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Refinement of the Crystal Structure of the Solid Electrolyte $\alpha(Cs_{0.55}Rb_{0.45})Cu_4Cl_3(I_{1.9}Cl_{0.1})$

S. GELLER AND T. SAKUMA*

Department of Electrical Engineering, University of Colorado, Boulder, Colorado 80309

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The crystal structure of metastable $\alpha(Cs_{0.55}Rb_{0.45})Cu_4Cl_3(I_{1.9}Cl_{0.1})$ at room temperature has been refined from single crystal X-ray diffraction data. The crystal on which the structure analysis was done belongs to space group $P4_132$, isostructural with $RbAg_4I_5$, and has a lattice constant of 10.100 ± 0.003 Å. As predicted, the substitution of Cs^+ for Rb^+ does not have a significant effect on the conduction passageways in the α phase.

1. Introduction

In two recent papers (*1*, *2*), we have reported the results of electrical conductivity vs temperature measurements, thermal analyses, and preliminary X-ray investigation of materials in the system $(Cs_{1-y}Rb_y)Cu_3(I_{2-x}Cl_x)$, and conclusions drawn therefrom. Four solid phases, designated α, α', β, γ, exist in this system above 295 K. The first of these exists across the whole range of composition. When $x = 0$, the α' and β phases exists only when $y \leq 0.36$; thus when $y \leq 0.36$, the α phase transforms directly to the γ phase.

It has been pointed (*2*) out that all melting in the system is incongruent and that small crystals of the α, α', and β phases are quenchable, but generally contain more cesium and more chloride than the starting material. The α phase is quenchable only when $y > 0.36$, where the α' phase does not exist. In this paper, we report briefly on the results of the refinement of the structure of $\alpha(Cs_{0.55}Rb_{0.45})Cu_4Cl_3(I_{1.9}Cl_{0.1})$ and how they support conclusions given in Ref. (*2*).

2. Experimental

Details of preparation of the starting constituents, starting compounds and crystals, have been given elsewhere (*2*). A crystal was isolated from the bulk material and ground to a sphere (*3*) of 0.14-mm diameter. This crystal was eventually aligned such that a fourfold axis, taken as [001], was the rotation axis.

The data were collected with a Buerger-Supper diffractometer automated by a NOVA 1200 computer. Zr-filtered Mo*K*α radiation was used in the range $5° \leq 2\theta \leq 60°$. The scan rate was 1°/min; the scan width was (1.5 + 0.7 Lp) where the L is the Lorentz and p the polarization correction. Background was counted at $\frac{1}{4}$ the scan time, before and after the scan.

The lattice constant of the specimen was

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* On leave from Department of Physics, Ibaraki University, Mito 310, Japan.

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10.100 ± 0.003 Å, as deduced from the highest angle lines of a powder photograph of some of the material taken with Cr$K\alpha$ radiation. The composition deduced (*2*) from this lattice constant is $(Cs_{0.55}Rb_{0.45})Cu_4Cl_3(I_{1.9}Cl_{0.1})$. This composition was later corroborated by the least squares refinement.

The X-ray density of $(Cs_{0.55}Rb_{0.45})Cu_4Cl_3(I_{1.9}Cl_{0.1})$ is 4.622 g/cm^3. For Mo$K\alpha$ radiation, the linear absorption coefficient is 19.10 mm^{-1}, giving 1.34 for μR. Absorption corrections were applied to the data. The number of independent observed intensities exceeding the threshold count of 100 used in the refinement was 178; the total number of accessible intensities in the range $5° \leq 2\theta \leq 60°$ was 342.

3. Refinement of the Crystal Structure

3.1 Least Squares Calculations

The NUCLS5 (*4*) program was used to carry out the least squares refinement of the structure. Starting parameter values were the final values of the analogous parameters of $RbCu_4Cl_3I_2$ (*5*). The final R value, $R = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$, is 0.060; the standard error of an observation of unit weight is 0.92 based on the following weighting scheme:

$$\sigma = 0.035\,F, \qquad F \geq 100$$
$$\sigma = 3.5 + 0.035\,(100 - F), \qquad F < 100$$
$$w = 1/\sigma^2.$$

The atomic scattering factors used in the calculations are from the paper by Cromer and Mann (*6*).

In the final least squares cycle all parameters, except the eightfold Cu$^+$-ion-site positional parameter, were varied; its value was fixed at 0.160 (*5*). The total Cu$^+$ multiplicity was constrained to be 0.667. The introduction of the imaginary parts of anomalous dispersion (*7*) contributions to the atomic scattering factors slightly favored the space group $P4_132$ over $P4_332$. The final parameters based on $P4_132$ are given in Table I. Variation of the $(I_{0.95}Cl_{0.05})$ and $(Cs_{0.55}Rb_{0.45})$ multipliers indicated that there was no significant deviation from the formula given.

