Copper(I) halide–phosphorus adducts: a new family of copper(I) ion conductors

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Abstract

Ion exchange experiments and impedance spectroscopy investigations were performed on adducts of copper(I) halides to phosphorus and polyphosphorchalcogenide polymers, respectively. All compounds under investigation except one showed an ion exchange reaction ($Cu^+ \leftrightarrow Ag^+$) in an aqueous silver nitrate solution at room temperature and are therefore considered to contain mobile copper ions. Impedance measurements on $(CuI)_8P_{12}$, $(CuI)_3P_{12}$ and $Cu_3P_{15}I_2$ demonstrated that the total conductivity of $(CuI)_8P_{12}$ and $(CuI)_3P_{12}$ is predominantly ionic with corresponding activation energies of 0.45 and 0.59 eV, respectively, while the conductivity of $Cu_3P_{15}I_2$ is mainly electronic with a related activation energy of about 0.72 eV.

Keywords: Copper(I) ion conductor; Impedance spectroscopy; Ion exchange; Copper(I) halide; Phosphorus polymers

Materials: $(CuI)_8P_{12}$; $(CuBr)_8P_{12}$; $(CuI)_3P_{12}$; $(CuI)_2P_{14}$; $(CuI)_5P_{16}S$; $(CuI)_5P_{16}Se$; $Cu_3P_{15}I_2$; $Cu_{12}P_{20}Br_{10}$; $Cu_{13}P_{15}Br_{12}$

1. Introduction

Recently we have prepared a series of compounds containing formally neutral or negatively charged phosphorus polymers and polymeric phosphorus chalcogenides respectively surrounded by copper(I) halides. A survey of these phases is given in Table 1. In all of them the phosphorus polymers are arranged in rod packings and are surrounded only by copper ions in the first coordination sphere. Phosphorus halogen contacts do not appear. The copper ions are tetrahedrally coordinated by 1 to 3 phosphorus atoms and 3 to 1 halide ions respectively. CuX_4-tetrahedra (X = halogen) as typical for the copper(I) halide structures do not occur. One hint for a possible

Cu$^+$-ion mobility is the structural disorder of copper ions observed in the phases $(CuI)_8P_{12}$ ($\equiv Cu_2P_3I_2$) [1,2], $(CuBr)_8P_{12}$ [7], $Cu_{12}P_{20}Br_{10}$ [4] and $Cu_{13}P_{15}Br_{12}$ [7]. Möller and Jeitschko reported that $Cu_2P_3I_2$ undergoes an ion exchange reaction in an aqueous silver nitrate solution leading to the isotypic compound $Ag_2P_3I_2$, although transference measurements by the Tubandt method gave no evidence of copper ion conduction [1,2]. Nevertheless conductivity measurements on $Cu_2P_3I_2$ between Cu$^+$ blocking electrodes by means of impedance spectroscopy demonstrated predominantly ionic conductivity ($\sigma \simeq 1.90 \times 10^{-3}$ S/cm, $T = 186°C$) [3].

One important factor influencing ion mobilities is the bonding interaction between these ions and their surroundings. Therefore the number and charge of the phosphorus atoms coordinated to the copper ions might play a major role regarding whether they are

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Table 1
Survey of all hitherto known adduct compounds of copper(I) halides to phosphorus and polyphosphorchalcogenide polymers, respectively

Compound	Enclosed covalent structure elements		Ref.
$(CuI)_8P_{12}$ ($\equiv Cu_2P_3I_2$)		$^1_\infty[P_{12}^{\pm 0}]$	[1–3]
$(CuBr)_8P_{12}$	Neutral phosphorus polymers	$^1_\infty[P_{12}^{\pm 0}]$	[7,12]
$(CuI)_3P_{12}$		$^1_\infty[P_{12}^{\pm 0}]$	[5]
$(CuI)_2P_{14}$		$^1_\infty[P_{14}^{\pm 0}]$	[7,8]
$Cu_3P_{15}I_2$	Low charged polyanionic phosphorus	$^1_\infty[P_{15}^{1-}]$	[6]
$Cu_{12}P_{20}Br_{10}$	polymers	$^1_\infty[P_{20}^{2-}]$	[4]
$Cu_{13}P_{15}Br_{12}$		$^1_\infty[P_{15}^{1-}]$	[7]
$(CuI)_5P_{16}Ch$ (Ch = S, Se)	Neutral polymeric phosphorus	$^1_\infty[(P_{16}Ch)^{\pm 0}]$	[7]
$(CuI)_2P_{4-x}Ch_y$ (Ch = S, Se)	chalcogenides	?	[7]

