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A Study of Phase Stability in the Rubidium–Copper(I)–Chloride System

T. E. WARNER*

Research Centre in Superconductivity, University of Cambridge, Cambridge CB3 0HE, United Kingdom

AND D. J. FRAY

Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, United Kingdom

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An attempt was made to synthesize a previously reported copper(I) ion solid electrolyte: $Rb_4Cu_9Cl_{13}$. Analysis of the product material by powder X-ray diffraction revealed that this composition was comprised solely of the two cubic phases: $Rb_9Cu_{16}Cl_{25}$ and CuCl. Electrical conductivity measurements yielded a copper(I) ion bulk conductivity of 0.025 S m^{-1} at 293 K. © 1989 Academic Press, Inc.

The occurrence and synthesis of a copper(I) ion solid electrolyte of formula $Rb_4Cu_9Cl_{13}$ has been reported by Gaines and Geller (*1*, *2*). They report an ionic conductivity for a polycrystalline sample as 0.44 S m^{-1} at 300 K, with an enthalpy of activation of 0.21 eV (*1*). The purpose of this study is to establish the validity of this claim, and to hopefully synthesize polycrystalline pellets for solid state EMF measurements.

A 10-g sample of the composition $Rb_4Cu_9Cl_{13}$ was prepared in accordance with the description given by the above workers (*1*). Starting materials included rubidium chloride (99+% purity) and copper(I) chloride (99.99%) purity, both supplied by Aldrich Chemical Co. Ltd. Stoichiometric amounts of RbCl and CuCl were ground together with an agate pestel and mortar and then sealed in a Pyrex tube under a pressure of approximately 50 kPa argon. The sample was heated to 473 K in a Lenton LTF12 horizontal tube furnace. After fusion, the charge was slowly cooled to ambient temperature. The contents were removed from the Pyrex tube and reground to a fine powder. Pellets of 10 mm in diameter and approximately 2 mm in length were pressed in a Specac stainless steel die under a pressure of 640 MPa. The pellets were then inserted into a Pyrex tube and sealed under a pressure of approximately 50 kPa argon, and annealed at 423 K for approximately 60

* The author to whom correspondence should be addressed.

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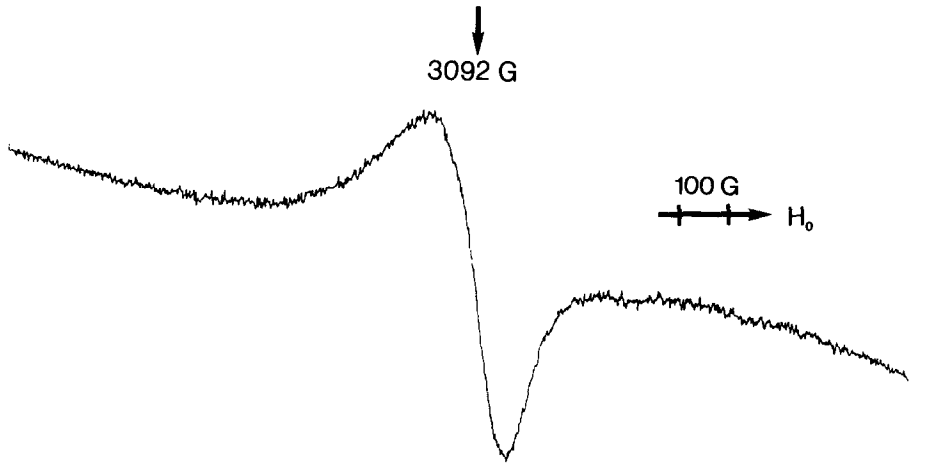

FIG. 1. First derivative X-band ESR spectrum of the annealed product recorded at 77 K showing a weak signal attributed to the impurity level of copper(II) ions.

hr before being cooled slowly to room temperature.