3.2 Interionic Distances

The interionic distances, calculated with the ORRFEC program (*8*) are given in Table II (compare Tables II of Refs. (*5*) and (*9*)). The differences of the Cu–Cl and Cu–

TABLE I

POSITIONAL AND THERMAL PARAMETERS AND STANDARD ERRORS

Ion position	$(Cs,Rb)^+$ 4*a*	$(I,Cl)^-$ 8*c*	Cl^- 12*d*	Cu^+ 24*e*	 24*e*	 8*c*
Multiplier	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{2}$	0.356(17)	0.247(15)	0.064(8)
x	$\frac{3}{8}$	0.0092(2)	$\frac{3}{8}$	0.520(2)	0.006(2)	0.160
y	$\frac{3}{8}$	$= x$	−0.1436(7)	0.297(2)	0.836(3)	$= x$
z	$\frac{3}{8}$	$= x$	$= (\frac{3}{4} - y)$	0.800(2)	0.211(2)	$= x$
β_{11}	0.0109(4)	0.0073(3)	0.0073(13)	0.018(3)	0.006(2)	0.012(3)
β_{22}	$= \beta_{11}$	$= \beta_{11}$	0.0089(9)	0.023(4)	0.023(5)	$= \beta_{11}$
β_{33}	$= \beta_{11}$	$= \beta_{11}$	$= \beta_{22}$	0.017(3)	0.015(4)	$= \beta_{11}$
β_{12}	0	0.0001(2)	−0.0026(6)	0.006(3)	0.001(2)	−0.002(2)
β_{13}	0	$= \beta_{12}$	$= \beta_{12}$	0.002(2)	0.000(2)	$= \beta_{12}$
β_{23}	0	$= \beta_{12}$	−0.0022(11)	0.010(2)	−0.002(3)	$= \beta_{12}$

I distances from those of $RbCu_4Cl_3I_2$ or $NH_4Cu_4Cl_3(I_{1.9}Cl_{0.1})$ are not statistically significant. Unfortunately these distances always have the largest limits of error, mainly because of the relatively low Cu^+-ion-site occupancy and the anharmonic motion of the Cu^+ ions.

One Cu(II)–Cu(III) distance is 0.10 Å longer, another 0.06 Å shorter, than the analogous distances in $RbCu_4Cl_3I_2$, but these differences are also not statistically significant.

The predicted (*10*) lattice constant at 20°C of a NaCl-type CsCl is 6.941 Å; thus the octahedral Cs–Cl distance is 3.471 Å. In RbCl (*10*), the analogous distance is 3.271 Å. An average $(Cs_{0.55}Rb_{0.45})$–Cl distance, in a solid solution of CsCl and RbCl, should be 3.361 Å, if the lattice constant vs composition relation is linear, which is likely for this structure. This is to be compared with the value 3.446(5) Å found (Table II) in $(Cs_{0.55}Rb_{0.45})Cu_4Cl_3(I_{1.9}Cl_{0.1})$; the latter is 0.085 Å larger than the former. For the $RbCu_4Cl_3I_2$ case, the analogous difference is 0.097 Å.

TABLE II

INTERIONIC DISTANCES AND STANDARD ERRORS

Atom types	No. of distances	Distance (Å)
I–I	3	4.270(3)
I–Cl	3	4.054(10)
I–Cl	3	4.171(1)
I–Cl	3	4.276(11)
Cl–I	2	4.054(10)
Cl–I	2	4.171(1)
Cl–I	2	4.276(11)
Cl–Cl	4	3.711(6)
Cl–Cl	2	5.73(2)
Chloride octahedron about $(Cs_{0.55}Rb_{0.45})^+$		
(Cs,Rb)–Cl	6	3.446(5)
Cl–Cl	6	3.711(6)
Cl–Cl	3	5.73(2)
Cl–Cl	3	5.895(11)
Tetrahedron about Cu^+ (*c*)		
Cu–I	1	2.64
Cu–Cl	3	2.39
I–Cl	3	4.276(11)
Cl–Cl	3	3.711(6)
Tetrahedron about Cu^+ (*e*) (0.520, 0.297, 0.800) II		
Cu–I	1	2.75(2)
Cu–Cl	1	2.30(2)
Cu–I	1	2.72(2)
Cu–Cl	1	2.42(2)
I–I	1	4.270(3)
Cl–Cl	1	3.711(6)
Cl–I	3	4.276(11)
Cl–I	1	4.171(1)
Tetrahedron about Cu (*e*) (0.006, 0.835, 0.211) III		
Cu–Cl	1	2.58(2)
Cu–I	1	2.69(3)
Cu–I	1	2.54(2)
Cu–Cl	1	2.32(2)
I–I	1	4.270(3)
Cl–I	1	4.054(10)
Cl–I	2	4.171(1)
Cl–Cl	1	3.711(6)
Cl–I	1	4.276(11)
Nearest-neighbor Cu+ sites		
Cu(*c*)–Cu(II)	3	1.53
Cu(II)–Cu(*c*)	1	1.53
Cu(II)–Cu(III)	1	1.64(3)
Cu(II)–Cu(III)	1	1.39(3)
Cu(II)–Cu(II)	1	1.79(4)
Cu(III)–Cu(II)	1	1.64(3)
Cu(III)–Cu(II)	1	1.39(2)

