a general survey of recent research on the halooxocuprates. Here, we focus on halooxocuprates in which the apical site is mainly occupied by halogen ions (occupancy, $g \geq 0.5$), although there are many reports on cuprates containing halogen ions. Studies on the compounds with the crystal structures which are illustrated in Figure 1b−d are reviewed. The structure b is constructed by alternately stacking the puckered A_2X_2 rock-salt block (A = alkaline earth, X = halogen) and the CuO_2 sheet. The structures c and d are made by inserting the so-called infinite-layer block and the fluorite block, respectively, into the structure b. It can be expected that there is a homologous series having various numbers of CuO_2 sheets (n) in the structure c. The structure b is considered as the first member of such a series. Structural types of the high-T_c cuprates are often denoted by the combination of element(s) and four indices,[3] for example Bi-2223, Tl-1234, Hg-1223, and so on. In this review, halooxocuprates with the 02(n − 1)n (structures b and c) and 0222 (structure d) structures are surveyed. Table 1 lists the compounds which are reviewed here.[1−26] They are classified by the contained halogen element and the cation occupying the site next to the apical site.

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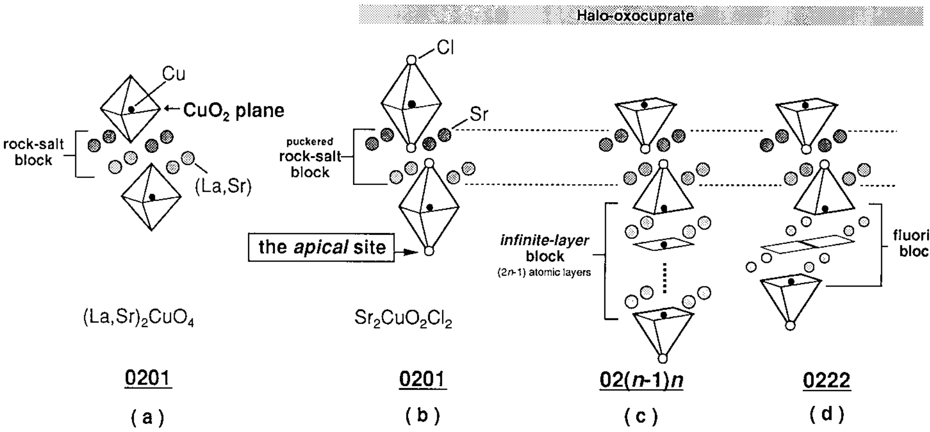

Figure 1. Schematic illustration of (a) 0201 cuprate, $La_{1.85}Sr_{0.15}CuO_4$, (b) 0201 oxychloride, $Sr_2CuO_2Cl_2$, (c) 02(n − 1)n halooxocuprates, and (d) 0222 halooxocuprates.

Table 1. Halooxocuprates with the 02(n − 1)n Structure, $A_2Ca_{n-1}Cu_n(O,X)_{2(n+1)+\delta}$ and the 0222 Structure, ALnCuO$_3$Cl

X	A	phase	chemical formula	a (Å)	b (Å)	c (Å)	T_c (K)	remarks[a]	ref
F	Sr	0201	$Sr_2CuO_2F_{2.6}$	5.394(1)	5.513(1)	13.468(3)	46[b]	f	2
		0201	$Sr_{1.8}Ba_{0.2}Cu(O,F)_{4+\delta}$	5.452(5)	5.481(5)	13.520(12)	68[b]	f	4
		0201	$La_{0.7}Sr_{1.3}Cu(O,F)_{4+\delta}$	3.9368(7)		13.075(4)	55[b]	f	5
		0212	$Sr_2Nd_{0.2}Ca_{0.8}Cu_2O_5F$	3.8609(7)		20.075(4)	85[b]	hp	6
		0212	$Sr_2CaCu_2O_{4.6}F_2$	3.843(1)		19.88(1)	99	hp	7
		0223	$Sr_2Ca_2Cu_3O_{6.2}F_{3.2}$	3.840(1)		26.17(1)	111	hp	7
		0234	$Sr_2Ca_3Cu_4O_{8+\delta}F_{2+y}$	3.852(2)		32.58(2)	40	hp	8
		0245	$Sr_2Ca_4Cu_5O_{10+\delta}F_{2+y}$	3.860(2)		39.17(1)	40	hp	8
F	Ba	0201	$Ba_2Cu_{1.1}O_2F_2$	3.922		14.56	34	hp	9
		0212	$Ba_2CaCu_{2.2}O_{4.4}F_{1.6}$	3.876		20.976	106	hp	9
		0223	$Ba_2Ca_2Cu_3O_{6.25+\delta}F_{1.3}$	3.860		27.42	109	hp	9, 10
Cl	Ca	0201	$Ca_2CuO_2Cl_2$	3.866		14.975	-		11
		0201	$(Ca,Na)_2CuO_2Cl_2$	3.8459(1)		15.1856(5)	28	hp	12,13
		0201	$(Ca,K)_2CuO_2Cl_2$	3.856		15.27	24	hp	14
		0212	$Ca_3Cu_2O_4Cl_2$	3.863		21.364	-		15
		0212	$(Ca,Na)_2CaCu_2O_4Cl_2$	3.85		21.45	49	hp	16
		0222	$CaSmCuO_3Cl$	3.901(1)		13.430(1)	-		17
		0222	$CaGdCuO_3Cl$	3.888(1)		13.389(1)	-		17
		0222	$CaErCuO_3Cl$	3.84		13.34	-	hp	18
Cl	Sr	0201	$Sr_2CuO_2Cl_2$	3.9716(2)		15.6126(2)	-		19
		0212	$La_{1.6}Sr_{0.4}CaCu_2O_5Cl$	3.827		19.42	34		20
		0201	$Sr_2Cu(O,Cl)_{4-\delta}$	3.94		15.6	-	hp	21
		0212	$(Sr,Ca)_3Cu_2(O,Cl)_{6-\delta}$	3.88		22.1	83	hp	22,23
		0223	$(Sr,Ca)_4Cu_3(O,Cl)_{8-\delta}$	3.881		28.63	35	hp	23
		0222	$SrNdCuO_3Cl$	3.956(1)		13.880(2)	-		17
Cl	Ba	0201	$Ba_2CuO_2Cl_2$	4.1026(3)		16.442(1)	-	hp	24
Br	Ca	0201	$Ca_2CuO_2Br_2$	3.875		17.264	-		11
		0212	$Ca_3Cu_2O_4Br_2$	3.8651(2)		23.620(1)	-		25
		0201	$(Ca,Na)_2CuO_2Br_2$	3.858		17.257	24	hp	26

[a] Remarks: hp, high-pressure synthesis; f, low-temperature fluorination. [b] Small Meissner volume fraction (<6.8% at 5 K).

