Cédric Tassel (Doctor Course student : 3rd year)(Supervised by Professor Hiroshi Kageyama)
Department of Chemistry
Graduate School of Science,
Kyoto University, Kyoto 606-8502, Japan.

Proposal number: [2009B1686]
Beamline used: BL02B2

TITLE

A Structural Study of New Fluorinated Ion-Exchanged Dion-Jacobson Perovskites

PURPOSE AND BACKGROUND

Low temperature topotactic reactions allow the preparation of compounds which cannot be synthesized through conventional solid state ceramic methods. And unlike these, allows the rational design of the structures which are necessary to control their chemical and physical properties.

Dion-Jacobson perovskite phases $AB_nT_{n+1}O_{3n+1}$ (A = Li, Na, K, Rb, Cs, B = La, Nd, Eu, Sr, Ca, Ba and T = Nb, Ta, Ti) consist of two-dimensional perovskite slabs separated by cations or cationic structural units. [1] The interlayer site can be modified using a wide range of reactions in order to intercalate, desintercalate and/or exchange the cations to give various new structures. [2] Furthermore their frame is of high interest due to the wide range of physical properties that low dimensionality induces such as superconductivity and magnetoresistivity. The use of bismuth for B and/or the d_0 state of the metal T also generates possible ferroelectricity and high photocatalytic activity.[3,4]

Previously, Wiley and coworkers studied the exchange properties of layered perovskites by exchanging the A^+ site alkaline ions with metal halides $(MX)^+$ (M = Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}… and X = Cl^-, Br^-) through a relatively low temperature topotactic reaction.[5] The resulting compound consist in diamagnetic ATO arrays with T remaining a d_0 element separating the magnetic MO_2X_4 octahedron layers.

These compounds were studied by some of us as they exhibit interesting low dimensional magnetic features. For instance, $(CuCl)LaNb_2O_7$ exhibits a singlet ground

state, spin-gap and a Böse-Einstein condensation under high fields. $(CuBr)LaNb_2O_7$ shows a collinear antiferromagnetic order, $(CuBr)Sr_2Nb_3O_{10}$ has a 1/3 plateau upon magnetization and $(CuCl)Ca_2Nb_3O_{10}$ has a spin-gap. [6]
By using powder diffraction, we were able to show that the structure in these compounds appears to be more complex and differs from one to another sample. We previously shown that $(FeCl)LaNb_2O_7$ and $(CuCl)LaNb_2O_7$ were showing distortions noticeable using synchrotron radiation involving octahedron tilting in the perovskite slabs and distortions in the interlayers. (Proposal No. 2006A1062)[7]

Electron doped ion-exchanged perovskite could be thus of great appeal as they would originally combine conducting layers separated by antiferromagnetic layer, which has only been studied with organic slabs and can exhibit interesting magnetically triggered phenomenons such as magnetically induced superconducticity in λ-$(BETS)_2FeCl_4$.[8]
We have been able to exchange the A' site of the conducting fluorinated $RbLaNb_2O_6F$ by CuCl to form $CuClLaNb_2O_6F$ similar to $CuClLaNb_2O_7$. The goal of this study is to determine structure of this new material.

EXPERMENTAL

$(CuCl)LaNb_2O_6F$ is synthesized from the fluorinated Dion-Jacobson compound $RbLaNb_2O_6F$ mixed with $CuCl_2$ at 325ºC for a week. Powders are mixed thoroughly in an argon filled glove box and pelletized. The pellets are then inserted in Pyrex tubes and sealed under vacuum. For synchrotron experiment, powders were inserted in a 0.1 mm of diameter capillary and exposed for 30 minutes to the beam at a 0.775Å wavelength. The collected data were analyzed using RIETAN-2000 for Rietveld refinement.

RESULTS

$CuClLaNb_2O_7$ has a 2a * 2b * c orthorhombic (pseudo-tetragonal $a \approx b$) cell with a = 3.8792 Å and c = 11.7282 Å. The unit cell of the fluorinated $CuClLaNb_2O_6F$ was calculated to be tetragonal with a = 3.87113 Å and c = 11.8633 Å. The c axis is strongly elongated which may indicate some preferential sites for fluorine. However the distinction of oxygen and fluorine is difficult using x-ray diffraction and the use of other methods will be necessary (e.g. NMR). The careful indexation of the synchrotron x-ray diffraction pattern indicated the presence of two peaks (1/2, 1/2, 0) and (1/2, 1/2, 2) belonging to a possible √2a * √2a * c unit cell. The detection of small impurity peaks and the small number of superstructural peaks does not allow the certainty of the space group.

We have attempted to refine the structure using the simple tetragonal unit cell, by excluding the superstructural peaks and the impurity peaks. The refinement gives reasonable agreement values Rwp = 7.15% and $\chi^2 = 3.56$ however several peaks are not correctly fitted (Fig. 3). The refinement using the $CuClLaNb_2O_7$ model with a $2a * 2b * c$ orthorhombic (pseudo-tetragonal $a \approx b$) did not lead to better values Rwp = 7.96% and $\chi^2 = 4.32$.

CONCLUSION

Using synchrotron x-ray diffraction, we showed that the fluorinated $(CuCl)LaNb_2O_6F$ exhibit superstructure peaks, however the crystal structure appears to be different from previous observed models and complementary studies of this material using other techniques (electronic and neutron diffraction) are necessary.

