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New magnetic materials obtained by ion-exchange reactions from non-magnetic layered perovskites

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Abstract

New layered magnetic materials, $(MCl)Ca_2Ta_3O_{10}$ ($M = Cu, Fe$), have been prepared by ion-exchange reactions of non-magnetic perovskite derivatives, $ACa_2Ta_3O_{10}$ ($A = Rb, Li$), in corresponding anhydrous molten salts. Powder x-ray diffraction patterns of the products are successfully indexed assuming tetragonal symmetry with cell dimensions $a = 3.829 \text{ \AA}$ and $c = 15.533 \text{ \AA}$ for Cu, and $a = 3.822 \text{ \AA}$ and $c = 15.672 \text{ \AA}$ for Fe. Being separated by the $Ca_2Ta_3O_{10}$ triple-layer perovskite slabs, the transition-metal chloride (MCl) network provides a two-dimensional magnetic lattice. Magnetic susceptibility measurements show that $(CuCl)Ca_2Ta_3O_{10}$ is in an antiferromagnetic state below 8 K, while $(FeCl)Ca_2Ta_3O_{10}$ has two anomalies at 91 and 125 K, suggesting successive phase transitions due to geometrical spin frustration.

1. Introduction

Geometrical spin frustration has received considerable interest from solid-state physicists over the last several decades. They have investigated models mostly comprising of rigid triangles with only one exchange interaction, including pyrochlore, Kagomé and triangular lattices, while little attention has been paid to systems based on squares [1]. Among the latter cases are the Shastry–Sutherland model [2] and the J_1 – J_2 model [3], both of which contain two distinct exchange interactions (see figure 1). In order to exploit inorganic materials with frustrated magnetic geometry, one usually takes the solid-state reaction route. This approach, however, can limit the control of specific structural features to only those obtainable within the bounds of a specific structure type (e.g. spinel or corundum).

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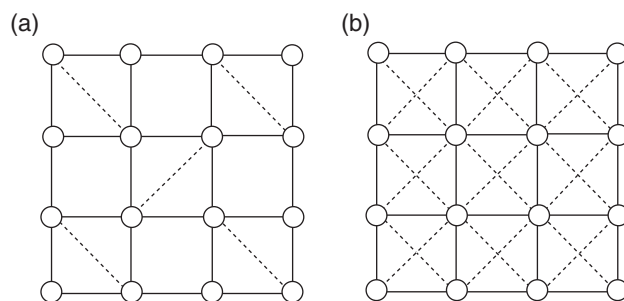


Figure 1. (a) Shastry–Sutherland model and (b) the J_1 – J_2 model. With inclusion of diagonal bonds (broken lines) to the square lattice, magnetic moments sitting on the corners (open circles) feel frustration.

Recently, low-temperature topotactic strategies such as intercalation/deintercalation have been found to be very effective for the design and construction of new magnetic materials. Some of the authors and their collaborators obtained $(\text{CuX})\text{LaNb}_2\text{O}_7$ ($X = \text{Cl}, \text{Br}$) from a non-magnetic double-layer perovskite host $\text{RbLaNb}_2\text{O}_7$ through an ion-exchange reaction with CuX_2 [4]. They further reported, using similar synthetic routes, the synthesis of a series of related materials, $(\text{CuX})\text{LaTa}_2\text{O}_7$, $(\text{CuCl})\text{Ca}_2\text{Nb}_3\text{O}_{10}$, $(\text{FeCl})\text{LaNb}_2\text{O}_7$ and so on [5–7]. In all compounds, the transition-metal ions carrying magnetic moments form layers of a two-dimensional square lattice, separated by magnetically inert perovskite slabs. Since each halogen ion is located at the centre of a square made by the neighbouring four magnetic ions, the nearest and next-nearest interactions are expected to be comparable. If this is the case, the magnetic properties are mapped onto the J_1 – J_2 model. In addition, these interactions appear to be tunable by modifying, for example, the size of perovskite slabs. Herein, we present the synthesis and magnetic character of the new magnetic materials $(\text{CuCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ and $(\text{FeCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$, the structures of which are likely to be isostructural with $(\text{CuCl})\text{Ca}_2\text{Nb}_3\text{O}_{10}$.