mobile or not. We suppose that coordination to neutral phosphorus atoms should be in favour while coordination to negatively charged phosphorus atoms probably fixes the copper ions due to stronger coulomb interactions and thus hinders their mobility. This is supported by the fact that in the polyphosphide $Cu_{12}P_{20}Br_{10}$ [4] only 3 copper positions which are neighboured to negatively charged phosphorus atoms are fully occupied. By contrast the remaining 9 (of 12) copper ions are spread over 16 only partly occupied positions where they are coordinated to neutral phosphorus atoms and iodide ions, respectively [4]. To investigate these circumstances more closely we performed ion exchange experiments on single crystals of the compounds listed in Table 1. In addition we carried out impedance spectroscopy investigations on $(CuI)_8P_{12}$ and $(CuI)_3P_{12}$ containing neutral phosphorus polymers and on $Cu_3P_{15}I_2$ with polyanionic phosphorus chains respectively (for structural details see Refs. [1,5,6]).

2. Experimental

Single crystals and samples for impedance measurements were prepared from CuI (powder, 99.999%, Aldrich), CuBr (powder, 99.999%, Aldrich), copper (shot, m5N, Johnson Matthey), red phosphorus (lump, 6N, Hoechst), sulphur (powder, 99.999%, Fluka) and selenium (shot, 99.999%, Johnson Matthey) by heating stoichometric amounts of the educts in evacuated silica tubes at temperatures between 400 and 500°C for several days. More detailed information will be given elsewhere [7].

Although the compact materials and single crystals are black and shiny and look almost metallic, most of them show dark red colour through very thin layers. Samples for impedance measurements were ground and sample purity was checked by powder X-ray diffraction. After grinding, both black powders and fibrous products were obtained. Round pellets for impedance measurements were made by cold pressing the ground materials in a 13 mm stainless steel die between gold leaf forming the electrodes with an applied pressure of about 6000 kg/cm². Densities between 86 and 89% of the theoretical density were obtained. Good electrode contact was checked by comparing impedance spectra from pellets sputtered with gold [3] and pellets with gold leaf on the top which came out to be identical. The pellets were placed in a two-terminal spring-loaded measuring cell connected to Pt leads. The cell was placed in a horizontal tube furnace, with a thermocouple very close to the sample. Temperature was automatically controlled and measured within a tolerance of ±1°C. In order to avoid oxidation of the samples at higher temperatures, argon gas which was first passed over hot copper filings (400°C) to remove traces of oxygen was flushed through the cell. All impedance measurements were made with an IM6 impedance measuring system (Zahner-Elektrik) in the frequency range of 100 mHz to 4 MHz with an applied a.c. voltage of 100 mV. The series resistance of the leads was about 0.5 Ω and was always much smaller than the sample resistance. It was thus neglected. Since the parallel capacitance of the measuring system was about 40 pF and in addition the apparent semicircles in the complex

impedance plane were extremely depressed, probably due to a wide distribution in grain size and anisotropy of shape, grain interior and grain boundary impedances could not be resolved. Therefore only total resistivities were extracted from the impedance spectra including the grain boundary resistance.

3. Results

3.1. Ion exchange experiments

Referring to Möller and Jeitschko $Cu_2P_3I_2$ shows an ion exchange reaction in an aqueous silver nitrate solution. According to the equation

$$Cu_2P_3I_2 + 4Ag^+ \rightarrow Ag_2P_3I_2 + 2Ag\downarrow + 2Cu^{2+}$$
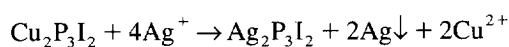
elemental silver is deposited on the material surface and the reaction solution becomes blue due to solvated Cu^{2+} ions [1,2]. Provided this is a real ion exchange reaction rather than a decomposition reaction (what we are investigating more accurately now), it proves copper ion mobility and supports interpretation of the impedance spectra. Its kinetics should be closely related to the copper ion conductivities and determination of the exchange ratio might reveal the number of mobile ions.

