$T_c$ dependence on the number of CuO$_2$ planes in multilayered Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$(O,F)$_2$ superconductors

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Abstract. Multilayered cuprates of Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$(O,F)$_2$ with $n = 5 - 9$ have been synthesized by using high pressure synthesis method in order to investigate the variation of $T_c$. The temperature dependence of susceptibility showed that the $T_c$ (about 80 K) does not depend on $n$ for $n = 5 - 9$. This result can be explained using the carrier imbalance model in multilayered cuprates. Charge reservoir layers supply most of the carriers to adjacent CuO$_2$ planes (OP) and the OP keeps the $T_c$ constant even for large $n$.

1. Introduction

Multilayered cuprates are generally described by the formula of MCa$_{n-1}$Cu$_n$O$_{2n}$, where M is a charge reservoir layer (CRL) such as HgBa$_2$O$_y$, Bi$_2$Sr$_2$O$_y$, Tl$_2$Ba$_2$O$_y$, Ba$_2$(O,F)$_y$, etc. The Ca$_{n-1}$Cu$_n$O$_{2n}$ has an infinite layer (IL) structure and the $n$ means the number of CuO$_2$ planes between the CRL's. A crystal structure is constructed by an alternate staking of the CRL and IL. The CRL supplies carriers to the IL i.e. CuO$_2$ planes. The multilayered cuprates are characterized by existence of two or more crystallographically inequivalent CuO$_2$ planes in a unit cell: outer planes (OP) with pyramidal (five) oxygen coordination and inner planes (IP) with square (four) oxygen coordination.

The number of CuO$_2$ planes dependence of $T_c$ in the multilayered cuprates is an interesting problem in high-$T_c$ superconductivity. In case of Tl- or Hg-system, after the $T_c$ reaches maximum at $n=3$ or 4, the $T_c$ decreases with increasing $n$ up to 6 or 7, respectively [1,2]. The $T_c$ has been shown to finally become zero in some cases [3,4,5]. Thus, the problem is still controversial [6]. Assuming that the carriers are almost equally shared with all the CuO$_2$ planes, the $T_c$ should decrease with $n$ and finally become zero because of the decrease of the average carrier concentration per a CuO$_2$ plane.

Systematic investigation of the multilayered cuprates by Nuclear Magnetic Resonance (NMR), however, has revealed that the carriers are quite unequally distributed to crystallographically inequivalent CuO$_2$ planes [7,8,9], i.e. outer planes (OP) adjacent to the CRL always have more carriers than the inner planes (IP) and the difference of carrier concentration between the OP and IP increases with $n$. Then, the $n$ dependence of $T_c$ should not be as simple as it is generally believed.

We have synthesized multilayered superconductors of Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$(O,F)$_2$ (F-02(n-1)n) with $n = 5 - 9$ by using high pressure synthesis method in order to verify the above problem.
2. Sample preparation

A lot of cuprates whose apical oxygen is partially or fully substituted by F, Cl or Br so-called $0_2(n-1)n$ structure have been found so far [10]. The homologous series of $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2$ ($\text{F}-0_2(n-1)n$) studied in this paper is one of the halooxocuprates. The physical properties were investigated for $\text{F}-0234$ with various F content [11].

Sample preparation of $\text{F}-0_2(n-1)n$ ($n = 3$ and 4) was described in elsewhere [12,11]. Samples of $\text{F}-02(n-1)n$ ($n = 5$ - 9) were prepared as follows. Source materials were $\text{CaF}_2$, $\text{CuO}$, $\text{Cu}_2\text{O}$, $\text{Ca}_2\text{CuO}_3$ and precursors with a nominal composition of $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ or $\text{Ba}_2\text{Ca}_3\text{Cu}_6\text{O}_{10}$. The precursors of $\text{Ba}_{2.5}\text{Cu}_3\text{O}_{1.8}$ ($\gamma \sim 7.5$) and $\text{Ba}_{2.5}\text{Cu}_3\text{O}_{1.4}$ ($\gamma \sim 13.7$) were prepared from a mixture of $\text{Ca}_2\text{CuO}_3$, $\text{CuO}$ and $\text{BaO}_2$ by heating at 940 °C and 880 °C for 12 h in an oxygen flow, respectively. An oxygen content of the precursors was estimated from weight change by the heating. Combining the source materials, a mixture with a nominal composition of $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2$ ($n = 5$ - 9, $\delta < \pm 0.1$) was obtained. The excess oxygen $\delta$ in the nominal compositions was almost fixed in order that the amount of carriers created by the CRL become almost same for all the as-synthesized samples.