2. Synthesis

Synthetic methods for the compounds are given in Table 1. No remark means the preparation was accomplished by means of a conventional solid state reaction method. The 0201 superconductor with A = Sr (partly Ba), X = F is prepared by fluorinating F-free precursors, $(Sr,Ba,La)_2CuO_{3+\delta}$, noted with “f” in the table. The fluorination is carried out by heating the precursors at low temperatures, 200−300 °C, in a F_2-containing gas which needs to be handled with a great care because of its toxicity.[2] A more convenient fluorination method has been developed, that is, heat treatments of the precursors with reagents, instead of the toxic gas.[27] Several kinds of fluorination reagents, such as NH_4F,[28] NH_4HF_2,[29−31] MF_2 (M = Cu, Zn, Ag and Ni),[32] and XeF_2,[33] have been used instead of a F_2-containing gas. In the table, the compounds noted by “hp” are synthesized under high pressure (1.5−6 GPa). Either a flat-belt-type or cubic-anvil-type apparatus is utilized for generation of such high pressure. A graphite tube in a pressure-transmitting medium works as a furnace. Starting materials, which are mixed and pelletized in air or a drybox, are then charged into a gold or platinum capsule (sometimes no capsule is used). It is then placed into the graphite heater. BN or NaCl is placed between the heater and the capsule (sometimes the bare sample pellet) for electrical insulation. Recent activities in searching for new materials using the high-pressure technique have significantly increased the number of superconducting halooxocuprates and related compounds.

3. Oxyfluoride (X = F)

A. Sr-Based 0201 Oxyfluoride. Sr_2CuO_3 has a structure related to the K_2NiF_4-type [orthorhombic; a = 12.968(2) Å, b = 3.913(1) Å, and c = 3.499(1) Å] in

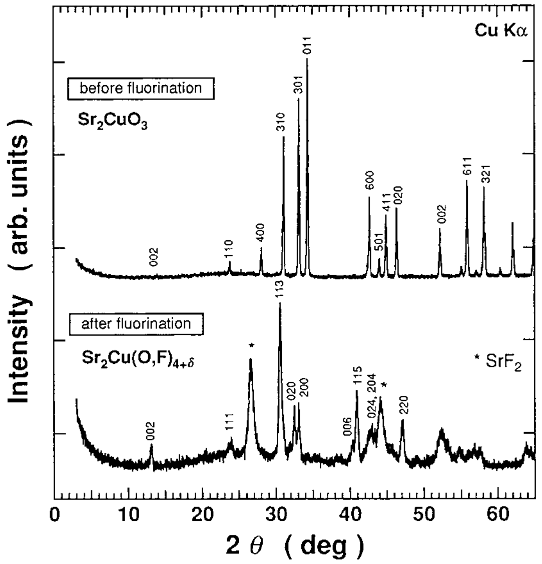

Figure 2. X-ray powder diffraction patterns for Sr_2CuO_3 before and after fluorination.[4]

which ordered oxygen vacancies form one-dimensional CuO chains.[1] Al-Mamouri et al.[2] found that the phase drastically changes by low temperature fluorination. Figure 2 shows X-ray powder diffraction (XRD) patterns for Sr_2CuO_3 before and after fluorination.[4] The pattern drastically changes from the ambient phase of Sr_2CuO_3 to an orthorhombic K_2NiF_4 structure with lattice parameters of $a = 5.394(1)$ Å, $b = 5.513(1)$ Å, and $c = 13.468(3)$ Å. The distance of Cu−Cu in the CuO_2 sheet is estimated to be 3.856 Å, being comparable to other p-type superconducting cuprates. In the XRD pattern after the fluorination, peaks due to SrF_2 are also seen. During the fluorination, fluorine easily reacts with strontium to form SrF_2. No one has succeeded in preparing pure samples that does not contain this impurity. Al-Mamouri et al.[2] estimated the fluorine content of the resultant K_2NiF_4-type compound to be ~2.6 and Slater et al.[32] reported the existence of a continuous CuO_2 sheet in the resultant $Sr_2CuO_2F_{2.6}$, as revealed by a neutron diffraction study. X-ray emission and photoelectron studies revealed that fluorine is preferentially bonded to strontium.[34] These reported results suggest that the resultant oxyfluoride is a K_2NiF_4 phase which contains interstitial fluorine as well as fluorine completely occupying the apical site. In other words, $Sr_2CuO_2F_{2.6}$ seems to be constructed by alternately stacking the CuO_2 sheet and the Sr_2F_2 rock-salt block with interstitial fluorine. Diamagnetic signals are detected in the fluorinated Sr_2CuO_3 below 46 K, as shown in Figure 3.[4] It was found that partial substitution of barium for strontium pushes the T_c up to >60 K.[4,28,32] However, the intensity of the reported Meissner signals was too small to claim bulk superconductivity (less than 5% of the full Meissner signal). This weak diamagnetism makes identification of the superconducting phase difficult. Although some researchers explained that the small Meissner signals were attributable to a small particle size,[2,28,32,33,35] no one has provided a definite answer to this question at present. Other possibilities should be properly discussed.[31,36] It is necessary to develop a new synthetic method for preparing samples with Meissner signals large enough to claim bulk superconductivity.

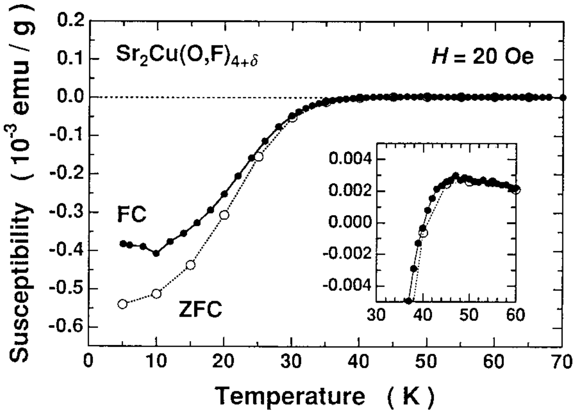

Figure 3. Temperature dependence of magnetic susceptibility detected from the fluorinated Sr_2CuO_3.[4]