Single crystals of the compounds listed in Table 1 were treated with a concentrated aqueous solution of $AgNO_3$ under a light microscope. In all cases the shiny crystals first became dull within several seconds or minutes due to elemental silver deposited on the surface. Crystals of the copper halide rich phases showed an almost immediate cracking and splitting into thin fibers along the needle axes, which is equivalent to the axes of the one-dimensional phosphorus polymers. This can be ascribed to the larger radius of the silver ion compared to that of the copper ion. After a while, thin fibers of elemental silver were growing on the crystal surfaces of all compounds except for $Cu_3P_{15}I_2$. Crystals of the latter only became dull but were neither breaking up nor showed any larger amount of deposited silver indicating a volume reaction. Thus it can not be decided whether $Cu_3P_{15}I_2$ is penetrated by the silver ions or simply reacts at the surface. An arrangement of the compounds according to their relative reac-
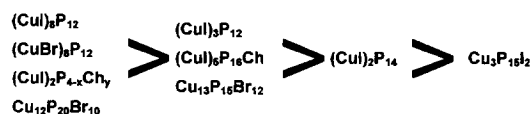

Fig. 1. Sequence of the relative reactivities regarding the ion exchange reaction in an aqueous silver nitrate solution.

tivities that were roughly estimated from the optically observed rate of silver deposition leads to the sequence shown in Fig. 1.

For $(CuI)_8P_{12}$, $(CuI)_3P_{12}$ and $Cu_{12}P_{20}Br_{10}$ the ratio of exchanged copper was determined by titration of Cu^{2+} in the reaction solution after treating about 1 g of the ground material for 24 h with a concentrated silver nitrate solution. For $(CuI)_8P_{12}$ the exchange ratio came out to be ca. 98%. Taking into consideration small losses of exchanged copper during the separation of the reaction solution from the solid residue this is in good agreement with the results of Möller and Jeitschko who proved complete exchange by EDX investigations [1,2]. Exchange ratios of 86% and 93% were found for $(CuI)_3P_{12}$ and $Cu_{12}P_{20}Br_{10}$, respectively.

3.2. Impedance measurements

Typical impedance spectra of polycrystalline samples of $(CuI)_8P_{12}$, $(CuI)_3P_{12}$ and $Cu_3P_{15}I_2$ plotted in the complex impedance plane are shown in Fig. 2. They represent the raw data and are neither corrected for the geometry of the samples nor for the parallel capacitance of the measuring system. The electrical properties of a polycrystalline mixed electronic–ionic conductor between ion blocking electrodes that are reversible for the electronic charge carriers might approximately be described by the equivalent circuit of Fig. 3a yielding an impedance spectrum of the shape given in Fig. 3b [9]. The semicircles 1 and 2 at the high frequency end are related to the grain and the grain boundary response, respectively. They are followed by a linear raise ending up in the semicircular arc 3. The linear part is corresponding to a diffusion process caused by the polarisation of the sample and is often represented by a Warburg impedance element in the equivalent circuit [10], while the low frequency arc yields the response of
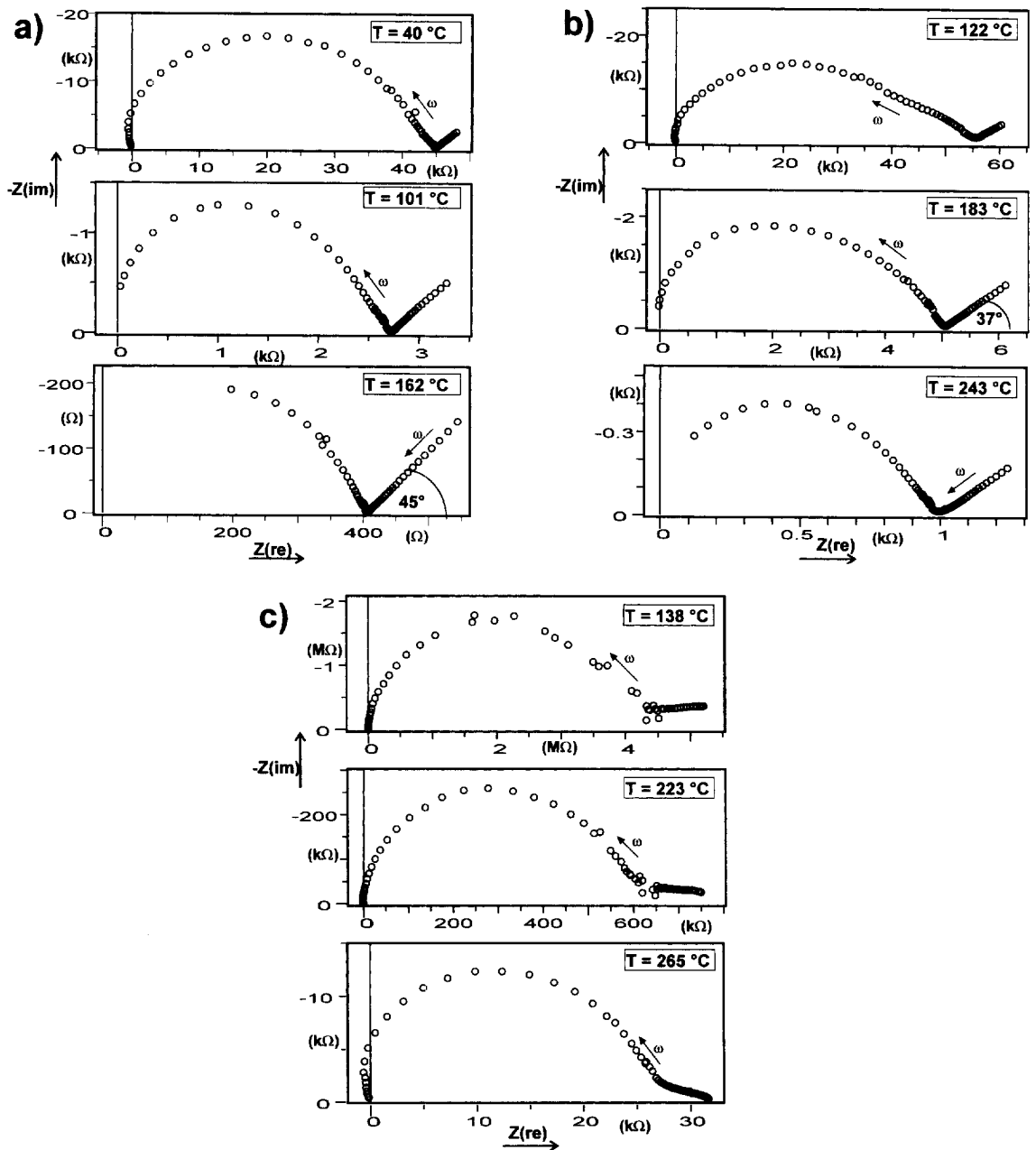
Fig. 2. Representative impedance spectra of polycrystalline samples of $(CuI)_8P_{12}$ (a), $(CuI)_3P_{12}$ (b) and $Cu_3P_{15}I_2$ (c) plotted in the complex impedance plane.