REFERENCES

[1] Dion, M.; Ganne, M.; Tournoux, M. *Mater. Res. Bull.* 1981, *16*, 1429. (b) Dion, M.; Ganne, M.; Tournoux, M.; Ravez, J. *Rev. Chim. Miner*. 1984, *21*, 92. (c) Jacobson, A. J.; Johnson, J. W.; Lewandowski, J. T. *Inorg. Chem*. 1985, *24*, 3729.

[2] Schaak, R. E.; Mallouk, T. E. *Chem. Mater.* 2002, *14*, 1455, and references therein.

[3] Fennie, C. J.; Rabe, K. M. *Appl. Phys. Lett.* 2006, *88*, 262902

[4] Domen, K.; Yoshimura, J.; Sekine, T.; Tanaka, A.; Onishi, T. *Catal. Letter.* 1990, *4,* 339.

[5] (a) Kodenkandath, T.A. et al., *J. Am. Chem. Soc.* 1999, *121*, 10743. (b) Kodenkandath, T.A. et al. *Inorg. Chem.*, 2001, *40*, 710. (c) Kodenkandath, T.A. et al. *Proc. Mater. Res. Soc. Symp.,* 2001*, GG8.5.1*, 658. (d) Viciu, L. et al. *Inorg. Chem.,* 2002*, 41*, 3385. (e) Viciu, L. et al. *Chem. Mater.*, 2003, *15*, 1480. (f) Viciu, L. et al. *J. Solid State Chem.*, 2003, *175*, 88.

[6] (a) Kageyama, H.; et al. *J. Phys. Soc. Jpn.* 2005, *74*, 1702. (b) Kageyama, H.; et al. *Prog. Theo. Phys. Suppl.* 2005, *159*, 39 (c) Kageyama, H.; et al. *J. Phys. Soc. Jpn* 74, *2005*, 3158. (d) Kitada, A.; et al. *J. Phys. Soc. Jpn.* 76, *2007*, 093706-1-4. (e) Tsujimoto,

Y.; et al. *J. Phys. Soc. Jpn.* 2007, *76*, 063711-1-4. (f) Tsujimoto, Y.; et al. *J. Phys. Soc. Jpn.*, 2007, *76*, 063711-1-4 (g) Yoshida, M.; et al. *J. Phys. Soc. Jpn.* 2008, *77*, 104705-1-7.

[7] Oba, N.; et al. *J. Magn. & Magn. Mater.* 2007, *310*, 1337.

[8] Uji, S.; et al. *Nature*, 2001, *410*, 908-910.

FIGURE

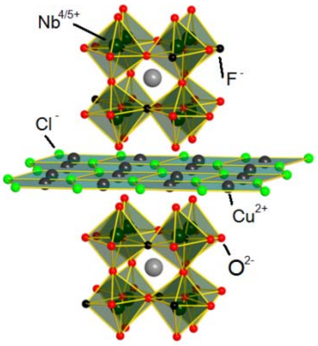

Figure 1. (CuCl)LaNb$_2$O$_6$F schematic structure.

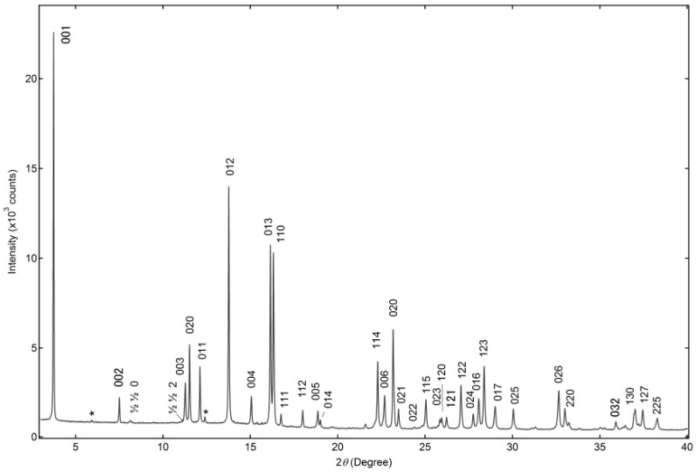

Figure 2. Indexation of the synchrotron x-ray diffraction pattern of (CuCl)LaNb$_2$O$_6$F.

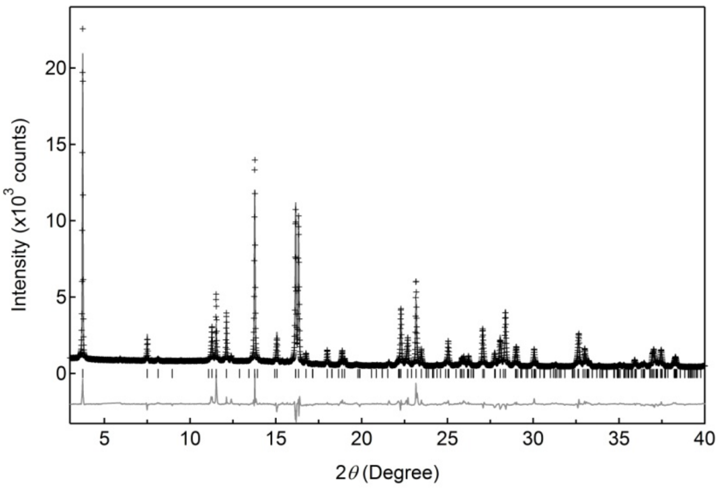

Figure 3. Rietveld refinement of (CuCl)LaNb$_2$O$_6$F. Dark crosses, black line, black ticks and gray line indicate the observed pattern, calculated pattern, peak positions and difference between observed and calculated pattern, respectively.