In 1981, Nguyen et al.[37] reported that there is a solid solution in the $La_{2-x}Sr_xCuO_{4-\delta}$ system at a range of $0 \leq x \leq 1.3$. One end member, $La_{0.7}Sr_{1.3}CuO_{3.35}$, has a tetragonal K_2NiF_4 structure, in which the $(La,Sr)_2O_2$ rock-salt block is complete and an appreciable amount of oxygen in the CuO_2 sheet is missing. This compound was similarly fluorinated at low temperatures by Chen et al.[5] They observed a drastic change in the XRD patterns of the sample before and after fluorination. The lattice parameters of the major phase changed from $a = 3.7547(5)$ Å and $c = 12.896(4)$ Å to $a = 3.9368(7)$ Å and $c = 13.075(4)$ Å. For the fluorinated sample, Meissner signals below 55 K were observed. They considered that the resultant oxyfluoride, $La_{0.7}Sr_{1.3}Cu(O,F)_{4-\delta}$, is responsible for the observed Meissner signals. Furthermore, they discussed the possibility of acquiring an n-type superconducting cuprate with an apical anion from their experimental data: (1) the observed elongation of the c-axis length implied incorporation of apical anion, (2) the large a-axis length was comparable with that of n-type superconducting cuprates, (3) the superconducting volume fraction was improved by annealing in nitrogen gas. Similar results were reported for fluorinated samples of $Nd_{0.7}Sr_{1.3}Cu(O,F)_{4-\delta}$ ($a = 3.9288(5)$ Å, $c = 12.2630(2)$; $T_c = 44$ K)[38] and $Pr_{0.7}Sr_{1.3}Cu(O,F)_{4-\delta}$ ($a = 3.9372(3)$ Å, $c = 12.9496(2)$ Å; $T_c = 15$ K).[39] Here the indentification of the superconducting phase is also a problem, since the fluorinated samples did not exhibit Meissner signals large enough to claim bulk superconductivity. If the synthetic method to prepare high-quality samples were developed and the above-mentioned possibility of the n-type superconductor with apical anion were proven, it would be of particular interest to researchers studying the mechanism of high-T_c superconductivity.

B. Sr-Based 02(n − 1)n Oxyfluoride (n = 2−5). Kawashima et al.[7,8] prepared Sr−Ca−Cu−O−F samples with a variety of nominal compositions under a high pressure of 5.5 GPa. Samples containing the 02(n − 1)n phase (n = 2, 3, 4 or 5) as a major phase were successfully synthesized. It is well-known that a similar homologous series exists in the Sr−Ca−Cu−O system.[40−46] In this F-free system, the c-axis lengths are ~12.43, 20.74(6), 27.22(2), and 33.82(2) Å for n = 1, 2, 3, and 4, respectively.[42] The relationship between the lattice parameter c and the number of CuO_2 planes n for the high-temperature-synthesized homologous series is shown in Figure 4. The reported parameter for the

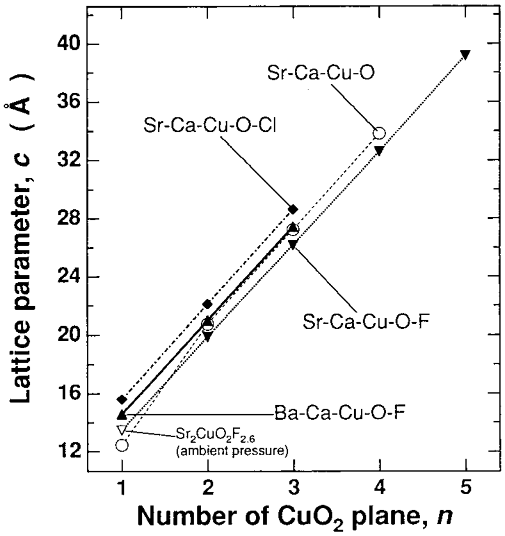

Figure 4. Relationship between lattice parameter *c* and the number of the CuO_2 plane *n* for the high-pressure-synthesized 02($n-1$)*n* homologous series in Sr−Ca−Cu−O (open circles),[42] Sr−Ca−Cu−O−F (filled inverted triangles),[7,8] Ba−Ca−Cu−O−F (filled triangles),[9,10] Sr−Ca−Cu−O−Cl (filled diamonds).[21,23] For comparison, the value for $Sr_2CuO_2F_{2.6}$ prepared at ambient pressure is also plotted (open inverted triangle).

firstmember of the Sr−Ca−Cu−O−F system, $Sr_2CuO_2F_{2.6}$,[2] prepared by low-temperature fluorination, is also plotted. For the Sr−Ca−Cu−O−F system, the parameter *c* increases linearly with increasing *n*. This implies that every member has an almost identical structure for the rock-salt block. The appreciable differences in the *c*-axis length between the Sr−Ca−Cu−O and Sr−Ca−Cu−O−F systems are seen. This suggests that fluorine is actually incorporated into the structure. A gradual increase in the parameter *a* with increasing *n* is observed. Generally, the parameter *a* of a homologous series of superconducting cuprates comes close to 3.851 Å, which is the *a*-axis length of the infinite-layer compound $CaCuO_2$, with increasing *n*.[47] However, such a tendency is not seen in the Sr−Ca−Cu−O−F homologous series. Probably, Sr incorporation into the Ca site in the infinite-layer block expands the *a*-axis length.

The partial pressures of oxygen and fluorine inside the sample capsule during high-pressure synthesis are crucially important to obtain samples of a certain phase with a suitable carrier concentration for high-T_c. Kawashima et al.[8] prepared samples with nominal compositions of $Sr_2CaCu_2O_{4+\delta}F_{2+y}$ and $Sr_2Ca_2Cu_3O_{6+\delta}F_{2+y}$ and found that these samples exhibited the highest T_cs of 99 and 111 K when $2\delta + y = 1.1$ and 1.6, respectively. The detected Meissner curves exhibited single-step transitions with quite large intensities.

Isobe et al.[6] prepared 0212 oxyfluoride samples containing rare earth elements, $Sr_2LnCu_2O_5F$ (Ln = Y, La, Nd, Sm, Gd, Dy, Er, and Yb), under a high pressure of 6 GPa. They successfully synthesized single-phase samples. X-ray Rietveld analysis suggested that the sample is essentially isostructural to the 0212-type $La_2SrCu_2O_6$[48] with half of the apical sites replaced by fluorine. Their sample of $Sr_2Nd_{0.2}Ca_{0.8}Cu_2O_5F$ exhibited superconductivity with T_c = 85 K and a Meissner volume fraction of 6.8% at 5 K. They considered that a small grain size, weak intergrain coupling, and/or weak pinning force is responsible for the small Meissner signals. It is well-known that the occurrence of superconductivity in Ln−(Sr,Ca)−Cu−O with the 0212 structure is very sensitive to cationic ordering.[49] It seems that the 0212 oxyfluoride containing rare earth has similar sensitivity.