2. Experimental details

A triple-layered Dion–Jacobson phase, $\text{RbCa}_2\text{Ta}_3\text{O}_{10}$, was prepared by a solid-state reaction method from Rb_2CO_3 (Alfa, 99%), CaCO_3 (Alfa, 99.99%) and Ta_2O_5 (Alfa, 99.999%). Stoichiometric quantities of CaCO_3 and Ta_2O_5 with a 25% molar excess of Rb_2CO_3 were weighed and ground thoroughly inside an argon-filled glove box, annealed overnight at 850 °C followed by an additional thermal treatment at 1050 °C for 24 h. The excess of RbCO_3 was added to balance that lost due to volatilization. The product was washed with distilled water and dried at 150 °C overnight. $\text{LiCa}_2\text{Ta}_3\text{O}_{10}$ was obtained by an ion exchange reaction from LiNO_3 (Alfa, 99.98%) and $\text{RbCa}_2\text{Ta}_3\text{O}_{10}$ in a 10:1 molar ratio at 300 °C. After 24 h, the product was thoroughly washed with warm water and acetone and then dried at 150 °C overnight. To prepare $(\text{MCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ ($M = \text{Cu}, \text{Fe}$), $\text{ACa}_2\text{Ta}_3\text{O}_{10}$ ($A = \text{Li}, \text{Rb}$) were mixed with a two-fold molar excess of ultra-dry MCl_2 (Alfa, 99.99%) and then pressed into pellets with a hand press inside an argon-filled glove box. Reactions were carried out in sealed, evacuated ($<10^{-3}$ Torr) Pyrex tubes at 320 °C for 7 days and 350 °C for 12 days for $M = \text{Cu}$ and Fe , respectively. The final products were washed with warm water and acetone to eliminate the excess copper chloride and alkali metal by-product.

Chemical analyses were based on energy dispersive spectroscopy (EDS) of sets of individual grains. These are carried out on a JEOL (model JSM-5410) scanning electron microscope (SEM) equipped with an EDAX (DX-PRIME) microanalytical system. X-ray

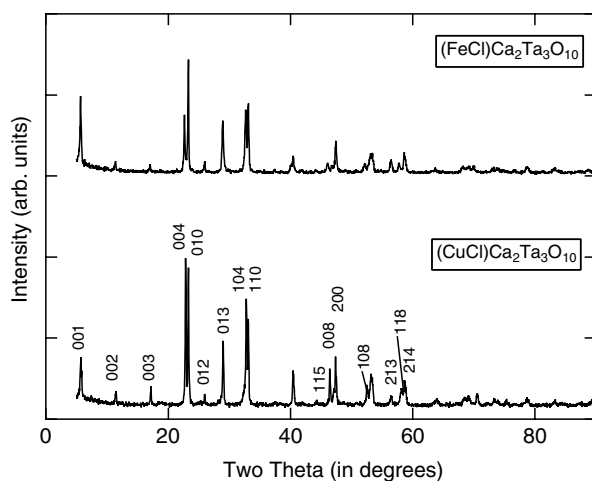


Figure 2. Powder x-ray diffraction patterns for (lower) $(\text{CuCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ and (upper) $(\text{FeCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$.

powder diffraction data were collected on a Philips X'Pert-MPD diffractometer equipped with a graphite monochromator and $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$). The pattern was recorded in step-scanning mode between 5° and 90° with a 0.02° step width and step time of 1 s. Unit cells were refined by a least-squares method with a homemade program, which runs on a Macintosh computer. Magnetic susceptibility measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS) over the temperature range 2–300 K in an applied field of $H = 0.1 \text{ T}$.

