| MLF Experimental Report | 提出日 Date of Report<br>2013/04/08 |
|---|---|
| 課題番号 Project No.<br>PM0001<br>実験課題名 Title of experiment<br>Development of the maximum entropy method using a time-of-flight (TOF) neutron powder diffractometer<br>実験責任者名 Name of principal investigator<br>Ryoji Kanno<br>所属 Affiliation<br>Tokyo Institute of Technology | 装置責任者 Name of responsible person<br>Touru Ishigaki<br>装置名 Name of Instrument/(BL No.)<br>BL 20 iMateria<br>実施日 Date of Experiment<br>2013/02/04 – 2013/02/06 |

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Powdered $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ were synthesized by a solid state reaction. The starting materials were mixed and pelletized in an inert condition and then it was enclosed in the evacuated pyrex tube. Then the pellets were sintered at 120°C for several days with intermediate grinding. Phase identification was applied by the X-ray diffraction measurement. It is well known that $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ showed high ionic conductivity (0.34 $Scm^{-1}$ at 298 K)[1].

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Neutron diffraction data of $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ were taken in the temperature range from 10 K to 298 K on a time-of-flight (TOF) neutron powder diffractometer at iMateria (BL20) using the double frame. The data measured at 10 K and 298 K was taken for 17 h for MEM refinement. The specimen of ca. 1.875 g is contained in a cylindrical vanadium cell with 8 mm diameter and 37.5 mm height. The specimen was filled in the cell under a helium gas atmosphere. The data were analyzed by the Rietveld method using the Z-Rietveld program and maximum entropy method using Z-MEM.

The Rietveld refinement was applied based on the model with the space group of $P4_132$ reported by Kanno *et al.* [2] : $a$ = 10.0134 Å, Rb at 4*a* (0.375, 0.375, 0.375), Cu1 at 24*e* (0.5213, 0.2921, 0.7968), Cu2 at 24*e* (0.0008, 0.8407, 0.2110), Cu3 at 8*c* (0.1643, 0.1643, 0.1643), I/Cl1 at 8*c* (0.01107, 0.01107, 0.01107) and Cl2 at 12*d* (0.125, 0.15057, 0.20057). Figure 1 shows a Rietveld analysis result using neutron diffraction data of $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ measured at 298 K. Structural parameters are summarized in Table 1. Occupancy values, positions and isotropic thermal parameters of each sites

2. 実験方法及び結果（つづき） Experimental method and results (continued)

were determined from present results. Structural changes against temperatures, nuclear density distribution have been investigated.

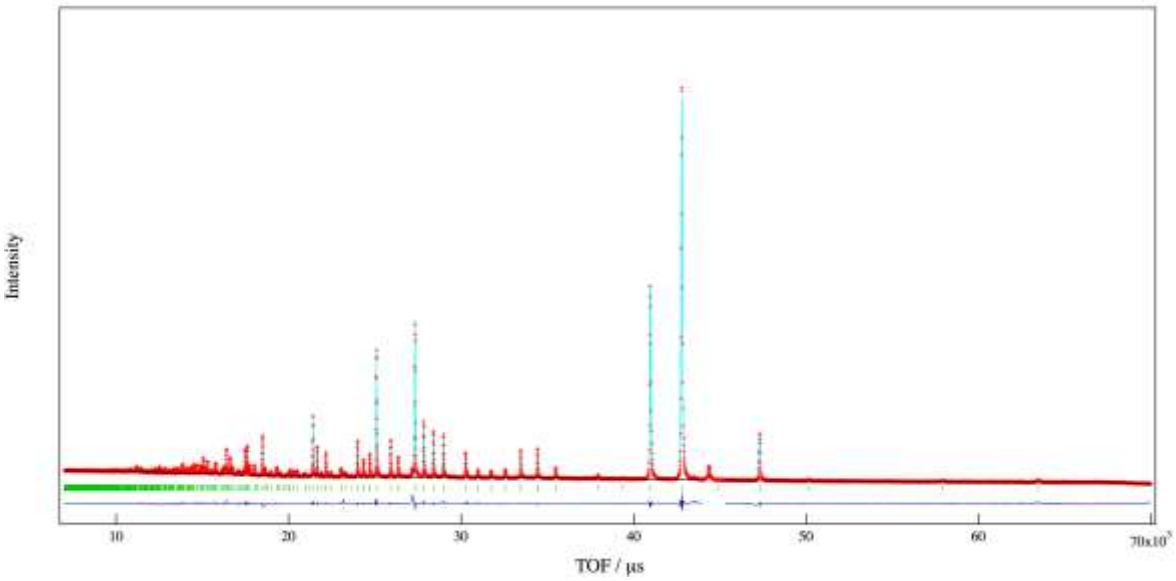


Fig. 1. Rietveld refinement pattern for $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ measured at 298 K.

Table 1 Rietveld refinement results for $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ measured at 298 K.

| | | | *g* | *x* | *y* | *z* | *Uiso* |
|---|---|---|---|---|---|---|---|
| Rb1 | 4 | *b* | 1 | 3/8 | 3/8 | 3/8 | 0.04763(15) |
| Cu1 | 24 | *e* | 0.3584(10) | 0.51893(6) | 0.29593(6) | 0.79503(7) | 0.0884(5) |
| Cu2 | 24 | *e* | 0.2636(9) | -0.00354(7) | 0.83189(6) | 0.21422(7) | 0.0579(5) |
| Cu3 | 8 | *c* | 0.1176(12) | 0.15956(11) | =x(Cu2) | =x(Cu2) | 0.0501(14) |
| I1 | 8 | *c* | 0.9 | 0.01263(2) | =x(I1) | =x(I1) | 0.03053(8) |
| Cl1 | 8 | *c* | 0.1 | =x(I1) | =x(I1) | =x(I1) | =Uiso(I1) |
| Cl2 | 12 | *d* | 1 | 1/4 | 0.150319(10) | 0.400319(10) | 0.03216(6) |

Unit cell: tetragonal $P4_132$ (213); $a$ = 10.014301(5) Å

[1] T. Takahashi *et al.*, *J. Electrochem. Soc.*, **126**, 1954 (1979).
[2] R. Kanno *et al.*, *J. Solid State Chem.*, **102**, 79 (1993).