Electrical conductivity of cuprous bromide in the temperature range of 30-490 °C

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The electrical conductivity (dc) of solid CuBr has been determined employing the cell configuration Cu/CuBr/Cu over a wide range of temperature (30 – 490 °C) which allowed the phase transformations: γ-CuBr $\leftrightarrow$ β-CuBr and β-CuBr $\leftrightarrow$ α-CuBr. With the measured conductivities, activation energy and pre-exponential factors have been evaluated over the studied range of temperature. Transport properties in the respective phases are discussed and compared with those reported in the literature. Though the order of magnitude of observed conductivity is same as that reported in literature, the observed values are higher than those reported earlier. The electrical conductivity of γ-CuBr increases rapidly with temperature, from $2.51 \times 10^{-3}$ Ω\textsuperscript{-1}m\textsuperscript{1} at 50 °C to 16.08 Ω\textsuperscript{-1}m\textsuperscript{1} at 400 °C. After the first phase transition of γ-CuBr $\leftrightarrow$ β-CuBr, the electrical conductivity attains a value of 148 Ω\textsuperscript{-1}m\textsuperscript{1} and increases further with increase in temperature. The conductivity increases by about 30 % on β-phase $\leftrightarrow$ α-phase transition (maximum value 377.60 Ω\textsuperscript{-1}m\textsuperscript{1} at 487 °C). Activation energies for conduction of γ-CuBr are found to be 85.58 kJ mol\textsuperscript{-1} (30-225 °C) and 145.35 kJ mol\textsuperscript{-1} (320-380 °C) whereas for β-CuBr it is 22.45 kJ mol\textsuperscript{-1} and for the superionic α-phase it is 2.38 kJ mol\textsuperscript{-1}.

**Keywords:** Conductivity, Cuprous bromide, Activation energy, Phase transformations

Conductivity measurement of CuBr has been an important topic of research for several decades\textsuperscript{1,6}. The electrical conductivity of cuprous bromide was first studied by Friederich and Meyer\textsuperscript{7}, who suggested that CuBr shows metallic type conduction. Later, its specific conductivity determined by Fischer\textsuperscript{8} using CuBr pellet sandwiched between Pt electrodes supported the suggestion of Friederich & Meyer\textsuperscript{7} and Frers\textsuperscript{9} who studied the electrical conductivity of CuBr across the temperature range 200-330 °C and concluded that between these temperatures conductivity turns gradually from metallic to pure electrolytic.

Tubandt\textsuperscript{10} studied the electrical conductivity of CuBr with respect to temperature and concluded that CuBr follows a linear temperature-conductivity relationship. He made a distinction between electronic and ionic conductivity of CuBr suggesting that below 300 °C, CuBr behaves as an electronic conductor and above 300 °C, it acts as a mixed conductor. Wagner & Wagner\textsuperscript{11} applied the polarization technique to estimate the contribution of electronic and ionic conductivity. They concluded that electronic contribution makes only a small contribution to the total conductivity of sample equilibrated with copper above 300 °C. Thus, the total conductivity is essentially ionic. Maidonovskaya et al.\textsuperscript{12} used emf measurements and concluded that CuBr samples showed hole conductivity at 50-350 °C and ionic conductivity due to Frenkel defects\textsuperscript{13} at $>$300 °C. They also studied the effect of concentration of halogen to the ionic conductivity of CuBr and found that participation of ionic conductivity increased with the decrease of halogen concentration. Wojakowska & Krzyzak\textsuperscript{14} also studied electrical conductivity of CuBr in the high temperature range of 500 – 1050 K. They reported the electrical conductivity of γ-CuBr as $2.1 \times 10^{-3}$ Ω\textsuperscript{-1}m\textsuperscript{1} at 500 K and $\sim22.2\Omega^{-1}m^{-1}$ at 653 K, β-CuBr as 215.5 Ω\textsuperscript{-1}m\textsuperscript{1} at 740 K and α-CuBr as 350 Ω\textsuperscript{-1}m\textsuperscript{1} at 753 K. Melting of the α-phase involved ~30 % decrease in conductivity and they reported the electrical conductivity of liquid CuBr at 770 K to be 250 Ω\textsuperscript{-1}m\textsuperscript{-1}. However, in the liquid state the electrical conductivity increased slowly with temperature up to 270 Ω\textsuperscript{-1}m\textsuperscript{-1} at 1050 K.