3. Result and discussion

The synthesis of $(\text{MCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ ($\text{M} = \text{Cu}, \text{Fe}$) is achieved by a single-step ion exchange reaction involving the replacement of the alkali-metal cation A of the perovskite host, $\text{ACa}_2\text{Ta}_3\text{O}_{10}$, by M^{2+} and Cl^- :

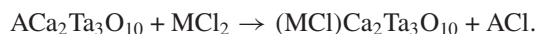


Figure 2 presents x-ray diffraction patterns at room temperature for $(\text{CuCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ and $(\text{FeCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ obtained from $\text{LiCa}_2\text{Ta}_3\text{O}_{10}$ and $\text{RbCa}_2\text{Ta}_3\text{O}_{10}$, respectively. Both profiles could be readily indexed on tetragonal unit cells and no trace of the impurity phase was found within the experimental resolution of the present experiment. The final products are green and light brown in colour for the Cu and Fe compounds, respectively. The EDX experiment revealed that no residual alkali metal is present in the products and the $\text{M}:\text{Cl}:\text{Ca}$ compositions were approximately found to be 1:1:2.

It is to be noted that, when $\text{RbCa}_2\text{Ta}_3\text{O}_{10}$ and $\text{LiCa}_2\text{Ta}_3\text{O}_{10}$ were used as the hosts in the formation of $(\text{CuCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ and $(\text{FeCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$, respectively, the products were of poor quality in that the reactions were incomplete, the products were poorly crystalline and a minor impurity was formed. It is known in many Dion–Jacobson-type layer perovskites that alkali-metal cation mobilities within the hosts are greater for the smaller alkali metals and hence correlate highly with the reaction time [5, 7, 8]. This tendency is consistent with what happened in $(\text{CuCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$, but not in $(\text{FeCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$. Further study is needed to clarify the origin of the discrepancy in the latter compound. It may be possible that the

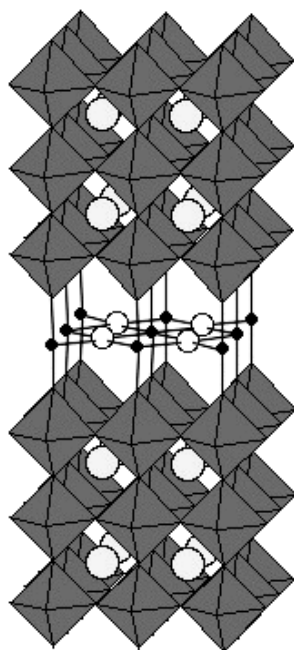


Figure 3. Idealized structural representation of $(MCl)Ca_2Ta_3O_{10}$ ($M = Cu, Fe$) with the MCl layer sandwiched by slabs of corner-sharing TaO_6 octahedra. The white, grey and black spheres are chlorines, calciums and coppers/irons, respectively.

Table 1. Tetragonal unit cell parameters for the parents and the exchange products.

Compounds	a (Å)	c (Å)	Cell volume (Å ³)
$RbCa_2Ta_3O_{10}$	3.857(3)	15.044(3)	223.8
$LiCa_2Ta_3O_{10}$	3.851(1)	28.339(2) ^a	420.3
$(CuCl)Ca_2Ta_3O_{10}$	3.829(3)	15.533(4)	227.7
$(FeCl)Ca_2Ta_3O_{10}$	3.822(3)	15.672(4)	228.9

^a Due to staggered stacking of perovskite slabs, the c in $LiCa_2Ta_3O_{10}$ is nearly double relative to the other compounds. Thus, the spacing between Li ions in successive layers is 14.169 Å.

diffusion of reactants to and products away from the reaction interface is more important than cation mobilities.

As seen in table 1, unit cells obtained from the analysis show that the spacing between the perovskite layers is expanded significantly on reaction relative to the starting materials. Moreover, the observed patterns without any extinct reflections are quite similar to those of the known $(CuCl)Ca_2Nb_3O_{10}$ ($P4/mmm$) [5], except for slight differences in peak positions due to small variations in cell parameters. This indicates that the two compounds should be isostructural with $(CuCl)Ca_2Nb_3O_{10}$. It is known from structural studies that the increase observed in c is due to the formation of extended metal-halide arrays between the perovskite layers [4–7]. The divalent metal cations (M) bridge between apical oxygens of the perovskite layers while surrounded by four chloride ions: the octahedra edge-share with each other and corner-share with the octahedra of the perovskite layers. Figure 3 illustrates an idealized crystal structure.

