JOURNAL OF MATERIALS SCIENCE 25 (1990) 3780–3784

Electrical conductivity of $CuSn_5Br_{11}$ in solid and molten states

A. WOJAKOWSKA, E. KUNDYS
Department of Inorganic Chemistry, Medical Academy, 50139 Wrocław, Poland

The electrical conductivity of solid and molten $CuSn_5Br_{11}$ and $SnBr_2$ compounds was determined using classical a.c. bridge techniques and sealed capillary-type cells with platinum electrodes. The experiments allow us to suspect the solid compound $CuSn_5Br_{11}$ to be a fast Cu^+ ion conductor. The specific conductance of the molten compound is nearly the same as that of the molten stannous bromide, so its conduction can be regarded as being mostly due to motion of the anions.

1. Introduction

The new intermediate compound $CuSn_5Br_{11}$ was discovered during the phase equilibrium studies of the $SnBr_2$–CuBr system [1]. Electrical conductivity investigations were undertaken because high values for its ionic conductivity in the solid state were expected, as in the case of $CuPb_3Br_7$, a compound with high Cu^+ ion conductivity [2, 3] existing in the related $PbBr_2$–CuBr system.

The bromide systems are studied less frequently than those of the chlorides or even the iodides. Only a few phase diagrams of the binary CuBr systems with other bromides are known [1]. Practically no data exist for the electrical conductivity of molten salt mixtures with CuBr or $SnBr_2$ as a component [4], apart from those for very dilute solutions of CuBr in molten $HgBr_2$ [5]. The specific conductance of the solid as well as molten stannous bromide is unknown. The molten cuprous bromide conductivity data [6] are based only on three experimental points [7]. On the other hand, the conductivity of the solid cuprous bromide has been studied more thoroughly. The works of Tubandt and his co-workers [7–9] and the paper of Wagner and Wagner [10] seem to be the most frequently cited.

The crystal structures and electrical conductivities of the cuprous halides resemble those of silver iodide. Room temperature γ-phases with the zincblende lattice transform into β-phases with the wurtzite lattice. High-temperature cubic α-phases, with a high degree of lattice disorder, are fast ion conductors. Lower silver halides, having a higher bond ionicity [11], crystallize with the NaCl structure and do not form polymorphic modifications. Therefore, the copper (I) ion conductors can be found not only in iodide systems but also in the chloride and bromide ones.

The detection of unusually high ionic conductivities of the solid complex silver compounds of the type MAg_4I_5 (where M = K, Rb, NH_4) [12, 13] gave rise to interest in analogous copper (I) salts. KCu_4I_5 was reported to have a similar conductivity [14] to KAg_4I_5 [12, 13]. No compound resembling the well-known $RbAg_4I_5$ was found in the system CuI–RbI. It was only when some of the iodide ions were replaced by chloride ions (the cation/anion radius ratio in CuCl is near that of AgI) that $Rb_4Cu_{16}I_7Cl_{13}$ was obtained [15], in which the copper/rubidium mole ratio is the same as that of silver/rubidium in $RbAg_4I_5$. This compound, like $RbAg_4I_5$, is characterized by high values of specific conductivity at ambient temperature and a low activation energy for conduction. $Rb_4Cu_{16}I_7Cl_{13}$ has, at present, found practical use in solid state batteries [16]. The CuCl + RbCl mixtures containing 67 to 90 mol % CuCl also have relatively high conductivity at room temperature [17]. The CuCl–RbCl phase diagram [18, 19] involves many compounds and probably because of this complexity, various formulae are claimed by different authors for the compound with the best conductivity, e.g. $RbCu_4Cl_5$ or $RbCu_3Cl_4$ [17], $RbCu_3Cl_4$ [20], $Rb_3Cu_7Cl_{10}$ [18], $RbCu_2Cl_3$ [21, 22]. The CuCl–TlCl system contains the intermediate compound $Tl_3Cu_2Cl_5$ which has a high copper ion conductivity, but decomposes when cooled [23]. The search for the fast ion conductors in the bromide and iodide systems resulted in the detection of the new compounds $CsCu_9Br_{10}$ and $CsCu_9I_{10}$ [15, 24]. Their stability ranges, however, are situated several hundred degrees above room temperature and are very narrow (about 15 K) [15].