electronic conduction in parallel to a diffusion capacitance.

For $(CuI)_8P_{12}$, previous investigations have shown that the grain boundary capacitance C_{gb} was re-

markably small ($C_{gb} \cong 7 \times 10^{-11}$ F/cm) and close to that of the grains ($C_g \cong 2 \times 10^{-12}$ F/cm) leading to similar time constants τ ($\tau = R \times C$) for bulk and grain boundary response [3]. Since the parallel
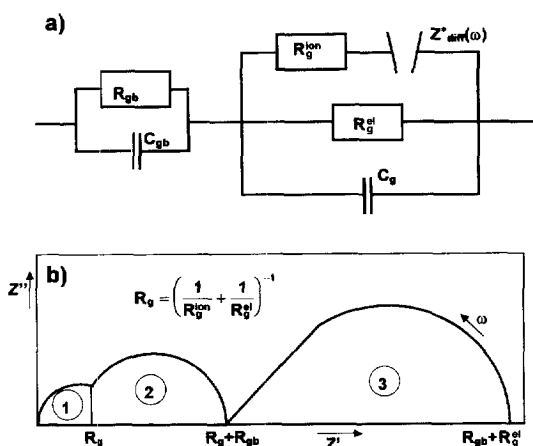
a)

Fig. 3. Equivalent circuit to approximate the electrical properties of a polycrystalline mixed electronic–ionic conductor between ion blocking but electronically reversible electrodes [9] (a) and the corresponding complete impedance spectrum (b).

capacitance of the measuring system (not considered in the equivalent circuit of Fig. 3a) was of the same order of magnitude here (≈ 40 pF) grain interior and grain boundary semicircle are not resolved but are included in the depressed high frequency semicircle of the spectra. This also applies for the spectra of $(CuI)_3P_{12}$ and $Cu_3P_{15}I_2$.

In the case of $(CuI)_3P_{12}$ (Fig. 2b) an additional semicircle can be identified at low temperatures. Since it was almost completely fused with the high frequency arc over a large temperature range, the related resistance could not be separated from the sum of bulk and grain boundary resistance. The origin of this arc is yet unclear. Provided it can be modelled by an additional parallel RC-element in series to the circuit of Fig. 3a the related capacitance can be estimated according to the equation $\omega_{max} \times R \times C = 1$ which holds at the frequency where the semicircle reaches its maximum. It then turns out to be of the order of 10^{-3} F at 122°C and shows a noticeable temperature dependence. Further experiments are necessary to clarify the origin of this effect.