The solid state structure of CuBr is temperature dependent\textsuperscript{15}. γ-CuBr has the cubic zinc-blende structure\textsuperscript{15} at low temperature which shows a mixed ionic-electronic conductivity\textsuperscript{11}. However, it is a fact that above 573 K, the electronic conductivity is negligible\textsuperscript{16}. The γ-phase transforms to the β-phase at 658 K having hexagonal wurtzite structure\textsuperscript{15} with a high ionic electronic conductivity\textsuperscript{17,18} of around 100 Ω\textsuperscript{-1}m\textsuperscript{-1}. α-CuBr is a superionic phase similar to α-AgI and is stable in the temperature range\textsuperscript{19,21} of 742 –759 K. Buhrer & Halg\textsuperscript{15} and Kvist et al.\textsuperscript{22} reported that bromide ions form a rigid bcc sub-lattice while Cu\textsuperscript{+} ions are distributed statistically on tetrahedral positions\textsuperscript{15,22}. It is interesting to note that the electrical...
conductivity of \( \alpha \)-CuBr is even higher than that of \( \alpha \)-AgI at the same temperature.

Review of relevant literature reveals that significant work has been done on structural and transport properties of solid and molten CuBr in order to analyze structure and ionic motion in different phases\(^{17,18,22-25} \). However, some detailed experimental data are still desirable. The main objective of the present work is to carry out the conductivity measurements of CuBr in low as well as high temperature regions including the phase transition \( \gamma \)-phase \( \leftrightarrow \) \( \beta \)-phase, \( \beta \)-phase \( \leftrightarrow \) \( \alpha \)-phase. Cuprous halides are interesting from both the scientific and technological point of view. Moreover, economically copper compounds may be a good alternative to the silver conductors. The use of CuBr is gaining popularity due to the highly mobile cuprous ions and also that it seems to possess superionic conductivity (SIC).

**Experimental**

Cuprous bromide was prepared by treating solutions of copper sulphate (AR, Sigma) with sodium bisulphate (AR, Sigma) and potassium bromide (AR, Sigma) with continuous stirring. This solution was poured into a large beaker containing doubly distilled water. Cuprous bromide was precipitated and allowed to settle down. The solution of supernatant liquid in the beaker was decanted off. The solid mass remaining in the beaker was rinsed with water and acetone for at least 3–4 times to remove as much cupric bromide and other impurities from the solution till the supernatant liquid was almost colorless. Cuprous bromide was vacuum filtered with the help of Buckner funnel and washed with acetone and absolute alcohol while filtering. Cuprous bromide after the filtration was dried at 50 °C in a vacuum oven for 10 h and was stored in vacuum desiccators. The product obtained was characterized by scanning electron microscopy (SEM) (LEO 430, Leo Ldta, Cambridge, UK and Polaron sputter coater, Electron Optic Services, Inc. Ottawa, Canada), X-ray diffraction (PW 2404, Phillips, Pananalytical, The Netherlands) and electron paramagnetic resonance spectroscopy (E-112 ESR Spectrometer, Varian, USA).

Pellets of cuprous bromide were prepared in a KBr punch and die machine (model 341-20 Loomis Engineering and Manufacturing Co., USA). The diameter of the pellet was 1.16 cm, thickness was 4 mm and the area of the pellet was 1.06 cm\(^2\).

The electrodes and the pellets of cuprous bromide were assembled in order to charge the cell of configuration Cu/CuBr/Cu and contacts were ensured by screwing the top electrode into the bottom part of the cell. The full cell assembly was placed in an oven for heating at 200 °C for 4 h for annealing. The cell was kept in a resistance furnace in horizontal position. A variac was used to control the temperature, which was monitored by Pt-Rh thermocouple and external thermometer. The conductivities were measured at different temperatures ranging between 30 and 490 °C using a digital conductivity meter (Hewlett Packard HP 3457A multi meter) in the voltage range 30 mV-300 V with accuracy ±0.0005 V, current range 300 µA–1 A with accuracy±0.0005 A). The circuit diagram for conductivity and current is shown in Fig. 1.

**Results and discussion**

The CuBr used in this investigation has been characterized on the basis of impurity present in it. Only Cu\(^{2+}\) impurity has been taken in account, since it is the only inorganic cation which is likely to play an active role on the transport properties of CuBr. Transport property is an intrinsic property of CuBr material and effective only when an impurity atom (bromine atom) enters into the lattice (of a given crystalline material) or produces any perturbation in the lattice by forming an electron deficient bond in the crystal lattice. Scanning electron microscopy (SEM) image of the cross-sectional cell structure is shown in Fig. 2.

