Synthesis and magnetic properties of Cu oxides with low-dimensional structure

M Kato, Y Nogi, S Hongo and K Hirota
Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, JAPAN
E-mail: makato@mail.doshisha.ac.jp

Abstract. We report the synthesis and magnetic properties of Cu oxides with low-dimensional structure. For CuSb$_{2-x}$Ti$_x$O$_6$ compounds with tri-rutile type structure, magnetic susceptibility showed that a characteristic temperature, $J/k_B$, where a broad maximum of $\chi$ appears due to the short-range antiferromagnetic order, decreases with increase of $x$. Thus, it is considered that a hole carrier doped by Ti substitution results in the decrease of $J/k_B$. Furthermore, it was found that the antiferromagnetic long-range order at the transition temperature ($T_N$), around 8.5 K for $x = 0.0$, still remains in the substituted compounds for $x = 0.3$, which indicates the one-dimensional interaction along the diagonal direction is dominant. CuNb$_{2-x}$Ti$_x$O$_6$ compounds have zig-zag chain structure in the edge-sharing CuO$_6$ octahedra. Temperature dependences of $\chi$ were found to be well analyzed by the alternating 1DHAF model. Hole doping into this material is realized by substituting Ti$^{4+}$ ions for Sb$^{5+}$ ions.

1. Introduction
Many layered Cu oxides such as high-$T_c$ superconductors [1] generally show unconventional electric and magnetic properties based on the strongly correlated electron behaviors. Among them, tri-rutile type CuSb$_2$O$_6$ phase with two-dimensional (2D) tetragonal CuO$_2$ layers is known as a low-dimensional antiferromagnetic compound [2, 3]. Magnetic interactions between Cu atoms mainly consist of a Cu-O-Cu side direction of the square lattice ($J_1$) and a Cu-O-O-Cu super-exchange interaction ($J_2$) along the diagonal direction. These two magnetic interactions are geometrically frustrated, leading to the unconventional magnetic behaviors. Magnetic susceptibility $\chi$ of CuSb$_2$O$_6$ is well analyzed by the one-dimensional (1D) Heisenberg antiferromagnetic (1DHAF) model with half-integral spin [4]. On the other hand, this compound undergoes the so-called collinear ordered antiferromagnetic transition [5]. From these results, the magnetic properties of CuSb$_2$O$_6$ phase has been described by 1DHAF with the dominant $J_2$ interaction. Recently, the ground state of the 2D layered cuprates has been found to depend on the ratio of $J_2/J_1$; the system undergoes from Néel ordered state to a collinear state with increasing $J_2/J_1$. Moreover, a spin-singlet state has been predicted around the region with $J_2/J_1 \sim 0.5$ [6]. The ground state of 2D layered cuprates also can be varied by doping a carrier. A CuNb$_2$O$_6$ compound, with the similar chemical composition to CuSb$_2$O$_6$, has chains of edge-sharing CuO$_6$ octahedra [7], as schematically shown in Fig. 1. It also has chains of edge-sharing NbO$_6$ octahedra, which form washboard-like planes by the linkage of corner oxygens. The Cu atoms have the valency of +2 and carry spin $S = 1/2$, forming a quasi-1D localized spin system. For this compound, two polymorphs, orthorhombic and monoclinic, have been reported [8, 9],
where the magnetic susceptibility $\chi$ of the monoclinic phase was measured in the region of temperature $T$ between 10 K and 300 K and analyzed by introducing isolated spin dimers with the singlet-triplet excitation of 40 K. In this paper, we study synthesis and magnetic properties of Cu$M_2$$_x$Ti$_x$O$_6$ ($M =$ Sb, Nb) compounds to investigate what magnetic characteristics are found in such low-dimensional quantum spin systems by a chemical substitution on this compound.

2. Experimental

Samples of CuSb$_{2-x}$Ti$_x$O$_6$ ($0.0 \leq x \leq 0.6$) were prepared by a conventional solid state reaction (SSR). Starting materials of CuO (purity 99.999%), Sb$_2$O$_3$ (99.99%) and TiO$_2$ (99.99%) were mixed carefully, subsequently pressed in the form of a cylindrical pellet. Then, the pellet was heated in air at 750°C for 1 day. The resulting intermediate is reground, pressed and then heated further for 2 days at 800°C.

It has been difficult to synthesize CuNb$_{2-x}$Ti$_x$O$_6$ compounds with a conventional SSR method. Thus, polycrystalline samples of CuNb$_{2-x}$Ti$_x$O$_6$ phases were synthesized by citric acid complex polymerization (CCP) methods. Starting materials of Cu(NO$_3$)$_2$$\cdot$3H$_2$O (99%), Nb($\text{OC$_2$H$_5$}$)$_5$ (99.99%) and Ti($\text{OC$_2$H$_5$}$)$_4$ (99.99%) were dissolved in C$_3$H$_4$(OH)(COOH)$_3$ (99%) and HOC$_2$H$_4$OH (99.5%) solution, then heated at 60-80°C for 12 hours. Obtained polymerized complex was dried at 150°C for 12 hours. The precursor was heated at 400°C for 1 day to decarbonate, and then heated at 650-700°C for 2 days with intermediate grinding.

