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Structural Study of a High Ionic Conductor $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$

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Abstract

The structure of a high ionic conductor $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ at low temperature has been reinvestigated by use of angle-dispersive neutron powder diffraction. All the diffraction data have been analyzed with integrated software REMEDY consisting of RIETAN-2000 for whole-pattern fitting and MEED for calculating densities of electrons or atomic nuclei by the maximum-entropy method. The resulting nuclear-density maps have reconfirmed that Cu1–Cu2 chains are the main conduction pathways in this material, as previously suggested from the Rietveld analysis of neutron powder diffraction data.

Introduction

A high ionic conductor $Rb_4Cu_{16}I_7Cl_{13}$ has a room-temperature (RT) conductivity of 0.34 S/cm, which is the highest among ionic conductors that have been prepared so far [1]. Geller *et al.* [2] have determined its crystal structure at RT using single-crystal X-ray diffraction. To understand a transition from a normal conduction state to a high conduction one at around 200 K, Kanno *et al.* [3] have studied structural changes of $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ at low temperatures using time-of-flight (TOF) neutron powder diffraction. They found that no structural phase transition occurs at the low temperatures and that copper ions gradually migrate from a 'nonconducting' Cu3 site to a 'conducting' Cu2 site at about 200 K. However, the conventional Rietveld analysis of the TOF neutron diffraction data is not effective in learning structural details in such a highly disordered system. In addition, reflections with $d > 3.4$ Å were excluded from their Rietveld refinements, which may lead to give systematic errors in occupation factors of mobile atoms.

In this study, we have reinvestigated the structural changes of $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ at low temperatures from 11 K to 280 K using angle-dispersive neutron powder diffraction. A neutron wavelength of ca. 1.50 Å was chosen to collect reflection intensities with a maximum lattice-plane spacing, *d*, of ca. 7.5 Å, giving 110 reflections. All the diffraction data were analyzed with integrated software REMEDY [8] consisting of RIETAN-2000 for whole-pattern fitting and MEED for a maximum-entropy method (MEM) to determine nuclear-density distribution of mobile ions.

Experimental

A powder specimen of $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ was prepared with the same procedure as reported previously [3]. Neutron powder diffraction data were taken at 11, 40, 70, 100, 130, 160, 190, 220, 250 and 280 K on the HB-4 powder diffractometer at the High Flux Isotope Reactor of Oak Ridge National

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Laboratory. About 8 grams of the sample were contained in a cylindrical V can 12 mm in diameter, 30 mm in height, and 150 μm in wall thickness. The neutron beam was monochromatized with Ge(115) set at $2\theta_M = 87^\circ$. The wavelength calibrated from diffraction data of Si (NIST SRM 640b) was 1.50108 Å. Soller slit collimators of 12′ and 20′ were positioned before and after the monochromator, respectively. Intensity data between 11.00° and 135.20° were collected with a step size of 0.05° using an array of 32 ^{3}He detectors with 6′ Soller collimators. A closed-cycle He refrigerator was used to change the temperature of the sample. A holding time for ensuring the equilibration of the sample temperature was about 0.5 h.

Results & Discussion

Neutron diffraction data in a 2θ range from 11.00° to 135.20° were analyzed with RIETAN-2000 [4]. Coherent scattering lengths used for the refinements were 7.08 fm (Rb), 7.718 fm (Cu), 5.28 fm (I), and 9.5770 fm (Cl) [5]. The split pseudo-Voigt function of Toraya was selected as a profile shape function, with partial profile relaxation applied to 110 and 111 reflections [4]. The structural model of Kanno *et al.* [3] was used in all the refinements: space group $P4_132$ with Rb at 4*a*, Cu1 and Cu2 at 24*e*, Cu3 at 8*c*, I/Cl1 at 8*c*, and Cl2 at 12*d* site. Occupation factors, *g*, of Cu ions were refined under a linear constraint of $g(\mathrm{Cu3}) = 2 - 3g(\mathrm{Cu1}) - 3g(\mathrm{Cu2})$. I atoms and part of the Cl atoms were assumed to occupy randomly the 8*c* site with a *g* ratio of 0.9 : 0.1. Because isotropic atomic displacement parameters, *B*, of I/Cl1 and Cl2 converged to nearly the same values with large estimated standard deviations (e.s.d.'s), they were constrained to be equal to each other to reduce the number of structure parameters. A small amount (mass fraction: ca. 2 %) of $Rb_{18}Cu_{31}Cl_{49}$ [6] was detected as an impurity phase, which was included in the Rietveld analyses.