Nevertheless, the linear raise of the impedance curves of $(CuI)_8P_{12}$ and $(CuI)_3P_{12}$ at low frequencies indicates that the total conductivity is dominated by copper ion conduction. By contrast, the spectra of $Cu_3P_{15}I_2$ only show a small low frequency semicir-

cle with related capacitances of 10^{-8}–10^{-7} F. There are several possible explanations for this. First it might be equivalent to arc no. 3 in Fig. 3. Second it can be interpreted in terms of a charge transfer resistance for the electronic charge carriers in parallel to a double layer capacitance. And last it might be related to the response of space charge regions formed at the grain–grain boundary interface [11] which would also fit to the remarkable atmosphere dependence found for the apparent sample resistance. Regardless of which of these interpretations is the right one, the nature of the total conductivity must be considered as mainly electronic.

Specific conductivity values including both bulk and grain boundary resistance were extracted from the impedance spectra by taking either the intersection of the declined low frequency spike with the real axis (in the case of $(CuI)_8P_{12}$ and $(CuI)_3P_{12}$) or by taking the real part of the intersection of the high and the low frequency semicircle (in the case of $Cu_3P_{15}I_2$), respectively. Fig. 4 shows the temperature dependence of the specific conductivities. Activation energies of 0.45 eV ($T = 70$–280°C) for $(CuI)_8P_{12}$, 0.59 eV ($T = 120$–280°C) for $(CuI)_3P_{12}$ and of about 0.72 eV ($T = 60$–280°C) for $Cu_3P_{15}I_2$ were extracted from the extrapolated slopes in the Arrhenius type $\log \sigma$ vs. $1/T$ plots.

4. Discussion

The fact that all compounds under investigation, except for $Cu_3P_{15}I_2$, undergo an ion exchange reaction in an aqueous silver nitrate solution proves that at least a certain amount of copper ions in those phases are mobile. Nevertheless, the experiments also imply that any quantitative interpretation such as the calculation of the ratio of mobile copper ions from the ratio of exchanged copper is questionable. Breaking of the crystals during the exchange reaction clearly indicates mechanical destruction or deformation of the original structure. Therefore the mobilities of the copper ions probably change in the course of the experiment. Copper ions that originally were fixed possibly become mobile due to the lattice distortions.

The exchange ratio of 98% found for $(CuI)_8P_{12}$ is in accordance with its crystal structure showing

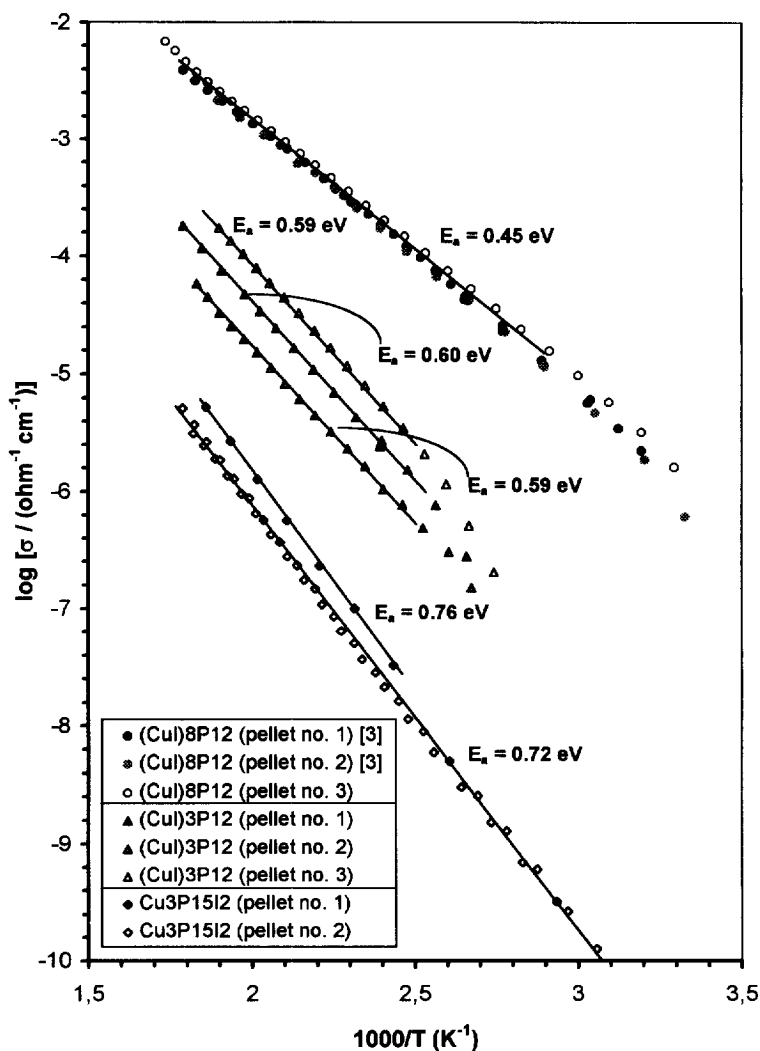Fig. 4. Conductivity data for polycrystalline samples of $(CuI)_8P_{12}$, $(CuI)_3P_{12}$ and $Cu_3P_{15}I_2$.