The phase identification was performed by X-ray diffraction measurements (Rigaku, Rint-2200) using the monochromatic Cu Kα radiation. Magnetic susceptibility ($\chi$) was measured by SQUID magnetometer (Quantum Design, MPMS-5T) in the temperature range from 2 to 300 K under the magnetic field of 0.1 or 1 T. In the measurement of $\chi$, the magnetic field was applied before cooling the sample (Zero-field cooling, ZFC) because none of the sample is ferromagnetic.

3. Results and Discussion

In Fig. 2, we show XRD patterns for CuSb$_{2-x}$Ti$_x$O$_6$ ($0.0 \leq x \leq 0.6$) samples obtained by SSR methods. Samples with Ti composition of $0.0 \leq x \leq 0.3$ were found to be indexed by monoclinic tri-rutile type structure. The sample with higher Ti content indicates small diffraction peaks due to CuO, although the lattice parameters were found to vary with increasing $x$. Thus, we have succeeded in synthesize the solid solution of CuSb$_{2-x}$Ti$_x$O$_6$ with tri-rutile type structure up to $x = 0.6$.

Temperature dependences of magnetic susceptibility for CuSb$_{2-x}$Ti$_x$O$_6$ ($0.0 \leq x \leq 0.6$) are shown in Fig. 3. The sample of $x = 0$ indicates the broad maximum at about 60 K due to the
Figure 2. XRD patterns of CuSb$_{2-x}$Ti$_x$O$_6$ with tri-rutile type structure.

Figure 3. Temperature dependence of magnetic susceptibility for CuSb$_{2-x}$Ti$_x$O$_6$ compounds with tri-rutile type structure. The Curie-Weiss paramagnetic components are subtracted from the raw data for the samples with $x \geq 0.1$.

short-range antiferromagnetic interaction of low-dimensional structure as previously reported [3]. The Curie-Weiss paramagnetic components are subtracted from the raw data for the samples with $x \geq 0.1$ using the following estimation. The data of magnetic susceptibility were analyzed by the 1DHAF model presented by Bonner and Fisher (BF) [4] with CW term as follows.

\[
\chi = (1 - A)\chi_{BF} + A\chi_{CW} + \chi_0
\]

\[
\chi_{BF} = \frac{N_A g^2 \mu_B^2}{k_B} \times \frac{0.25 + 0.14995z + 0.30094z^2}{1 + 1.9862z + 0.68854z^2 + 6.60626z^3}
\]

\[
\chi_{CW} = \frac{N_A g^2 \mu_B^2 S(S + 1)}{3k_B(T - \Theta)}
\]

Here, $A$ represents the ratio of BF and CW term, $\chi_0$ a constant parameter of $\chi$, $N_A$ Avogadro’s number, $g$ ($g'$) g-factor, $\mu_B$ Bohr magnetron, $k_B$ Boltzmann constant, $S$ spin quantum number, $\Theta$ Weiss temperature, and $z$ denotes $J/k_B T$. The raw data of temperature dependence of $\chi$ were performed by least-square curve fitting with parameters of $J$, $g$ ($g'$), $A$ and $\chi_0$. As a result, the value of $J/k_B$ decreases with increasing $x$. We summarize the values of $J/k_B$ and $T_N$ in Fig. 4 with data for other solid solutions of CuSb$_{2-x}$T$_x$O$_6$ ($T = Sn, Ta, Nb$) [10]. One can note that $J/k_B$ for Ta and Nb-substituted system has still finite value at higher concentration. This can be caused by the invariant carrier concentration because Ta and Nb is pentavalent as same as Sb. On the other hand, $J/k_B$ for Sn-substituted system rapidly decrease with $x$ due to the doped holes by tetravalent Sn. Thus, the rapid decrease of $J/k_B$ is also expected for Ti-substituted system, however, the experimental data of $J/k_B$ are almost intermediate between
Ta- and Nb-substituted systems. In the present stage, the reason of the magnetic behavior of Ti-system is unclear yet, although these behaviors should be caused by structural and magnetic interactions between Cu atoms in 1DHAF. Furthermore, it was found that the antiferromagnetic long-range order at the transition temperature \( T_N \), around 8.5 K for \( x = 0.0 \), still remains in the substituted compounds for \( x = 0.3 \), which indicates the one-dimensional interaction along the diagonal direction is dominant.

