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Synthesis of New Electron-Doped Cuprates $Li_xSr_2CuO_2X_2$ (X= Cl, Br, I)

Tetsuya Kajita[a, b], Masatsune Kato[a, b], Takashi Noji[a, b] and Yoji Koike[a, b]

[a] *Department of Applied Physics, Tohoku University, 6-6-05 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan*
[b] *CREST, Japan Science and Technology Corporation (JST)*

Abstract. We have successfully synthesized a new electron-doped superconducting cuprate $Li_xSr_2CuO_2I_2$ by the electrochemical Li-intercalation technique. The electrochemical intercalation was carried out at room temperature under a constant potential of 500 mV vs. Li/Li^+ using a three-electrode cell. It has been found that Li^+ ions tend to be intercalated readily with the increase of the ionic radius of X^- in $Sr_2CuO_2X_2$ (X = Cl, Br, I). The magnetic susceptibility measurements have revealed the appearance of superconductivity with the superconducting transition temperature T_c = 4.5 K in $Li_{0.25}Sr_2CuO_2I_2$, which is lower than T_c = 8.0 K in $Li_{0.15}Sr_2CuO_2Br_2$.

Keywords: Superconductor, Li-intercalation, Electron-doping, $Li_xSr_2CuO_2X_2$ (X = Cl, Br, I)
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In our previous works, we have succeeded in synthesizing new electron-doped cuprates $Li_xSr_2CuO_2X_2$ (X = Cl, Br) by the electrochemical Li-intercalation technique [1,2]. As shown in Fig. 1, the compound $Sr_2CuO_2X_2$ is a layered perovskite with the K_2NiF_4 structure and essentially isostructural to the well-known hole-doped high-T_c superconductor $(La,Sr)_2CuO_4$. In the rock-salt layer of Sr^{2+} and X^-, X^- ions shift away from the CuO_2 plane, which is due to the larger radius of X^- than that of O^{2-} and the smaller Coulomb attraction between Cu^{2+} and X^- than between Cu^{2+} and O^{2-}. This leads to the formation of $X^- $-$X^-$ double layers, so that Li^+ ions can be intercalated between the electronegative X^- layers, which are weakly bound through the van der Waals force. It has been found that $Li_xSr_2CuO_2Br_2$ shows superconductivity with the superconducting transition temperature T_c = 8.0 K, while no superconductivity appears in $Li_xSr_2CuO_2Cl_2$. The type of carriers doped into the CuO_2 plane changes from hole-like to electron-like with the increase of the a-axis length from 3.78 Å in $(La,Sr)_2CuO_4$ to 3.97-3.99 Å in $Sr_2CuO_2X_2$ (X = Cl, Br), indicating the large a-axis length would be important for the appearance of electron-doped superconductivity. Therefore, it is interesting to study whether the value of T_c increases for X = I with the larger a-axis length of 4.03 Å than those for X = Cl and Br.

In this paper, we report the synthesis of a new electron-doped cuprate $Li_xSr_2CuO_2I_2$ and discuss the superconductivity of $Li_xSr_2CuO_2X_2$ (X = Cl, Br, I).

Polycrystalline host samples of $Sr_2CuO_2I_2$ were synthesized as follows [3]. First, polycrystals of $SrCuO_2$ were prepared from stoichiometric amounts of $SrCO_3$ and CuO powders. The powders were mixed, ground and heated in air at 925 °C for 10 h. The products were then pulverized, pressed into pellets and sintered at 950°C for 20 h. Next, the obtained single-phase samples of $SrCuO_2$ were mixed with a stoichiometric amount of SrI_2 and pressed into pellets. Then the pellets were sintered at 580°C for 24 h in an evacuated quartz ampoule in order to suppress the volatilization of iodine, though no ampoule was necessary in the case of X = Cl and Br. The obtained samples of $Sr_2CuO_2I_2$ were highly unstable in air due to the hygroscopic nature. In the case of X = Cl and Br, the obtained samples of $Sr_2CuO_2X_2$ were mixed with naphthalene, pelletized and then sintered again in air to obtain porous samples which are suitable for the homogeneous intercalation of Li. In the case of X = I, however, porous samples were not prepared, because the volatilization of iodine was inevitable in the process of the volatilization of naphthalene. The electrochemical Li-intercalation was carried out at room temperature in an argon-filled glove box using a three-electrode cell. The working electrode was a pellet of $Sr_2CuO_2I_2$ which was covered with Ni meshes. Li sheets were used as the counter electrode and the reference electrode. As an electrolyte, 1.0 M $LiClO_4$
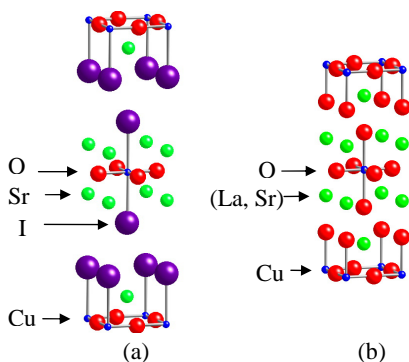
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FIGURE 1. Crystal structures of (a) $Sr_2CuO_2I_2$ and (b) $(La, Sr)_2CuO_4$.