The mixture is pressed into a pellet and encapsulated with Au. Conditions such as pressure, temperature and composition (oxygen content etc.) must be adjusted carefully to control phases in samples. The samples of $\text{F}-0223$ and $\text{F}-0234$ phases are usually prepared under a pressure of 4.5 GPa. We found that lower pressure is better for preparation of $\text{F}-02(n-1)n$ phases ($n \geq 5$). The samples were synthesized under a pressure of 3.5 - 4 GPa at about 1000 - 1100 °C for 2 hours. A sample including a $\text{CaCuO}_2$ infinite layer compound (IL) as a major phase was intentionally synthesized under a pressure of 2.5 GPa using a mixture with a nominal composition of $\text{Ba}_2\text{Ca}_6\text{Cu}_7\text{O}_{14}(\text{O,F})_2$ ($n = 5$ - 9).

As-synthesized samples were characterized by powder X-ray diffraction and susceptibility (field cooling method) measurements. Chemical compositions of the crystal grains were measured using an energy dispersive X-ray analyzer attached to a scanning electron microscope (SEM-EDX).

Fig. 1 X-ray diffraction patterns of $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2$ ($n = 5$ - 9) samples and a sample including a $\text{CaCuO}_2$ infinite layer compound (IL) as a major phase. Peaks that can be indexed as $\text{F}-02(n-1)n$ and the IL are shown by closed and open circles, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of $\text{F}-02(n-1)n$ ($n = 5$ - 9) phases together with the sample including the IL as a major phase. The lattice constants of the IL are $a=3.856$ Å and $c=3.178$ Å. As shown in Fig. 1, characteristic peaks of $(1 0 2n+3)$ between $2\theta = 36^\circ$ and $38^\circ$ systematically shift with $n$, which agrees with results of simulation. Peaks that can be indexed by $(00L)$ are not observed at low angle ($2\theta < 25^\circ$) for $\text{F}-0278$ and $\text{F}-0289$ probably due to stacking fault defects.
The average interval of \( c/2 \) is about 3.194 Å and the \( a \)-axis length is located between 3.85 and 3.86 Å for the samples \((n = 5 - 9)\). It means that almost the same size of a unit cell of the IL increases in the crystal structure with increasing \( n \). Average composition ratios of the grains in the F-0278 and F-0289 samples were respectively Ba:Ca:Cu =1.98:7.04:7.99 and 1.99:8.20:8.81 which are almost as same as the starting compositions. Although the samples have stacking fault defects, the average \( n \) in the F-0278 and F-0289 samples will be almost 8 and 9, respectively.

Fig. 2 shows the temperature dependence of susceptibility of F-02\((n-1)n \) \((n = 5 - 9)\) samples and the sample including the IL as a major phase. Multilayered cuprates necessarily include more or less stacking fault defects or another different \( n \) phases. If the sample includes the stacking fault defects or plural phases and each phase has a different \( T_c \), the transition must be multi-step. Actually, a two-step transition is observed for the F-0245 sample, because it includes the minor phase of F-0234 that has higher \( T_c \) than the main phases of F-0245. The fact that the samples show almost the same \( T_c \) and the sharp transitions demonstrates that the \( T_c \) does not depend on \( n \) for \( n \geq 5 \).

![Fig. 2](image-url)  
**Fig. 2** Temperature dependence of susceptibility of Ba\(_2\)Ca\(_n\)-1Cu\(_n\)O\(_{2n}\)(O\(_{0.8}\)F\(_{1.2}\)) \((n = 5 - 9)\) and the sample including a CaCuO\(_2\) infinite layer compound as a major phase.

The onset \( T_c \) of F-02\((n-1)n \) \((n = 1 - 9)\) are plotted in Fig. 3. The \( T_c \) is almost constant (about 80 K) for \( n = 5 - 9 \) while it strongly depends on \( n \) around \( n = 3 \). The constant \( T_c \) can be understood using the carrier imbalance model in multilayered cuprates revealed by the NMR study: the carrier concentration of the OP (\( N_{h}(OP) \)) is always larger than the \( N_{h}(IP) \) and the difference between the \( N_{h}(OP) \) and \( N_{h}(IP) \) increases with \( n \). According to this model, the OP can always have enough carriers for superconductivity even for large \( n \) while the carrier density of the IP is quite small. Actually, coexistence of superconductivity at OP and antiferromagnetism at IP has been found in Hg-1245 [13,14]. The scenario is essentially the same for the case when apical oxygen is partially replaced by fluorine. The present study will indicate that the CRL actually supplies most of the carriers to adjacent CuO\(_2\) planes (OP) and the OP keeps the \( T_c \) constant for \( n = 5 - 9 \).
Fig. 3. Variation of $T_c$ as a function of $n$ for $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2$ ($n = 1 - 9$). The $T_c$ for $n = 3 - 9$ were obtained from the samples synthesized from nominal compositions of $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O}_{0.8}\text{F}_{1.2})$. The $T_c$ for $n = 1$ and 2 are maximum ones obtained so far.

4. Summary

The $T_c$ has been shown to be almost constant for multilayered cuprates of $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2$ ($n = 5 - 9$). The carrier imbalance model was used to explain this result: charge reservoir layers supply most of the carriers to adjacent CuO$_2$ planes (OP) and the OP keeps the $T_c$ constant. According to this model, the $T_c$ will be constant even for $n \geq 10$.

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