C. Ba-Based 02($n-1$)*n* Oxyfluoride ($n = 1-3$). The Ba−Ca−Cu−O−F system was studied by Zenitani et al.[9] and Iyo et al.[10] using high-pressure techniques. Nearly single-phase samples of the n = 1, 2, and 3 members were synthesized. For the first member, a sample with a nominal composition of $Ba_2Cu_{1.1}O_2F_2$ was prepared.[9] The lattice parameters of the obtained 0201 phase were a = 3.922 Å and c = 14.56 Å. Zhang and Osamura[50] synthesized a F-free tetragonal Ba_2CuO_x with lattice parameters a = 3.9923(2) Å and c = 12.9686(2) Å. It was considered that fluorine incorporation in the structure altered the unit cell dimensions significantly. Bulk superconductivity below 34 K was observed in the 0201 oxyfluoride. For this series of oxyfluorides, a systematic decrease in *a* was observed with increasing *n*. The parameter *c* is longer than that for the Sr−Ca−Cu−O−F system, as shown in Figure 4. This observed difference in the parameter *c* is quite reasonable, considering the ionic radii of barium and strontium [$r(^{IX}Ba^{2+})$ = 1.47 Å, $r(^{IX}Sr^{2+})$ = 1.31 Å].[51] The parameter *a* approaches 3.851 Å, with increasing *n* (see Table 1). This change in the parameter *a* suggests that the volume fraction of the infinite-layer block $CaCuO_2$ actually increases with increasing *n*. The complete ordering of barium and calcium along the *c*-direction is probably attained. The T_cs of 106 and 109 K were recorded for the n = 2 and 3 samples, respectively. It was concluded that the samples of the third member were in an under-doped state, since they were prepared in rather low oxygen partial pressure[9] and a convex curve was observed for the temperature dependence of resistivity above T_c.[10] It is expected that further hole injection would raise the T_c of this member.

4. Oxychloride (X = Cl)

A. Ca-Based 02($n-1$)*n* Oxychloride (n = 1 and 2). Before the discovery of high-T_c superconductivity, the first member, $Ca_2CuO_2Cl_2$, had been well-known.[11] The second member of this oxychloride series, $Ca_3Cu_2O_4Cl_2$, was prepared by Sowa et al.[15] in 1989. It was expected that proper carrier doping would make them superconducting, because of the similarity in crystal structure to high-T_c superconductors. In 1994, Hiroi et al.[12] reported that partial substitution of sodium for calcium by using a high-pressure technique can introduce hole carriers into $Ca_2CuO_2Cl_2$, and bulk superconductivity with T_c = 26 K is induced. After that, Zenitani et al.[16] attempted sodium doping into $Ca_3Cu_2O_4Cl_2$ and successfully synthesized the superconducting oxychloride $(Ca,Na)_2CaCu_2O_4Cl_2$ with T_c = 49 K. Although Na^{1+} has a larger ionic radius than Ca^{2+} [$r(^{IX}Na^{1+})$ = 1.24 Å, $r(^{IX}Ca^{2+})$ = 1.18 Å],[51] the lattice parameter *a* decreased for both cases. This implies successful carrier doping with holes into the CuO_2 plane.[52] Results of an X-ray microanalysis[12] and neutron powder diffraction study[53] supported sodium incorporation in $(Ca,Na)_2CuO_2Cl_2$, but uncertainty remained because of difficulty in detecting sodium. Tatsuki et al.[14] used potassium

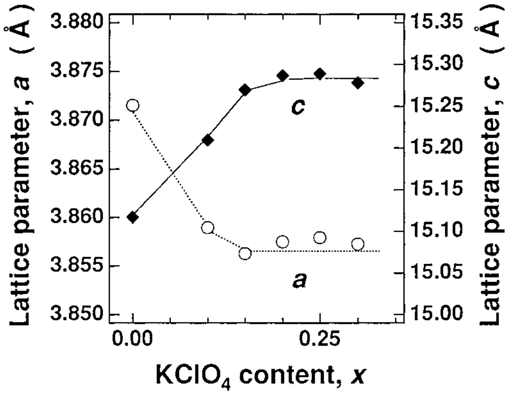

Figure 5. Lattice parameters vs x for the samples prepared at 900 °C for 30 min under the high pressure of 5 GPa from nominal compositions of $Ca_2CuO_2Cl_2 + xKClO_4$ ($0 \le x \le 0.3$).[14]

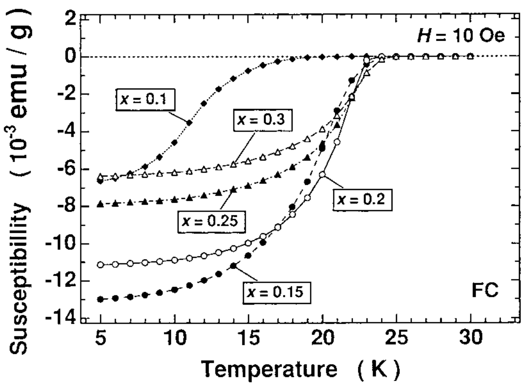

Figure 6. Temperature dependence of magnetic susceptibility for the samples prepared at 900 °C for 30 min under the high pressure of 5 GPa from nominal compositions of $Ca_2CuO_2Cl_2 + xKClO_4$ ($0 \le x \le 0.3$).[14]

instead of sodium as a dopant cation to confirm alkali metal doping. They successfully synthesized a nearly single-phase sample of $(Ca,K)_2CuO_2Cl_2$ exhibiting bulk superconductivity below 24 K. They prepared samples with compositions of $Ca_2CuO_2Cl_2 + xKClO_4$ ($0 \le x \le 0.3$) under high pressure of 5 GPa. Nearly single-phase samples with the K_2NiF_4 phase were obtained. Figure 5 shows the changes in lattice parameters against the amount of $KClO_4$, x. Although K^{1+} has a much larger ionic radius than Ca^{2+} [$r(^{IX}K^{1+}) = 1.55$ Å],[51] a decrease in the lattice parameter a was also observed. X-ray microanalyses using transmission and scanning electron microscopes (EDX-TEM, EDX-SEM) indicated that the crystal grains of the main phase really contained calcium, potassium, copper, and chlorine and their atomic ratio was 1.90:0.12:1.00:0.97. The Meissner curves for the samples are shown in Figure 6. The observed superconductivity seemed to be caused by hole-doping via partial substitution of potassium for calcium. Although the contribution of oxygen substitution for chlorine and interstitial anions to hole-doping is possible, it would not be substantial.

In experiments involving high-pressure synthesis, $KClO_3$ and $KClO_4$ are often used as an oxidizer.[45,46,54] They release oxygen during heat treatment. It is generally expected that potassium and chlorine do not react with other elements and inert KCl remains. However, it was confirmed that potassium is actually not inert in the experiments of ref 14.

