ESRF	**Experiment title:** Structural study of perovskite-type materials with complex distortions	**Experiment number**: HS4018
Beamline:	**Date of experiment**: from: 02.12.2009 to: 04.12.2009	**Date of report**: 01.09.2010
Shifts: 6	**Local contact(s)**: Andrew Fitch	*Received at ESRF:*

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Report:

The experiment was aimed at the structural investigation of several perovskite-type compounds at different temperatures. Initially, we planned to study four compounds, (CuX)$LaNb_2O_7$ with X = Cl, Br and Sr_3MO_6 with M = Mo, W. However, the reduced beam time (6 shifts instead of 9) and the demand for exploring a wide temperature range (both above and below room-temperature), restricted our study to two out of the four compounds, (CuCl)$LaNb_2O_7$ and Sr_3WO_6. We were also able to collect the preliminary data for (CuBr)$LaNb_2O_7$, but the detailed investigation of this material should be performed in future.

(CuCl)$LaNb_2O_7$ is a quantum magnet with unusual low-temperature properties. These properties remain poorly understood due to the lack of accurate structural information. Previous X-ray and neutron diffraction studies proposed the tetragonal crystal structure with $a_{sub} = b_{sub} \sim 3.87$ Å and $c \sim 11.87$ Å. In this structure, the perovskite-type [$LaNb_2O_7$] blocks and the flat [CuCl] layers have the four-fold symmetry and stack along the *c* direction. Electron diffraction and nuclear magnetic resonance evidenced a lower symmetry and a larger unit cell. However, no structure determination was performed. Using the superior intensity of the beam and the high resolution avilable at ID31, we were able to observe the superstructure reflections (see Fig. 1) and to refine the structure in the correct unit cell.

The room-temperature structure has the $2a_{sub} \times 2a_{sub} \times c$ unit cell and the *Pbca* symmetry. We found that the superstructure reflections originate from two types of the structural distortion. The NbO_6 octahedra tilt in the $a^-b^-c^+$ pattern, while the Cu and Cl atoms are displaced in order to achieve two shorter and two longer Cu–Cl bonds (in contrast to the four equivalent Cu–Cl bonds in the tetragonal crystal structure).

The two types of the distortion are, to a certain extent, independent. Upon heating the sample, we observed two successive phase transitions (Fig. 1). Above 500 K, the superstructure reflections with $h + k = 2n$ disappeared, while above 640 K the remaining reflections with $h + k = 2n + 1$ vanished as well (see Fig. 1). The two groups of the superstructure reflections are basically responsible for the tilting distortion of the octahedra

and for the distortion in the [CuCl] layers, respectively. Above 500 K, the $LaNb_2O_7$ blocks acquire the four-fold symmetry, the unit cell is reduced to $a_{sub} \times 2a_{sub} \times c$, and the symmetry is *Pbmm*. Above 640 K, the ordered arrangement of the short Cu–Cl bonds is destroyed, leading to the overall tetragonal *P*4/*mmm* symmetry and the $a_{sub} \times a_{sub} \times c$ unit cell.

The phase transitions at 500 K and 640 K are clearly visible as kinks in the temperature dependence of unit cell parameters (see Fig. 2). Both transitions are of the second-order. We have verified that the structural changes follow the symmetry rules and are consistent with the second-order phase transition. Below room temperature, the structure remains nearly unchanged. We have performed extensive band structure calculations and obtained a reliable microscopic spin model that is in good agreement with the experimental data and resolves the long-standing puzzle of the magnetic properties of $(CuCl)LaNb_2O_7$. The results are published in Phys. Rev. B **82**, 054107 (2010).