FIGURE 2. Temperature dependence of the magnetic susceptibility, χ , of $Li_{0.25}Sr_2CuO_2I_2$ (● , ○) and $Li_{0.15}Sr_2CuO_2Br_2$ (▲ , △)dmeasured in a magnetic field of 3 Oe on warming after zero-field cooling (ZFC) and on field cooling (FC).

dissolved in propylene carbonate (PC) was used. The Li-intercalation was performed under a constant potential of 500 mV (vs. Li/Li$^+$) using a potentiostat. The total amount of Li intercalated into $Sr_2CuO_2I_2$ was estimated according to the simple Faraday law and also from the ICP analysis. The magnetic susceptibility was measured using a SQUID magnetometer in a magnetic field of 3 Oe.

$Li_xSr_2CuO_2I_2$ with $0.10 \leqq x \leqq 0.28$ were successfully obtained through the Li-intercalation within a half day. On the other hand, the maximum value of x in $Li_xSr_2CuO_2Cl_2$ was less than 0.10 despite the Li-intercalation for 1 week. Probably, Li$^+$ ions were intercalated readily owing to the large ionic radius of I$^-$.

The temperature dependence of the magnetic susceptibility, χ , of $Li_{0.25}Sr_2CuO_2I_2$ is shown in Fig. 2. A single-step diamagnetic response due to the Meissner effect is observed below 4.5 K. The superconducting volume fraction at 2 K, which is estimated from the χ value on zero-field cooling, is ~2 %. The value of T_c = 4.5 K is independent of x, while the superconducting volume fraction at 2 K is below 2 %.

The above results suggest that a phase separation takes place in the sample as in the case of $Li_xSr_2CuO_2Br_2$. The sample may include a pristine phase with $x = 0$, a superconducting phase with $x = x_{sc}$ and an amorphous phase of Li-Sr-Cu-O-I with $x > x_{sc}$. In particular, $Li_xSr_2CuO_2I_2$ may include a large amount of the pristine phase, because the surface area into where Li$^+$ ions are intercalated is small for the non-porous sample. In fact, non-porous samples of $Li_xSr_2CuO_2Br_2$ showed no superconductivity. The phase separation is also observed in several alkali-matal-intercalated superconductors such as $Li_xCsSr_2Nb_3O_{10}$ [4] and Na_xHfNCl [5]. One possible reason of the phase separation is as follows. When Li$^+$ ions are intercalated, the lattice is deformed. In order to minimize the energy loss due to the deformation, it is likely that Li$^+$ ions tend to be intercalated into the same layer, leading to the phase separation.
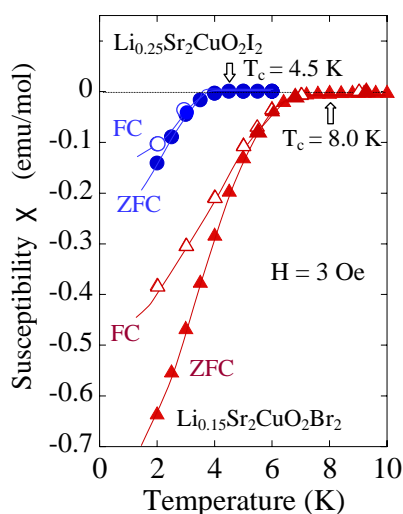
The increase of the a-axis length, namely, the increase of the Cu-O bond length in the CuO_2 plane decrease of the Madelung potential at the Cu site, so that electronegative electron carriers tend to be readily introduced into the CuO_2 plane, as discussed in our previous reports [1, 2]. Accordingly, the Li-content x_{sc} for X = I is expected to be larger than that for X = Br. Therefore, it may follow that the superconducting phase in $Li_xSr_2CuO_2I_2$ is situated in the heavily overdoped regime, so that T_c = 4.5 K for X = I is lower than T_c = 8.0 K for X = Br. A higher T_c value may be obtained in the present system by controlling the carrier concentration.

In conclusion, a new electron-doped superconducting cuprate $Li_xSr_2CuO_2I_2$ with T_c = 4.5 K has successfully been synthesized by the electrochemical Li-intercalation technique. The suppression of the phase separation in the Li-intercalation compounds is an important issue to obtain a higher T_c value. Anyway, Li-intercalated oxyhalides with the K_2NiF_4 structure are good candidates for new electron-doped superconductors.

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