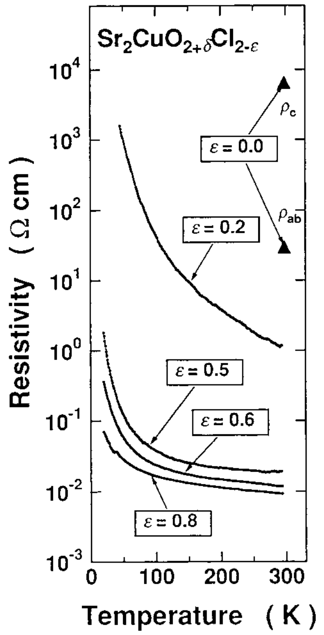

Figure 7. Temperature dependences of electrical resistivity for $Sr_2CuO_{2+\delta}Cl_{2-\epsilon}$ samples ($0 \le \epsilon \le 0.8$, $\epsilon \approx \delta$).[21] The data for the sample with $\epsilon \approx 0$ are reported values for the single-crystal sample.[19]

B. Sr-Based 02(n − 1)n Oxychloride (n = 1−3). The existence of $Sr_2CuO_2Cl_2$ has also been well-known since 1970s.[1,55] Vaknin et al.[56] reported that a three-dimensional antiferromagnetic structure is identified below the Néel temperature $T_N = 251$ K by neutron diffraction. This T_N is similar to that for La_2CuO_4 ($T_N \sim 250$ K).[57,58] Theoretical studies of its electronic structure predicted that proper hole doping (0.35−0.38 per Cu) into $Sr_2CuO_2Cl_2$ would induce superconductivity with T_c around 25 K.[59,60] Hiroi et al.[13] reported that a similar way of hole doping to the case of $Ca_2CuO_2Cl_2$, i.e., sodium and potassium substituting for calcium, does not work for $Sr_2CuO_2Cl_2$.

To introduce hole carriers, anion substitution has been attempted by Jin et al.[22] and Tatsuki et al.[21] Samples of $Sr_2CuO_{2+\delta}Cl_{2-\epsilon}$ ($0 \le \epsilon \le 0.8$) were prepared using a high-pressure technique.[21] The chlorine content was analyzed by EDX-SEM. With increasing ϵ, the lattice parameters a and c gradually decrease to 3.93 and 15.57 Å, respectively. The copper valence and oxygen content were determined by iodometric titration. The results indicated that δ is nearly identical to ϵ and the copper valence increases to 2.48 with increasing ϵ. It is likely that the attempted anion substitution, namely apical oxygen doping, can work as a hole carrier doping method. Figure 7 shows the temperature dependences of electrical resistivity for the $Sr_2CuO_{2+\delta}Cl_{2-\epsilon}$ samples. As hole carrier doping proceeds, the resistivity appreciably decreases. However, neither a superconducting transition nor metallic conduction behavior is seen. The general picture of the antiferromagnetic insulator−superconductor−normal metal transition with hole doping[61] was not realized in this 0201 oxychloride. It is considered that the general picture is not applicable to materials with such an expanded CuO_2 plane.

On the other hand, it was reported that 80 K class superconductivity in the $n = 2$ member was actually induced by hole doping via this anion substitution

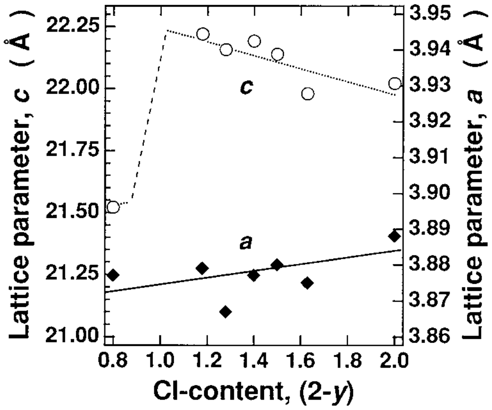

Figure 8. Lattice parameters vs Cl content, $(2 - y)$, for $Sr_{2.3}Ca_{0.7}Cu_2O_{4+\delta}Cl_{2-y}$. The Cl contents are the values analyzed by SEM-EDX. The samples are prepared at 1000 °C for 1 h under the high pressure of 5 GPa from nominal compositions of $Sr_{2.3}Ca_{0.7}Cu_{2.2}O_{4.6+y/2}Cl_{2-y}$.[62]

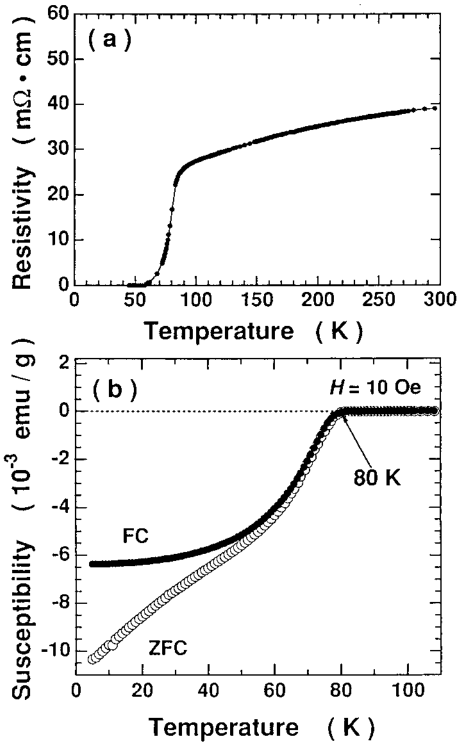

Figure 9. Temperature dependences of (a) electrical resistivity and (b) magnetic susceptibility for a high-pressure-synthesized sample with the nominal composition of $Sr_{2.3}Ca_{0.7}Cu_{2.2}O_{4.95}Cl_{1.3}$.[22]

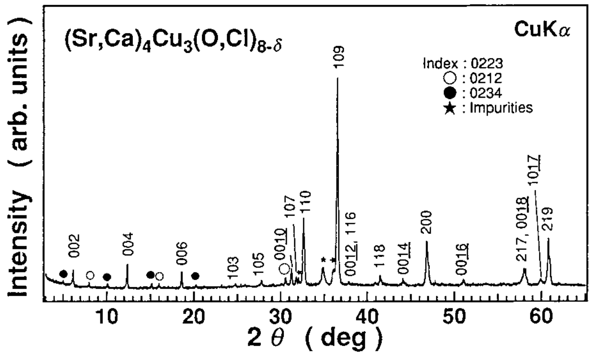

Figure 10. X-ray powder diffraction pattern for the sample prepared at 1100 °C for 4 h under the high pressure of 6 GPa from a nominal composition of $Sr_2Ca_2Cu_3O_7Cl$.[23]