At room temperature X-ray powder diffraction pattern of the prepared sample shown in Fig. 3 resembles that of \( \gamma \)-CuBr. The XRD patterns observed...
are in good agreement with literature value of CuBr and the observed peaks can be attributed to the cuprous bromide \( \gamma \)-phase\(^{26,27} \). The most intense peak corresponds to the peak centered at 27.12°, while two other relatively less intense peaks are centered at 45.03° and 53.36°. Comparison with literature data of X-ray diffraction pattern indicates that the cuprous bromide in the synthesized sample is present as the \( \gamma \)-phase in room temperature.

EPR spectra did not show the signal for in CuBr as evidenced from the EPR spectra, indicating the presences of Cu\(^+\) in the sample. In stoichiometric cuprous bromide crystal, Cu\(^+\) ion and Br\(^-\) ion have the configuration \( 3d^{10} \ 4s^0 \) and \( 4s^2 \ 4p^6 \), respectively. In the present sample of CuBr\(_x\), excess bromine atoms are incorporated into cuprous bromide lattice. Consequently bromine atoms will interact with the electron of Cu\(^+\) ion, as if Cu is converted to Cu\(^{2+}\) having \( 3d^9 \ 4s^0 \) configuration. This configuration creates on electron deficiency in copper of CuBr\(_x\), which acts as a positive hole in Cu Br crystal and is likely to play an active role in the transport properties of CuBr. There is a probability of oxidation of CuBr by moisture and eventually all Cu\(^+\) after conversion to Cu\(^{2+}\) forms its own lattice. However, since copper is in contact with CuBr pellet, this tendency of Cu\(^{2+}\) would be minimized. In other words, deficiency of Cu\(^+\) in CuBr created by Cu\(^{2+}\) is compensated by oxidation of Cu, i.e. Cu \( \rightarrow \) Cu\(^+\) + e\(^-\), keeping CuBr close to the original stoichiometry. Thus, a chain type of oxidation, that is Cu \( \rightarrow \) Cu\(^+\) \( \rightarrow \) Cu\(^{2+}\), sets in leading to predominance of contribution of Cu\(^{2+}\).

Temperature relationship of the electrical conductivity of CuBr in the temperature range 30-490 °C is illustrated in Fig. 4. An Arrhenius type equation, \( \sigma = \sigma_0 \exp (-E_a/RT) \), was found to follow the observed results in the temperature range where the dependence \( \ln \sigma = \frac{1}{T} \) could be approximated with a linear function.
Pre-exponential factors and activation energies were evaluated using this and the enthalpies of activation for conduction, $H_a$, was calculated using the equation $\sigma = A/T \exp(-H_a/RT)$, where $A$ is a constant. The values of pre-exponential factors, activation energies and enthalpy of activation are summarized in Table 1.

Our results on conductivity of $\gamma$-CuBr are similar to those reported in the literature (Wojakowska et al.\textsuperscript{14} and Biermann et al.\textsuperscript{28}). In the temperature range studied, the electrical conductivity of $\gamma$-CuBr increases rapidly with temperature, from $2.51 \times 10^{-3}$ $\Omega^{-1} \text{m}^{-1}$ at $50 \, ^\circ\text{C}$, $3.39 \times 10^{-3}$ $\Omega^{-1} \text{m}^{-1}$ at $100 \, ^\circ\text{C}$, $9.1 \times 10^{-3}$ $\Omega^{-1} \text{m}^{-1}$ at $200 \, ^\circ\text{C}$, $2.26 \times 10^{-2}$ $\Omega^{-1} \text{m}^{-1}$ at $230 \, ^\circ\text{C}$ to $16.08 \Omega^{-1} \text{m}^{-1}$ at $400 \, ^\circ\text{C}$. The curvature of the Arrhenius plot (Fig. 4) illustrates that the activation energy for conduction in the $\gamma$-CuBr increases with temperature. Wojakowska and Krzyzak\textsuperscript{14} observed two slopes in the temperature ranges of 500-590 K and 590-650 K, whereas we observed a third slope in the lower temperature range of 30-225 °C in addition to two slopes observed in almost the same temperature range as those of Wojakowska and Krzyzak\textsuperscript{14}. The activation energies corresponding to the temperature ranges 30-225 °C, 225-320 °C and 320-380 °C were found to be 85.58, 96.25 and 145.35 kJ mol$^{-1}$, respectively. However, the last value is closer to the results reported by Safadi et al.\textsuperscript{16} (154 kJ mol$^{-1}$ at 270 °C < $T$ < 385 °C) and Biermann & Oel\textsuperscript{28} (151 kJ mol$^{-1}$ in the high temperature limit of the $\gamma$-phase). It is well established that at 320 °C the transference number of Cu$^+$ ion starts to decrease considerably while electronic conductivity becomes more and more predominant\textsuperscript{11}. The enthalpy of activation for conduction of $\gamma$–CuBr, calculated for the entire range of temperature was estimated as 94.50 kJ mol$^{-1}$ (30-275 °C), 109.54 kJ mol$^{-1}$ (225-320 °C) and 140.35 kJ mol$^{-1}$ (320-380 °C).