Note. For simplicity, I is written instead of $(I_{0.95}Cl_{0.05})$.

4. Discussion

In the earlier paper (*2*) which included the results of conductivity vs temperature measurements, we had found that the conductivities of the α phases in the system $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ were about 25% lower than expected from the results obtained for the system $RbCu_4Cl_3(I_{2-x}Cl_x)$ (Ref. (*11*)). It was suggested that there was no a priori reason for such marked differences. At the

TABLE III

COMPARISON OF Cu^+-ION-SITE OCCUPANCIES IN DIFFERENT α PHASES, $MCu_4Cl_3(I,Cl)$

	M		
Site	NH_4^+	Rb^+	$(Cs_{0.55}Rb_{0.45})^+$
Cu(c)	0.74(14)	1.06(19)	1.54(19)
Cu(II)	7.34(67)	8.14(48)	8.54(41)
Cu(III)	7.82(74)	7.06(41)	5.93(36)

very least, the values at a particular temperature (for different y) should extrapolate to the value at that temperature for $RbCu_4Cl_3I_2$. They did not and, within experimental error, are constant for a particular temperature above 370 K, for $0.0 \leq y \leq 0.70$.

If the replacement of Rb^+ by Cs^+ does not affect the conduction passageways, then the only effect on the conductivity would be from change in charge carrier concentration, which decreases with decreasing y. The maximum effect on the conductivity from this source alone can be only 4% relative to $RbCu_4Cl_3I_2$, that is, the volume of the unit cell of $CsCu_4Cl_3I_2$ is 4% larger than that of $RbCu_4Cl_3I_2$. It has been assumed for this argument that the thermal expansion coefficient is the same for the α and α' phases for all y.

The structure refinement of $\alpha(Cs_{0.55}Rb_{0.45})Cu_4Cl_3(I_{1.9}Cl_{0.1})$ shows that the substitution of Cs^+ for Rb^+ does not have a noticeably unfavorable effect on the conduction passageways and therefore supports the hypothesis (*2*) that marked differences in conductivity as a function of y should not be expected. It also supports the hypothesis (*2*) that the difficulty encountered in attaining the conductivities of $RbCu_4Cl_3I_2$ is experimental in origin.

There is an interesting trend in the site occupancy of the Cu^+ ions. Table III gives the room temperature site occupancies (and standard errors) of the crystals of the chloroiodide solid electrolytes for which the structures have been refined. Although the standard error for each value is high, it appears that with increasing size of the alkali ion, the occupancies of the Cu(c) and Cu(II) sites increase, while (of necessity) the occupancy of the Cu(III) sites decreases. For comparison, the Ag^+-ion occupancies in $RbAg_4I_5$ are, respectively, 0.88(10), 9.38(29), and 5.50(28).

Undoubtedly, the site occupancies change with temperature; they should approach uniformity with increasing temperature. There is at least one indication, however, that within the occupancy ranges shown in Table III, the conductivities are not noticeably affected by the differences. This is obtained by comparing the room temperature conductivities of $RbCu_4Cl_3I_2$ (*11*) and $RbAg_4I_5$ (*12*), 0.39 and 0.27 Ω^{-1} cm^{-1}, respectively; the ratio is 1.44. The conductivity $\sigma = en\mu$, where e is the charge on the Cu^+ or Ag^+ ion, n the charge carrier concentration, and μ the mobility of the charge carrier. The ratio of the carrier concentrations is equal to the inverse of the ratio of the unit cell volumes which is 1.41, almost equal to the conductivity ratio. This suggests that the mobilities of the Cu^+ and Ag^+ ions in the two compounds are approximately the same, and therefore that the conduction passageways and charge carrier concentrations in the two are equally favorable.

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