structural disorder for all copper ions. By contrast, the crystal structures of $(CuI)_3P_{12}$ and $Cu_{12}P_{20}Br_{10}$ do not provide any obvious explanation for the corresponding exchange ratios of 86 and 93%, respectively. For example if we assume that only those copper ions linked to neutral phosphorus atoms are mobile, an exchange ratio of, at most, 75% is expected for $Cu_{12}P_{20}Br_{10}$. Further experiments are necessary to investigate the influence of the concentration of the silver nitrate solution as well as the duration of the treatment on both the exchange ratio and the exchange rate.

The impedance spectra of $(CuI)_8P_{12}$ and $(CuI)_3P_{12}$ demonstrate that in spite of the almost metallic appearance of the materials, the total conductivities are dominated by copper ion conduction. In the case of $(CuI)_8P_{12}$ the specific conductivities and the associated activation energy in the temperature range 70–280°C are in excellent agreement with previous investigations [3]. By contrast, the impedance measurements on 3 different samples of $(CuI)_3P_{12}$ revealed large differences concerning the specific conductivities. Only the activation energies came out to be identical. One possible explanation might be a

two-dimensional ionic conductivity in combination with non-random orientation of the grains due to anisotropy of the grain shape. This seems reasonable considering the layer character of the crystal structure [5]. The neutral phosphorus polymers in $(CuI)_3P_{12}$ are arranged in layers connected via copper and iodide ions with the 'surface' of the phosphorus polymers and this arrangement possibly provides the conduction pathways.

In contrast to $(CuI)_8P_{12}$ and $(CuI)_3P_{12}$, the total conductivity of the polyphosphide $Cu_3P_{15}I_2$ is predominantly electronic in nature although, from the impedance spectra, a small contribution of copper ion conduction can not be excluded. Since two of three copper ions in this compound are linked to negatively charged phosphorus atoms, this result supports the assumption that coordination of the copper ions to negatively charged phosphorus atoms hinders their mobility due to stronger coulomb interactions.

Despite the restrictions regarding the quantitative evaluation of the ion exchange experiments noted above, the results for $(CuI)_8P_{12}$, $(CuI)_3P_{12}$ and $Cu_3P_{15}I_2$ from impedance measurements are in good agreement with the extracted sequence of relative reactivities. Further impedance measurements on the remaining compounds of Table 1 must show if this is valid for all of them.

References

[1] M.H. Möller, W. Jeitschko, J. Solid State Chem. 65 (1986) 178.
[2] M.H. Möller, Dissertation, Dortmund, 1983.
[3] E. Freudenthaler, A. Pfitzner, D. Sinclair, Mater. Res. Bull. 31 (1996) 171.
[4] E. Freudenthaler, A. Pfitzner, Z. Kristallogr. 212 (1997) 103.
[5] A. Pfitzner, E. Freudenthaler, Angew. Chem. 107 (1995) 1784.
[6] A. Pfitzner, E. Freudenthaler, Z. Kristallogr. 210 (1995) 59.
[7] E. Freudenthaler, PhD thesis, Siegen, 1997.
[8] A. Pfitzner, E. Freudenthaler, Z. Naturforsch. 526 (1997) 199.
[9] J. Maier, Solid State Phenomena 39–40 (1994) 35.
[10] J.R. Macdonald, Impedance Spectroscopy, John Wiley and Sons, New York, 1987.
[11] J. Maier, Ber. Bunsenges. Phys. Chem. 90 (1986) 26.
[12] D. Özalp, PhD thesis, Gießen, 1993.