To prepare new solid electrolytes with high copper ion conductivities, the aliovalent cations e.g. Zn^{2+}, Cd^{2+} or Hg^{2+} were introduced into the crystal lattice matrix of cuprous halides. It was found in the system with zinc and cadmium salts, where extended solid solutions were reported [25, 26], that samples containing 20 to 37 mol % bivalent cation salt have higher conductivities than those of pure cuprous halides [14, 26]. The increased conductivity may be not only due to the solid solution formation but sometimes due to the compound formation as well, e.g. Cu_4CdCl_6 [14] or Cu_2ZnI_4 [27]. In the CuI–HgI_2 system, a compound Cu_2HgI_4 has been known for many years [28]. It has a relatively high ionic conductivity [29] at temperatures not much higher than room temperature – above 340 K.

The high conductivity of $CuPb_3Br_7$, the compound quoted at the beginning of this paper, containing only 25 mol % CuBr, is surprising when compared with the above fast ion conductors with high cuprous ion concentrations. The compound $CuSn_5Br_{11}$, which we have studied, is characterized by equally good electrical conductivity in spite of its still lower CuBr content.

2. Experimental procedure

$CuSn_5Br_{11}$ was obtained from appropriate amounts of CuBr and $SnBr_2$, heated at 520 K in vacuum-sealed ampoules of Thermisil glass for ~ 12 h. The preparation of the stannous and cuprous bromides was described in detail in the previous paper [1]. $SnBr_2$ was obtained by dissolution of tin in concentrated hydrobromic acid, followed by dehydration of the crystallized product. CuBr was synthetized in the sealed silica ampoules from $CuBr_2$ and copper. Both salts were carefully purified by repeated vacuum distillation.

The specific conductances of solid and molten electrolytes were determined as functions of temperature. Resistances were measured using an alternating current bridge of the type MEL 7/69 (Politechnika Śląska, Gliwice) or MK-rs (Politechnika, Wrocław) fed from an audio-frequency generator of the type BM 365 U (Tesla) or PW-13 (Zopan, Warszawa), respectively, with continuous frequency control. It was found that for molten samples the effect of the signal frequency on the measured resistances was negligible within the range 1 to 15 kHz. After crystallization this effect increased, but in the range from 1 to 6 kHz it did not exceed experimental error as long as the sample was not cooled below 340 K. The accuracy of the resistance determinations for molten salts was better than 0.5%. In the solid state it was generally of one order inferior to that for the molten salts.

Temperatures were measured using an Ni/Ni, Cr thermocouple (Philips) calibrated by freezing temperatures of known standards, and an RFT d.c.–a.c.–R digital voltmeter. The following dependence of the temperature, T (K), on the electromotive force of the thermocouple E (mV), satisfied within a limit of ± 0.3 K, was found

$$T = 273.2 + 25.31\,E - 0.04315\,E^2 \qquad (1)$$

The capillary type conductivity cells made of Thermisil glass were used. They permitted measurement of the conductivity of liquids as well as of solids. The furnace and cell assembly is presented schematically in Fig. 1. Two hollow cylindrical platinum electrodes (1) were placed in fixed positions on both sides of the capillary (2). The electrodes were fabricated from cylindrically shaped 16 mm × 7 mm × 0.1 mm platinum sheets welded to platinum support wires of 0.3 mm diameter. The platinum wires were led out through capillary tubes (3) and soldered to the screened cables connecting them with the bridge. The thermocouple (4) was positioned inside the glass tube guard with its bottom inside one of the cylindrical electrodes.

The conductivity cells used in this work were calibrated with fused potassium nitrate [6] and standard aqueous solutions of potassium chloride [4] and they had the following cell constants: $2644 \pm 12\,\mathrm{m}^{-1}$ and $11\,259 \pm 26\,\mathrm{m}^{-1}$.

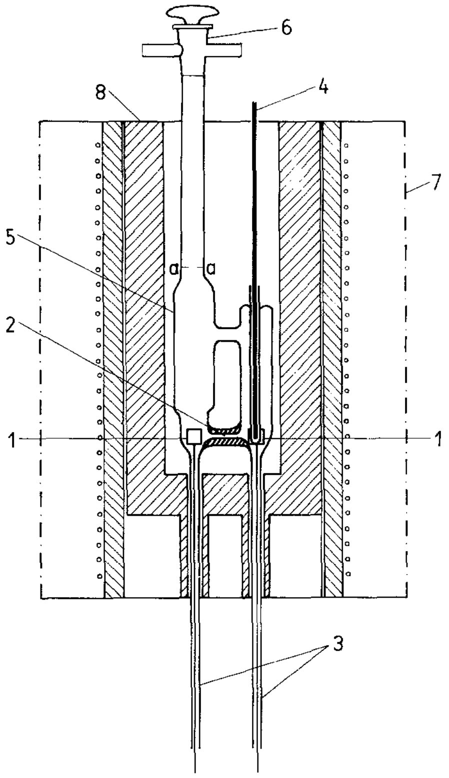

Figure 1 Conductivity cell assembly. 1, cylindrical part of the platinum electrode; 2, capillary; 3, guide tube; 4, thermocouple; 5, container; 6, tap; 7, furnace; 8, block.