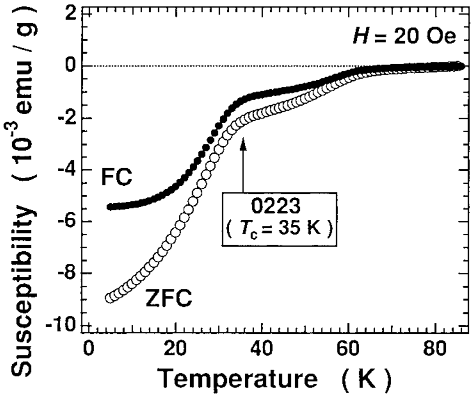

Figure 11. Temperature dependences of magnetic susceptibility for the sample prepared at 1100 °C for 4 h under the high pressure of 6 GPa from a nominal composition of $Sr_2Ca_2Cu_3O_7Cl$.[23]

method.[22,23,62] Samples with nominal compositions of $Sr_{2.3}Ca_{0.7}Cu_{2.2}O_{4.6+y/2}Cl_{2-y}$ were prepared and nearly single-phase samples with the 0212 structure were obtained. Figure 8 shows the lattice parameters vs Cl content $(2 - y)$, analyzed by SEM-EDX.[62] Upon decreasing the Cl content, the parameter a decreases monotonically. This behavior suggests successful hole carrier doping. The parameter c increases gradually with a decrease in the Cl content from 2.0 to 1.2 and then discontinuously decreases at 0.8. The increase in the parameter c is probably explained by the stretch in the puckered $(Sr,Ca)_2Cl_2$ rock-salt block due to the enhanced Coulomb repulsion between adjacent (monovalent) chlorine layers by introducing (divalent) oxygen. It seems that the observed discontinuous change in the parameter c at $(2 - y) = 0.8$ indicates the transformation of the basic phase unit from the oxychloride, $(Sr,Ca)_3Cu_2O_4Cl_2$, to the simple cuprate, $(Sr,Ca)_3Cu_2O_{6-\delta}$.[40-44] The compositional analysis using SEM-EDX and the Rietveld refinement of XRD data indicated that the obtained 0212 phase in the sample with a nominal composition of $Sr_{2.3}Ca_{0.7}Cu_{2.2}O_{4.95}Cl_{1.3}$ has a composition close to $Sr_{2.3}Ca_{0.7}Cu_2O_{4.8}Cl_{1.2}$. The temperature dependences of the electrical resistivity and magnetic susceptibility for the sample are shown in Figure 9. Bulk superconductivity at 80 K is clearly seen. A higher T_c of 83 K has been recently achieved in the same system after fine-tuning of the synthetic conditions.[23] Scott et al.[63] recently reported the formation of superconducting $Sr_3Cu_2O_5Cl$ ($T_c \sim 70$ K) in a diffusion couple of $Sr_2CuO_{3+\delta}$ and $KClO_3$ processed at 6 GPa and 950 °C. Their results clearly indicate that $KClO_3$ releases not only oxygen but also chlorine. They also suggested that identification of superconducting phases should be carefully done for materials high-pressure-synthesized with $KClO_3$.

Tatsuki et al.[23] synthesized a nearly single-phase sample of the third member. Figure 10 shows the XRD pattern of the sample. This sample exhibited a two-step transition at 35 and 70 K, as shown in Figure 11. It is considered that the former main transition is due to the 0223 phase. Since this T_c is much lower than those for other third members of the superconducting homologous series, proper adjustment of the hole content seems necessary to find the optimum T_c for this member.

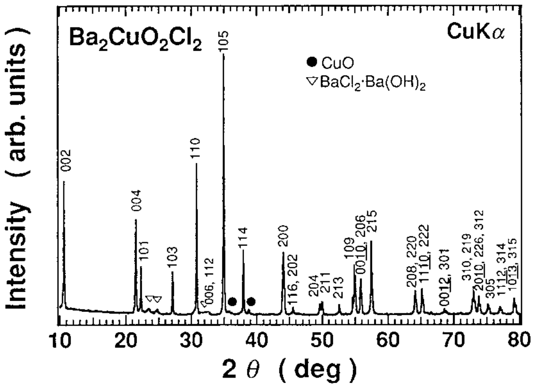

Figure 12. X-ray powder diffraction pattern for the sample prepared at 1000 °C for 1 h under the high pressure of 6 GPa from a nominal composition of $Ba_2CuO_2Cl_2$.[24]

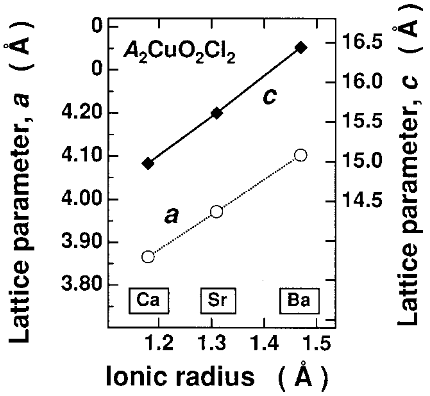

Figure 13. Lattice parameters for $A_2CuO_2Cl_2$ (A = Ca[11], Sr,[19] and Ba[24]) plotted against ionic radius of A (coordination number = 9).

Che et al.[20,64] tried to control the carrier concentration in a 0212 cuprate-containing lanthanum, $La_{1.6}Sr_{0.4}CaCu_2O_{6-\delta}$, by partial substitution of chlorine for oxygen. They reported that $La_{1.6}Sr_{0.4}CaCu_2O_5Cl$ prepared at ambient pressure exhibited bulk superconductivity at 34 K. A simple calculation gives a copper valence of +1.7 for this compound, implying that this material is possibly an electron-doped superconductor with apical anions. However, further studies on this superconductor should be done for the establishment of n-type superconductivity.