Table 1 exemplifies refined lattice and structure parameters of $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ at two temperatures together with *R* factors. Figures 1(a) and 1(b) show the dependence of *B* and *g* on temperature, *T*, for the three Cu sites, respectively. Though *B*(Cu1) and *B*(Cu3) are somewhat larger

Table 1. Structure parameters obtained by the Rietveld refinements of $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ at 11 and 280 K.

atom	site	*g*	*x*	*y*	*z*	*B* / Å^2
Rb	4*a*	1	3/8	3/8	3/8	0.60(9)
Cu1	24*e*	0.368(9)	0.5181(7)	0.2952(7)	0.8058(7)	2.02(18)
Cu2	24*e*	0.238(8)	–0.0015(9)	0.8321(9)	0.1984(8)	1.0(2)
Cu3	8*c*	0.18(4)	0.1638(11)	= *x*	= *x*	1.2(6)
I/Cl1	8*c*	0.9/0.1	0.0121(2)	= *x*	= *x*	0.51(3)
Cl2	12*d*	1	1/8	0.14925(12)	*y* + 1/4	= $B_{\mathrm{I/Cl1}}$
At 11 K: a = 9.91359(13) Å; R_{wp} = 6.43 %, R_e = 5.99 %, and R_B = 5.23 %.						
Rb	4*a*	1	3/8	3/8	3/8	3.55(19)
Cu1	24*e*	0.361(14)	0.5179(12)	0.2929(13)	0.7973(14)	6.9(5)
Cu2	24*e*	0.245(11)	0.0004(14)	0.8331(13)	0.2094(13)	4.4(5)
Cu3	8*c*	0.18(5)	0.1568(18)	= *x*	= *x*	6.6(16)
I/Cl1	8*c*	0.9/0.1	0.0123(3)	= *x*	= *x*	2.29(4)
Cl2	12*d*	1	1/8	0.15031(16)	*y* + 1/4	= $B_{\mathrm{I/Cl1}}$
At 280 K: a = 10.0005(2) Å; R_{wp} = 6.06 %, R_e = 5.78 %, and R_B = 6.25 %.						

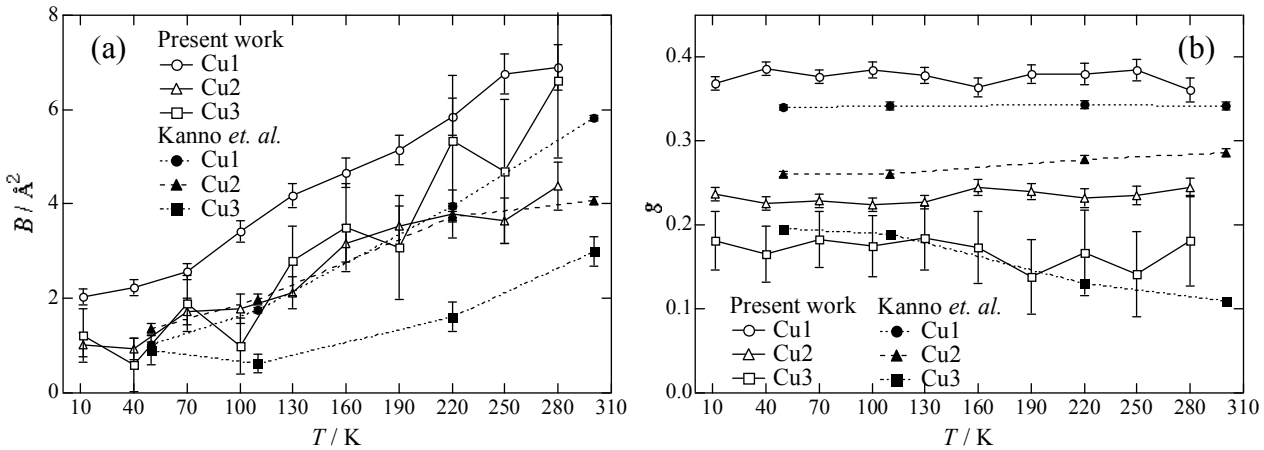

Fig. 1. Temperature dependence of isotropic atomic displacement parameters (a) and occupation factors (b) of the Cu sites..

than those obtained by Kanno *et al.* [3], but general tendencies for these parameters to vary with temperature are similar to each other.

After the Rietveld refinements, observed structure factors, F_o(Rietveld), estimated by Rietveld's procedure were analyzed with MEED [7] to determine three-dimensional nuclear densities. The resulting nuclear densities are believed to be more or less influenced by the imperfect structural model in the Rieveld refinements. To reduce these biases toward the structural model as much as possible, we executed MEM-based whole pattern fitting where structure factors were fixed at F_c(MEM). MEM analyses and whole-pattern fitting were repeated in this way until R_{wp} no longer decreased appreciably (REMEDY cycles [8]). This iterative procedure was particularly effective for high-temperature data where R_B decreased by 1% at most. Figure 2 exemplifies final whole-pattern fitting.