After the first phase transition of $\gamma$-CuBr $\rightarrow$ $\beta$-CuBr, the electrical conductivity attains a value of 148 $\Omega^{-1} \text{m}^{-1}$ and increases further with increase in temperature. However, it is relatively slower than in the $\gamma$-phase. To the best of our knowledge, this is the highest conductivity reported in literature though Wojakowska and Krzyzak\textsuperscript{14} reported the conductivity of $\beta$-CuBr to be about an order higher than that reported by Wagner and Wagner\textsuperscript{11}. The conductivity of $\beta$-CuBr at 470 °C is 260.5 $\Omega^{-1} \text{m}^{-1}$, and it has been established that $\beta$-CuBr is a purely ionic conductor\textsuperscript{1,16}. The energy of activation $E_a = 22.45$ kJ mol$^{-1}$ (Table 1) is in a close agreement with the value reported by Safadi et al.\textsuperscript{16} of 26 kJ mol$^{-1}$. The enthalpy of activation calculated from the ln($\sigma$) versus $T^{-1}$ curves is found to be 28.67 kJ mol$^{-1}$, which is close to 33 kJ mol$^{-1}$ (ref. 17), 30 kJ mol$^{-1}$ (ref. 18) and 31 kJ mol$^{-1}$ (ref. 14) reported earlier.

The conductivity increases by about 30 % on $\beta$-phase $\rightarrow$ $\alpha$-phase transition. For $\alpha$-CuBr we found the maximum value of the electrical conductivity as 377.60 $\Omega^{-1} \text{m}^{-1}$ at 487 °C, whereas Wojakowska and Krzyzak\textsuperscript{14} reported a value of 348 $\Omega^{-1} \text{m}^{-1}$ at 480 °C. Energy of activation and enthalpy of activation were evaluated from ln ($\sigma$T) versus $T^{-1}$ plot as 2.38 kJ mol$^{-1}$ and 8.78 kJ mol$^{-1}$, respectively (Table 1).

The relative role of ionic versus electronic conductivities as a function of temperature were studied. CuBr is a mixed ionic–electronic conductor, and the low temperature phase ($\gamma$-CuBr) shows a mixed ionic-electronic conductivity. The total electrical conductivity shows a considerable increase as the phase transition is approached. With increase of temperature, ionic conductivity increases whereas electronic conductivity was found to decrease. Above 200 °C the electronic conductivity is negligible. At 380 °C, the observed ionic conductivity was 144 $\Omega^{-1} \text{m}^{-1}$ and at 385 °C the $\gamma$-phase transforms to the $\beta$-phase having hexagonal wurtzite structure. The ionic conductivity was found to increase in the temperature range of 200-485 °C. Thus, there is a significant contribution of ionic conductivity towards total electrical conductivity of CuBr.

In the present study, the conductivity of CuBr in its different phases has been determined using cell configuration Cu/pellet/Cu over a wide range of temperature. The conductivity in $\beta$-phase is found to be the highest reported in the literature\textsuperscript{14,16,28} and is more than an order of magnitude higher than that reported by Wagner & Wagner\textsuperscript{11}. However, the present results in $\gamma$-phase are in close agreement with the literature values. Our results are more accurate having been obtained on the basis of a relatively large

\begin{table}[h]
\centering
\caption{Pre-exponential factors, activation energies and enthalpy of activation data for CuBr}
\begin{tabular}{|l|c|c|c|c|}
\hline
Phase & Temp. range & $\ln \sigma_0$ & $E_a$ & $H_a$ \\
(°C) & ($\Omega^{-1} \text{m}^{-1}$) & (kJ mol$^{-1}$) & (kJ mol$^{-1}$) \\
\hline
$\gamma$ & 30-225 & 16.54 & 85.58 & 94.57 \\
 & 225-320 & 20.15 & 96.25 & 109.54 \\
 & 320-380 & 29.08 & 145.35 & 148.35 \\
$\beta$ & 400-460 & 8.98 & 22.45 & 28.67 \\
 & 475-486 & 5.74 & 2.38 & 8.78 \\
$\alpha$ & 475-486 & 5.74 & 2.38 & 8.78 \\
\hline
\end{tabular}
\end{table}
number of measurement points with temperature difference of 10 °C. The higher value of conductivity in β-phase may be due to a lower resistance of the contact between the β-CuBr phase and the Cu electrode. However, such an interfacial resistance has not been confirmed.

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