C. Ba-Based 0201 Oxychloride. $Ba_2CuO_2Cl_2$ was successfully synthesized using a high-pressure technique.[24] Figure 12 shows the XRD pattern of the sample. Its lattice parameters were found to be a = 4.1026(3) Å and c = 16.442(1) Å. Comparison of the parameters with those for $Ca_2CuO_2Cl_2$ and $Sr_2CuO_2Cl_2$ is shown in Figure 13. Upon increasing the ionic radius of the alkaline earth element, the parameters reasonably increase. The parameter a is much larger than that for the infinite-layer compound $Ba_{1/3}Sr_{2/3}CuO_2$ ($a \approx 3.93$ Å).[65] MBa_2CuO_y (M = Sc and In) compounds with the 1201 structure have a comparably large parameter a of 4.12−4.23 Å.[66−68] It was reported that about 75% of the oxygen sites in the CuO_2 plane of these cuprates is vacant. $Ba_2CuO_2Cl_2$ seems to contain oxygen vacancies in the CuO_2 plane, similarly. SEM-EDX analysis revealed that the cation ratio Ba:Cu:Cl is 2:1:1.8. The oxygen content and the copper valence were analyzed to be 2.0 and 1.8, respectively, by iodometric titration. This observed formal valence of copper is close to that of heavily doped n-type superconductors,[69] in which either superconductivity or metallic conduction is expected. However, the sample was insulating at room temperature. The high resistivity is considered to be associated with the imperfect CuO_2 plane and/or poor overlapping between the Cu($d_{x^2-y^2}$) and O(p_x, p_y) orbitals. It is also possible that the existence of the apical anion suppresses conductivity in the electron-doped CuO_2 plane.

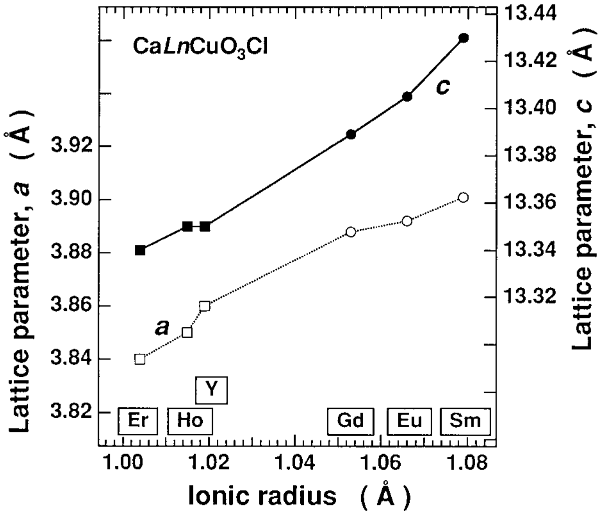

Figure 14. Lattice parameters for $CaLnCuO_3Cl$ (Ln = Sm, Eu, Gd,[17] Y, Ho, and Er[18]) plotted against ionic radius of Ln (coordination number = 8).

5. Oxybromide (X = Br)

A. Ca-Based 02(*n* − 1)*n* Oxybromide (*n* = 1 and 2). Progress in research on the Ca-based 02(n − 1)n oxybromides is analogous to that on the Ca-based 02(n − 1)n oxychlorides, aforementioned in section 4.A. The undoped insulating behavior of the first member had been already known before the discovery of high-T_c superconductivity.[11] The second member, $Ca_3Cu_2O_4Br_2$, was prepared by Huang et al.[25] in 1990. Zenitani et al.[12] have succeeded in making the first member superconducting by partial substitution of sodium or potassium for calcium using a high-pressure technique. Bulk superconductivity with $T_c \approx 24$ K is induced. For the second member, success in the hole doping has not been reported as yet.

6. Oxychlorides with the 0222 Structure

The 0222 oxychlorides $ALnCuO_3Cl$ (A = Sr, Ca; Ln = Nd, Sm, Eu, Gd) were synthesized at ambient pressure by Fuller and Greenblatt[17] in 1990. For $CaSmCuO_3Cl$, a single crystal was prepared and its structure was investigated in detail.[70] The smallest unit cell dimension among them is realized in the case of $CaGdCuO_3Cl$ [a = 3.888(1) Å, c = 13.389(1) Å]. The size of the CuO_2 plane is comparable to those of p-type superconducting cuprates, but is rather large.[71−73] Tatsuki et al.[18] tried to synthesize the 0222 oxychloride with a smaller CuO_2 plane under the high pressure of 6 GPa. They succeeded in preparing $CaLnCuO_3Cl$ (Ln = Er, Ho, Y) with the parameter a = 3.84−3.86 Å, while the 0222 phase is not stable for other rare earth elements. For the case of A = Ca, the lattice parameters

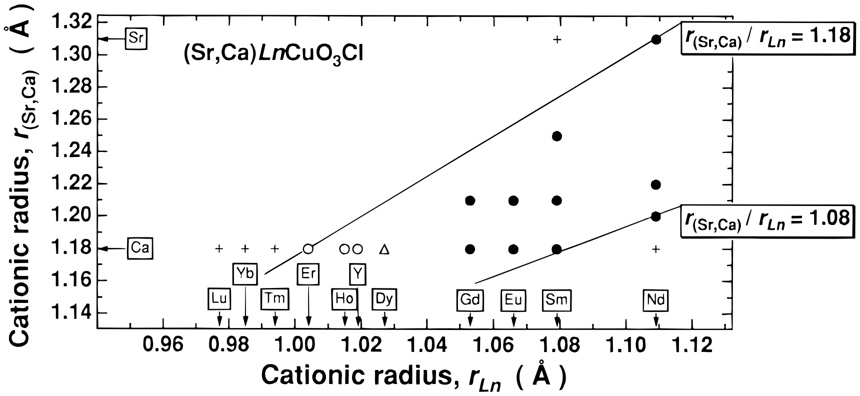

Figure 15. Previously examined compositions to synthesize the 0222-type (Sr,Ca)LnCuO$_3$Cl.[17,18] The coordination numbers of $r_{(Sr,Ca)}$ and r_{Ln} are 9 and 8, respectively. The circles (closed and open) and the triangle indicate the compositions at which the 0222 phase was obtained. The closed circles are for synthesis at ambient pressure, the other are for high-pressure synthesis. The pluses indicate failures.

are plotted against the ionic radii of Ln (coordination number = 8) in Figure 14. The parameters decrease reasonably with a decrease in the radius. The parameter $a = 3.84-3.86$ Å is quite suitable for the occurrence of p-type superconductivity. Tatsuki et al.[18] tried potassium doping in the same way as has been employed to synthesize a superconducting (Ca,K)$_2$CuO$_2$Cl$_2$.[14] They prepared samples with compositions of CaLnCuO$_3$Cl + xKClO$_4$ under high pressure. However, a spinel-phase LnCu$_2$O$_4$[74] that exhibits ferromagnetic-like characteristics[75] was stabilized. No one has succeeded in making the 0222 oxychloride superconducting yet.

The formation of the 0222 oxychloride is sensitive to the cationic radii of the constituent elements. Considering the structural similarity with the 0222[76] and Cu-1222[77] superconducting cuprates, larger alkaline earth and smaller rare earth elements seem to occupy preferentially the cationic sites in the rock-salt and fluorite blocks in the 0222 structure, respectively (see Figure 1). Figure 15 shows the previously examined compositions used to synthesize the 0222-type (Sr,Ca)LnCuO$_3$-Cl.[17,18] In the figure, the coordination numbers of $r_{(Sr,Ca)}$ and r_{Ln} are 9 and 8, respectively. The circles (closed and open) and the triangle indicate the compositions at which the 0222 phase was obtained. The pluses indicate failures. It is found that the 0222 oxychloride is stabilized in the range of $1.08 \leq (r_{(Sr,Ca)}/r_{Ln}) \leq 1.18$ in the (Sr,Ca)LnCuO$_3$Cl system.