The initial appearance of the annealed pellets was white, although their surface turned a pale green color on exposure to the atmosphere and/or light. The X-band electron spin resonance spectrum of this bulk material as recorded on a Varian E109 spectrometer is shown in Fig. 1. The spectrum revealed a somewhat anisotropic single line in the free-spin region ($g = 2$). This exhibited Curie-type susceptibility on warming from 77 to 300 K and is assigned to trace impurity level copper(II) ions (*3*). The X-ray powder diffraction pattern of the sample as obtained with a standard Philips diffractometer is shown in Fig. 2. The radiation was Cu$K\alpha$ of wavelength 0.15418 nm. The crystal lattice spacings are listed in Table I. These are attributed solely to the two phases $Rb_9Cu_{16}Cl_{25}$ and CuCl (*4*).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR THE ANNEALED PRODUCT ($Rb_9Cu_{16}Cl_{25}$ · CuCl)

$d_{obs.}$ (nm)	$I_{obs.}$	Assigned phase	*h k l*
0.579	vw	$Rb_9Cu_{16}Cl_{25}$	123
0.557	vw	?	
0.415	w	$Rb_9Cu_{16}Cl_{25}$	150
0.380	w	$Rb_9Cu_{16}Cl_{25}$	125
0.352	w	$Rb_9Cu_{16}Cl_{25}$	244
0.343	s	$Rb_9Cu_{16}Cl_{25}$	116
0.324	w	$Rb_9Cu_{16}Cl_{25}$	145
0.313	m	CuCl	111
0.306	vs	$Rb_9Cu_{16}Cl_{25}$	444
0.290	m	$Rb_9Cu_{16}Cl_{25}$	127
0.277	w	$Rb_9Cu_{16}Cl_{25}$	370
0.270	m	$Rb_9Cu_{16}Cl_{25}$	156
0.265	w	$Rb_9Cu_{16}Cl_{25}$	800
0.247	w	$Rb_9Cu_{16}Cl_{25}$	347
0.243	m	$Rb_9Cu_{16}Cl_{25}$	266
0.236	w	$Rb_9Cu_{16}Cl_{25}$	190
0.220	w	$Rb_9Cu_{16}Cl_{25}$	239
0.192	w	CuCl	220
0.186	s	$Rb_9Cu_{16}Cl_{25}$	
0.181	w	$Rb_9Cu_{16}Cl_{25}$	
0.163	w	CuCl	311

The total electrical conductivity was measured at frequencies between 10 Hz and 100 kHz using a Solartron 1255HF frequency response analyzer and an EG&G PAR Model 273 potentiostat. The conductivity cell was comprised of a pellet of the material (10 mm diameter, 2.1 mm length) of which a layer of copper was evaporated onto the two flat surfaces, and placed between two pieces of copper foil: Cu/$Rb_9Cu_{16}Cl_{25}$ · CuCl/Cu. In Fig. 3, the tangent of the slope in the impedance spectrum is