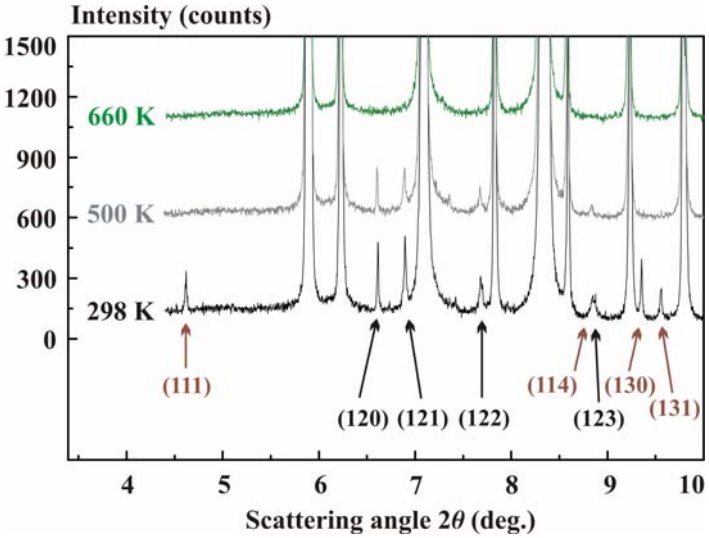

Fig. 1. XRD patterns of $(CuCl)LaNb_2O_7$ at 298 K, 500 K, and 660 K. The indices are given for the superstructure reflections only. The patterns are offset for clarity

Sr_3WO_6 is an elpasolite-type compound. The Sr cations in the B-position break the connectivity of the WO_6 octahedra and allow for their free rotations, opening a new route to the design of ferroelectrics. Synchrotron X-ray powder diffraction patterns at 300 K and 1173 K demonstrate that Sr_3WO_6 has two polymorphs with the *C*-centered triclinic (LT) and monoclinic (HT) structures (a_t = 10.09495(2) Å, b_t = 17.64750(5) Å, c_t = 11.81400(3) Å, α = 89.5470(2)°, β = 125.4528(2)°, γ = 90.2889(2)° for the LT phase and a_m = 10.21558(1) Å, b_m = 17.87382(2) Å, c_m = 11.95679(1) Å, β = 125.5911(1) for the HT phase). The transition between the LT and HT phases manifests itself by splitting of the reflections on going from the monoclinic to triclinic symmetry between 464 K and 506 K. We obtained the structural information on both LT and HT Sr_3WO_6 phases and provided a consistent description of the temperature evolution of the crystal structure. These results are relevant for understanding other elpasolite-type compounds and for the design of new ferroelectric materials. Published in Inorg. Chem. **49**, 6058 (2010).

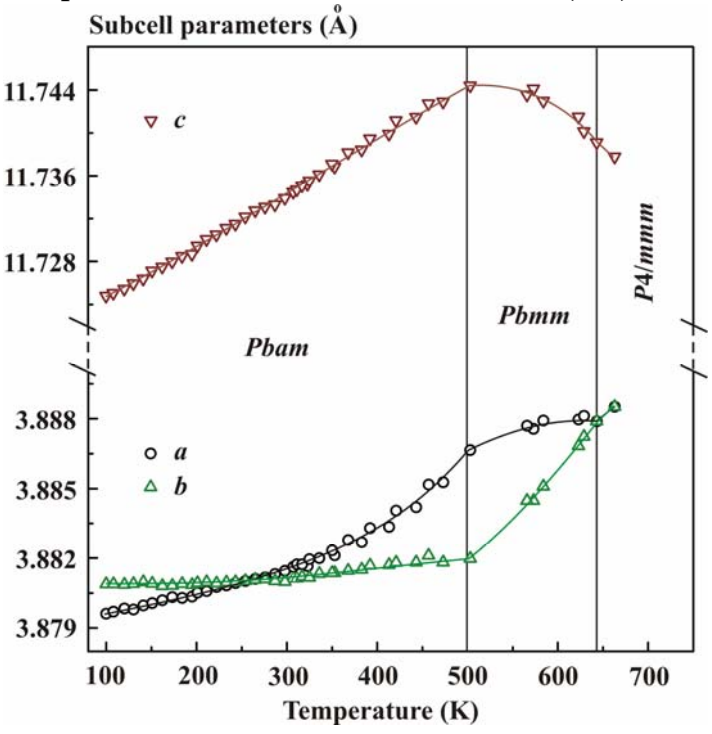

Fig. 2. Temperature dependence of the subcell parameters of $(CuCl)LaNb_2O_7$. The solid lines are guides-for-eye.