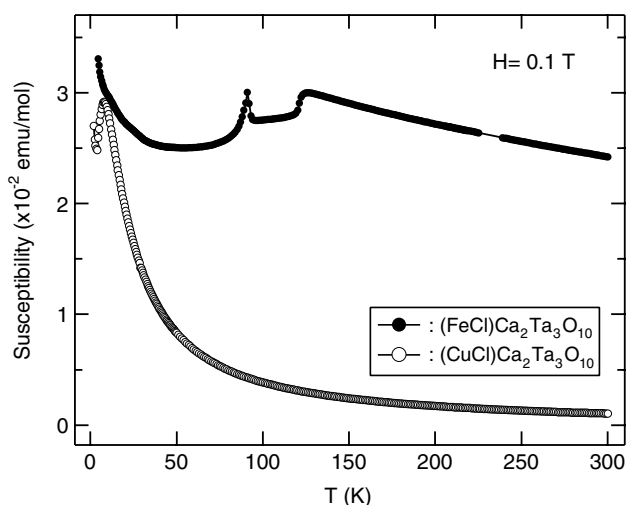


Figure 4. The temperature variation of the molar susceptibility of $(\text{CuCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ (open) and $(\text{FeCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ (full).

In figure 4, we show a plot of magnetization versus temperature for $(\text{CuCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$. The high-temperature data ($T > 170$ K) demonstrate the Curie–Weiss behaviour with an effective magnetic moment (P_{eff}) of $1.65 \mu_{\text{B}}$ and a Weiss temperature (θ) of 26 K. The P_{eff} value is nearly consistent with the presence of Cu^{2+} ions ($S = 1/2$) in a stoichiometric composition. The ferromagnetic interactions within the CuCl layer are derived from the positive value of θ . The compound shows an antiferromagnetic long-range ordering at $T_{\text{N}} = 8$ K. The magnetic structure is possibly composed of antiferromagnetic stacking of ferromagnetic layers. To support this magnetic structure, additional experiments such as neutron diffraction are necessary. It is worth pointing out that the triple-layered niobate $(\text{CuCl})\text{Ca}_2\text{Nb}_3\text{O}_{10}$ has a similar Néel temperature ($T_{\text{N}} = 10$ K) [5], while the double-layered one $(\text{CuCl})\text{LaNb}_2\text{O}_7$ has a maximum susceptibility at a somewhat higher temperature (16 K), accompanied by an unusually sharp drop with decreasing temperature [6]. The spacing between magnetic layers appears to play a crucial role in the magnetic character of these compounds.

The magnetic susceptibility of the $M = \text{Fe}$ compound, shown in figure 4, exhibits a more complex behaviour. Above 150 K, a Curie–Weiss law fit indicates that antiferromagnetic interactions are dominant. On cooling, the susceptibility shows a drop at 125 K, which is followed by a cusp at 91 K. This is an implication of successive magnetic phase transitions, possibly arising from the competition between J_1 and J_2 . A similar behaviour can be found in $(\text{FeCl})\text{LaNb}_2\text{O}_7$, although the niobate compound has lower transition temperatures, 18 and 87 K [7]. Determination of the magnetic structures for $(\text{FeCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$, as well as a qualitative and quantitative comparison with the niobate compounds, are important and are now in progress.

4. Conclusion

We have prepared layered magnetic materials, $(\text{CuCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$ and $(\text{FeCl})\text{Ca}_2\text{Ta}_3\text{O}_{10}$, using non-magnetic perovskite-based hosts through the topotactic ion-exchange reactions. This synthetic approach has an important advance to offer a wide variety of new magnetic materials.

Construction of different magnetic topologies, for instance the triangular lattice, could be realized if a host with hexagonal symmetry is chosen.

Acknowledgments

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