Figure 3 illustrates projections of nuclear densities in a *z* range from 0.42 to 0.58 onto the (001) plane at three temperatures. Cu atoms are localized at 11 K whereas pathways for Cu ions along Cu1–Cu2 chains are clearly visualized in Fig. 3(c). These density images lead us to conclude that the Cu1–Cu2 chain is the main conduction route in this material, as Kanno *et al.* pointed out.

As shown in the present study, MEM-based pattern-fitting using neutron powder diffraction data is useful to study highly disordered atomic configurations because crystal structures are adequately

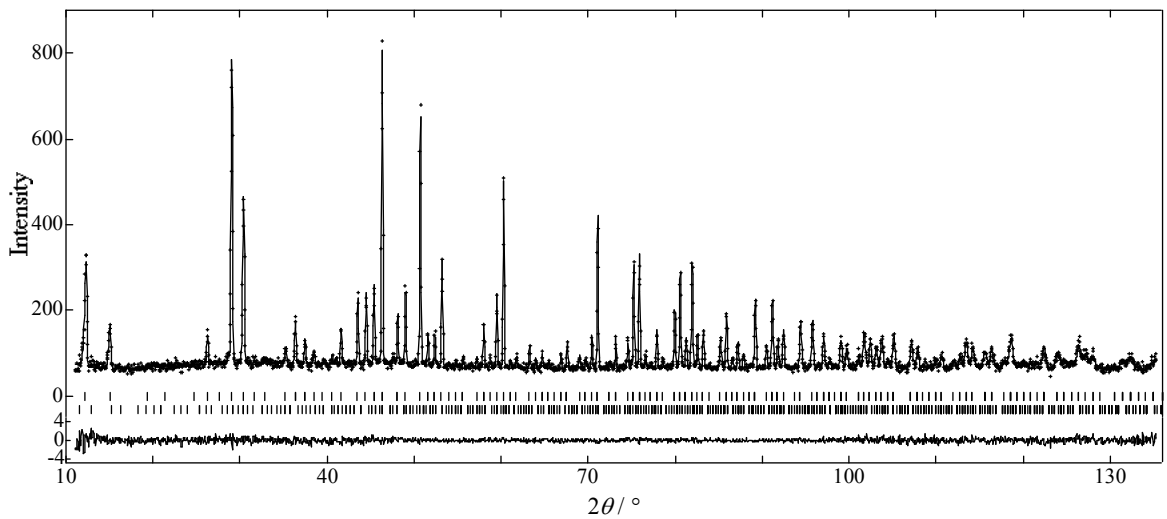

Fig. 2. Whole-pattern fitting of $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ at 11 K. Vertical markers indicate positions of possible Bragg reflections for $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ (upper) and $Rb_{18}Cu_{31}Cl_{49}$ (lower). Differences divided by the square roots of observed intensities are plotted at the bottom.

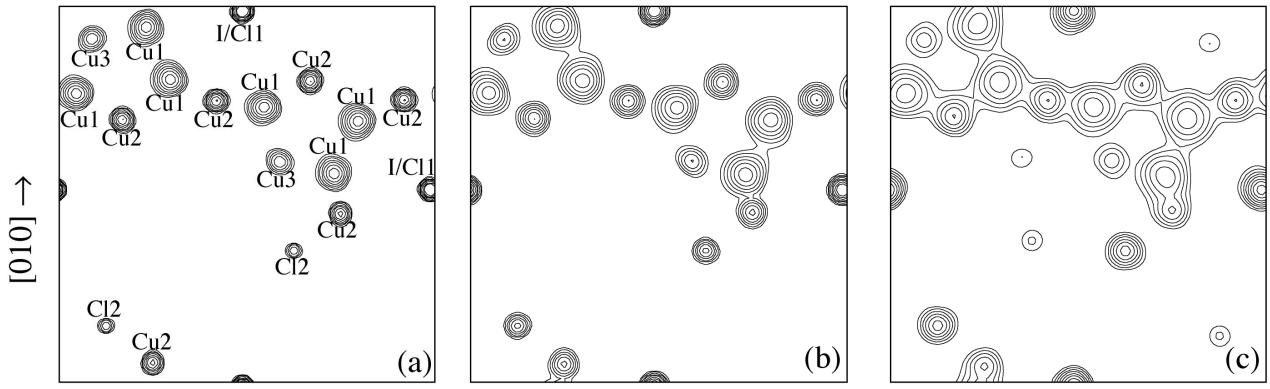

Fig. 3. Nuclear-density maps for $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ at (a) 11 K, (b) 130 K, and (c) 280 K with contours plotted for 2^{n+1} fm/Å^3 (n = 1 – 8).

represented not by structure parameters but by densities of atomic nuclei. We will further apply this technique to other ionic conductors.

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