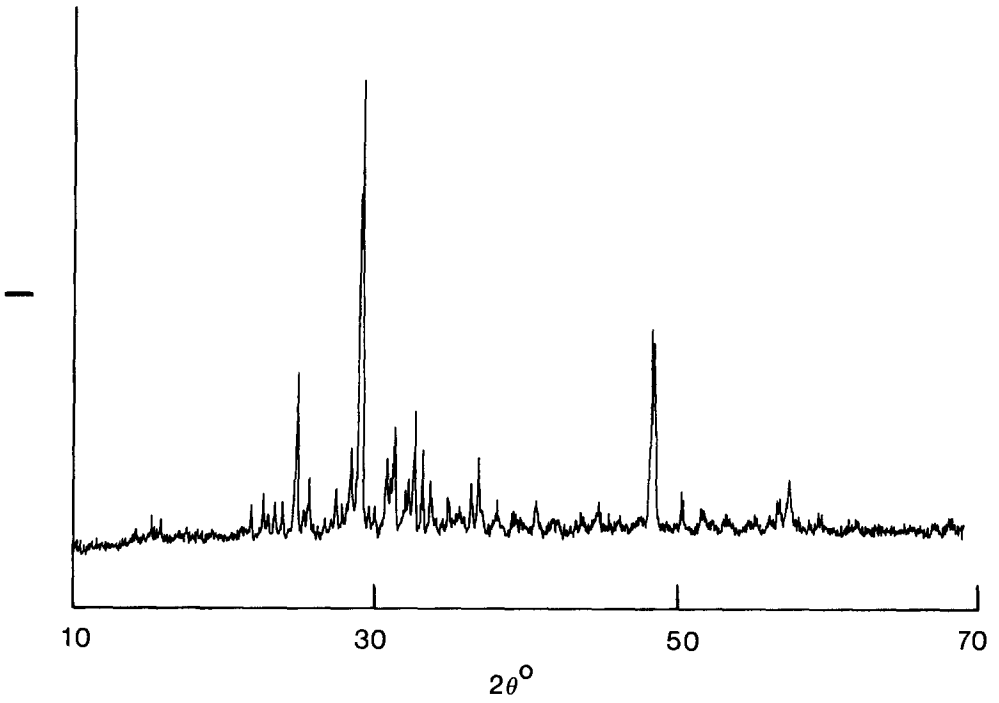

FIG. 2. X-ray powder diffraction pattern of the annealed product ($Rb_9Cu_{16}Cl_{25}$ · CuCl).

close to unity, which indicates Warburg-type behavior. The high frequency semicircle is due to the parallel combination of the grain boundary resistance and capacitance together with a series combination of the bulk resistance. Extrapolation of this semicircle at the high frequency end to the real axis yields the value of the intergranular resistance, namely, 1050 Ω. The corresponding conductivity was determined from the geometry of the pellet as 0.025 S m^{-1} (at 293 K).

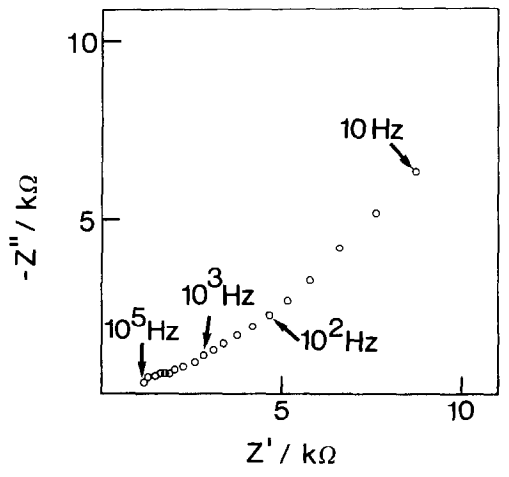

FIG. 3. Complex impedance spectrum of the annealed product ($Rb_9Cu_{16}Cl_{25}$ · CuCl) at 293 K.

The above synthesis was repeated under various conditions, namely, *in vacuo* (100 Pa) and also under a pressure of 50 kPa argon, both with slow cooling and with quenching in liquid nitrogen. Powder XRD data for each of these samples were identical with those given in Table I.

These results show clearly that the composition $Rb_4Cu_9Cl_{13}$ comprises the assemblage containing two cubic phases, namely, $Rb_9Cu_{16}Cl_{25}$ + CuCl at 423 K. Kanno *et al.* (*5*) have performed phase equilibria studies on the copper(I) chloride–rubidium chloride system, and have constructed the cor-

responding phase diagram containing the following six intermediate compounds: $Rb_3Cu_7Cl_{10}$, $RbCu_2Cl_3$, $Rb_9Cu_{16}Cl_{25}$, $Rb_{11}Cu_{14}Cl_{25}$, $RbCuCl_2$, and Rb_2CuCl_3. According to their results, the composition of 69.2 mol% CuCl (corresponding to $Rb_4Cu_9Cl_{13}$) would correspond to an equilibrium assemblage of $Rb_9Cu_{16}Cl_{25}$ + $Rb_3Cu_7Cl_{10}$, within the temperature range 424 to 438 K. The results from this current work suggest that this latter phase is itself segregated into $Rb_9Cu_{16}Cl_{25}$ + CuCl at 423 K.

Nonetheless, it is important to note that there is no evidence from the work of Kanno *et al.* (*5*) nor from this current study to suggest the existence of $Rb_4Cu_9Cl_{13}$ as a stable or even as a metastable phase within the temperature range 293 to 423 K.

Acknowledgments

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