7. Hole-Doping Routes into Halooxocuprates

To generate p-type superconductivity in the layered cuprates, one must create hole carriers in the CuO$_2$ planes by some doping method. As mentioned above, many superconducting p-type halooxocuprates have been synthesized. It was reported that the hole carriers were introduced by the following three methods: (1) anion substitution, (2) cation substitution, and (3) incorporation of interstitial anions.

The first method was successfully demonstrated in the synthesis of the (Sr,Ca)$_3$Cu$_2$(O,Cl)$_{6-\delta}$ superconductor.[22,23] It should be noted that the carrier concentration can be controlled by not only cation substitution but also anion substitution. In this superconductor, the apical sites are occupied by oxygen and chlorine, indicating a disorder in the apical site. It is interesting that the occurrence of superconductivity is insensitive to such a disorder. In the 02(n − 1)n superconducting cuprates without halogen, it is considered that the apical sites are considerably vacant, also indicating a disorder in the apical site.[40−46] These results suggest that the disorder at the apical sites does not destroy p-type superconductivity, although the possibility of some influence on T_c cannot be completely excluded.

The second method was demonstrated in synthesis of the Ca-based 02(n − 1)n superconducting oxychlorides and oxybromides with $n = 1$ and 2.[12,14,16,26] In the case of oxychloride superconductor with $n = 1$, the reported results of a composition analysis[14] and Rietveld refinement of X-ray[13] and neutron[53] powder diffraction data suggested the perfect occupation of the apical sites by chlorine. This implies that the existence of oxygen at the apical sites is not a must for p-type superconductivity. Interestingly, Hiroi et al.[13] reported that the apical chlorine goes away from the CuO$_2$ plane as the hole doping proceeds. There were some reports on the synthesis of p-type superconductors without an anion at the apical sites.[54,78] However, it seems that these results have not been fully established yet. The role of the apical anion is still controversial and should be investigated more intensively.

Al-Mamouri et al.[2] speculated that the third method works as a hole doping route in their S$_2$CuO$_2$F$_{2.6}$ superconductor prepared by fluorination at low temperatures. However, the identification of the superconducting phase in their fluorinated samples is controversial because of the small Meissner signals, as mentioned in section 3.A. Since the existence of a S$_2$-CuO$_2$F$_{2.6}$ superconductor is still not considered to be established, no one has demonstrated the third method to induce p-type superconductivity in halooxocuprates yet.

8. Problems

The clarification of the role of the apical anion in p-type high-T_c superconductors is very important in understanding the mechanism of the high-T_c superconductivity. It is expected that studies on superconductors having different ions at the apical site, e.g., oxygen, oxygen/halogen, halogen, “vacancy” would clarify this mechanism. To discuss the role of apical site ions, proper compositional and structural analyses of high-quality samples are needed. In sections 3−6, we reviewed many halooxocuprate compounds. Strictly speaking, no precise compositional analysis was carried out in most cases. Even incorporation of halogen ions in the structures was speculated from circumstantial evidence in many cases. It goes without saying that further discussion must be only speculative.

To perform reliable chemical composition analysis for both cations and anions, using, for example, the inductively coupled plasma (ICP) method, synthesis of high-quality samples which show a single phase in XRD and contain no impurity is necessary. When the samples contain some impurities, we need a microprobe to analyze the composition of the grains of the major phases. To extract information on the site occupancy for individual ions, for example by using X-ray Rietveld refinement, the crystallinity of the examined phases must be excellent. As mentioned in section 7, compositional and structural analyses which allow us to discuss hole-doping mechanisms were carried out for a few oxychlorides.[12−14,21−23,53,62] However, the reported data on other halooxocuprates are not sufficient to discuss the doping routes. A variety of halooxocuprates have been reported so far, but they were not understood at all. Development of preparation techniques for high-quality samples and precise analyses on them are needed to obtain some conclusive results.

9. Summary

We have reviewed halooxocuprates with the so-called $02(n-1)n$ ($n = 1-5$) and the 0222 structures, in which the apical site is mainly occupied by the halogen ions, F, Cl, and Br, (occupancy, $g \geq 0.5$). These compounds are prepared by the conventional solid-state reactions, low-temperature fluorination or high-pressure synthesis. The changes in the structural properties of the obtained halooxocuprates accompanied with substitution of ions having different valences and/or sizes were described. The oxyfluoride superconductors which are synthesized at ambient pressure are not well-established yet. The Meissner signals from the reported superconducting oxyfluorides have always been too small to identify the responsible superconducting phase correctly. The reports on $La_{1.6}Sr_{0.4}CaCu_2O_5Cl$, in which the formal Cu valence is +1.7, and $La_{0.7}Sr_{1.3}Cu(O,F)_{4+\delta}$, having a large lattice parameter a [=3.9368(7) Å], suggest possibilities of n-type superconductor with an apical anion. However, further investigation is needed for verification of superconducting behavior. Hole doping to induce p-type superconductivity has been successfully attained using high-pressure techniques. Anion and cation substitutions are performed as carrier doping methods into various halooxocuprates to induce p-type superconductivity. The maximum T_c of 111 K is recorded in the 0223 oxyfluoride superconductor. Hole and electron carriers are doped into $Sr_2Cu(O,Cl)_{4-\delta}$ and $Ba_2CuO_2Cl_2$, which have a rather large CuO_2 plane [lattice parameter $a = 3.93$ Å and 4.1026(3) Å, respectively]. In these oxychlorides, neither superconductivity nor metallic conduction is observed. It is considered that the size adjustment of the CuO_2 plane is necessary to induce high conductivity (or even superconductivity). The successful syntheses of superconducting halooxocuprates in which the apical sites are completely occupied by halogen indicates that the apical oxygen is not always necessary for p-type superconductivity. For well-established high-T_c superconductors, it has been found so far that all the p-type ones have an apical anion and all the n-type ones do not. Thus, the role of the apical anion should be further clarified. The synthesis of the 0222 $(Sr,Ca)LnCuO_3Cl$ oxychlorides with a variety of unit cell dimensions has been attempted. It is found that the 0222 oxychloride is stable in the range of $1.08 \leq (r_{(Sr,Ca)}/r_{Ln}) \leq 1.18$.

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