![Figure 4. Composition dependences of magnetic parameters for CuSb\(_2\)Ti\(_x\)O\(_6\) (\( T = \text{Ti, Sn, Ta, Nb} \)) estimated from the analysis using BF model.](image)

Figure 4. Composition dependences of magnetic parameters for CuSb\(_2\)Ti\(_x\)O\(_6\) (\( T = \text{Ti, Sn, Ta, Nb} \)) estimated from the analysis using BF model.

We show typical XRD patterns for CuNb\(_{2-x}\)Ti\(_x\)O\(_6\) compounds obtained by CCP methods in Fig. 5. Samples with Ti composition of \( 0.0 \leq x \leq 0.1 \) were found to be indexed by monoclinic CuNb\(_2\)O\(_6\) (\( m\)-CuNb\(_2\)O\(_6\)) type structure. The \( m\)-CuNb\(_2\)O\(_6\) type structure has been commonly synthesized by SSR method at low temperatures of about 700°C, although Ti-substituted system has not been obtained. On the other hand, single phase of orthorhombic CuNb\(_2\)O\(_6\) (\( o\)-CuNb\(_2\)O\(_6\)) compound, which is higher temperature phase, could not be synthesized by SSR nor CCP method. The sample with higher Ti content indicates small diffraction peaks due to impurity phases, although the lattice parameters were found to vary with increasing \( x \). Thus, we have succeeded in synthesize the solid solution of \( m\)-CuNb\(_{2-x}\)Ti\(_x\)O\(_6\) compounds up to \( x = 0.3 \).

Temperature dependences of magnetic susceptibility for CuNb\(_{2-x}\)Ti\(_x\)O\(_6\) (\( 0.0 \leq x \leq 0.3 \)) are shown in Fig. 6. The sample of \( x = 0 \) indicates the broad maximum at about 30 K due to the spin-gap formed by spin dimers on the zig-zag 1DHAF chains. The peaks of \( \chi \) shift towards low temperatures and almost disappears for \( x = 0.3 \), which means that the magnetic interaction between neighbor atoms decreases with \( x \). These data were found to be successfully analyzed by the alternating 1DHAF model proposed by Johnston (Johnston model) as follows [11].

\[
\chi = (1 - A)\chi_{AE} + A\chi_{CW} + \chi_0
\]  

(4)

In Eq. (4), \( \chi_{AE} \) represents the magnetic susceptibility of the alternating 1DHAF chains with
Figure 6. Temperature dependence of magnetic susceptibility for \( m \)-CuNb\(_{2-x}\)Ti\(_x\)O\(_6\) compounds.

Figure 7. Composition dependence of magnetic parameters for \( m \)-CuNb\(_{2-x}\)Ti\(_x\)O\(_6\) estimated from the analysis using Johnston model.

A parameter of \( \alpha \), the ratio of \( J_2/J_1 \); the system is a uniform 1DHAF chain (BF model) for \( \alpha = 1 \) and an isolated dimer model for \( \alpha = 0 \). Numerical formula should be referred to Ref. [11]. As a result, we have obtained magnetic parameters of \( \alpha \) and \( J_1 \) as shown in Fig. 7. One can note that \( J_1 \) decreases with \( x \) as mentioned above, and that \( \alpha \) increases with carrier doping. The increase in \( \alpha \) indicates that the system changes from alternating to uniform 1DHAF. Moreover, the doped holes are considered to be localized on 1DHAF chains because the temperature dependence of \( \chi \) is almost invariant at higher temperatures as shown in Fig. 6. From these behaviors, it should be concluded that the doped hole carriers result not in the itinerancy of the system but in the enhancement of magnetic exchange interaction on 1DHAF chains. Since these behaviors are similar to those of high-\( T_c \) Cu oxides, it is necessary to investigate the microscopic properties of strongly correlated electrons in CuNb\(_{2-x}\)Ti\(_x\)O\(_6\) compounds, which will be reported elsewhere.

4. Conclusion

The samples of solid-solution compounds, CuSb\(_{2-x}\)Ti\(_x\)O\(_6\) and CuNb\(_{2-x}\)Ti\(_x\)O\(_6\) were successfully synthesized using SSR and CCP methods, respectively. From magnetic susceptibility measurements for CuSb\(_{2-x}\)Ti\(_x\)O\(_6\) compounds, it is shown that a characteristic temperature, \( J/k_B \), where a broad maximum of \( \chi \) appears due to the short-range antiferromagnetic order, decreases with increase of \( x \). Thus, it is considered that a hole carrier doped by Ti substitution results in the decrease of \( J/k_B \). Hole doping into CuNb\(_2\)O\(_6\) is realized by substituting Ti\(^{4+}\) ions for Sb\(^{5+}\) ions. The doped hole carriers result not in the itinerancy of the system but in the enhancement of magnetic exchange interaction on 1DHAF chains.

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