In the calibrated conductivity cell, the gaps between the platinum wires and the extremities of their guide capillary tubes (3) were at first stopped with piceine sealing wax. Then appropriate amounts of salt (about 13 g) were put into the container (5) which was immediately connected to a vacuum pump through the tap (6). When evacuated the conductivity cell was sealed along the line "a–a" (see Fig. 1), put into the resistance furnace (7) and heated. The melted salt filled the capillary (2), electrode chambers and upper parts of the capillary tube guides (3), becoming crystallized in their lower parts when flowing down. Inside the conductivity cell, along the capillary (2) and two cylindrical electrodes (1), a zone of uniform temperature was ensured by suitable construction of a heavily lagged resistance furnace with a moulded steel block (8). A stand supporting the furnace ensured the possibility of tilting it. Alternating current power, regulated by an autotransformer, was supplied to the furnace. A signal temperature controller was used to hold the temperature steady.

Melt resistances were measured for several heating and cooling cycles. The rate of temperature change was, in general, lower than $1\,\mathrm{K\,min}^{-1}$ and practically stopped when the frequency dependence was measured. As the conductivity cell was sealed, the volume of the gaseous phase, as well as the temperature gradient above the melt were rather small, which prevented evaporation of the liquid. This was especially important in the case of the binary compound because a difference in the vapour pressure of the two components could cause a change of the melt composition.

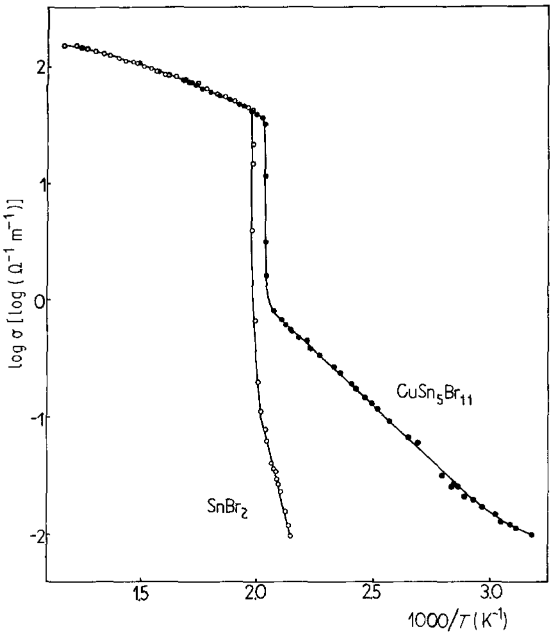

Figure 2 Temperature dependence of the specific conductivity for $CuSn_5Br_{11}$ and $SnBr_2$.

Afterwards the salt was crystallized by cooling the melt *in situ* at a very slow rate and resistances of the solid phase were measured. A solid sample was cooled or heated much more slowly than a liquid one (a few degrees per hour). Some results for samples kept at a given temperature for several hours or so, agreed with results based on dynamic measurements. This method of solid state conductivity determination is connected with difficulties arising from a possible appearance of fissures in the solidified mass or the electrode neighbourhood. In this study, however, this phenomenon has not been practically revealed.

3. Results

Resistances of molten and solid compounds $CuSn_5Br_{11}$ and $SnBr_2$ were measured as functions of temperatures and the results obtained at 5 kHz are presented in Fig. 2.

In the temperature range several tens of degrees above and below the melting point ($CuSn_5Br_{11}$ – 492 K, $SnBr_2$ – 505 K) the specific conductances follow Arrhenius temperature dependences

$$\log \sigma = \log A - \frac{E_a}{kT} \log e \qquad (2)$$

and appropriate data are shown in Table I. The logarithms of the specific conductance $\sigma(\Omega^{-1}\,m^{-1})$ were fitted to a function of the reciprocal of the absolute temperature T (K) by the method of least-squares using a computer program. The number of experimental data points, n, and the standard error of estimate, s, defined by

$$s = \left[\frac{\sum^{n} (\sigma_e - \sigma_c)^2}{n - q}\right]^{1/2} \qquad (3)$$

where σ_e is the experimental value at each temperature, σ_c the value calculated from the least-squares equation at the same temperature as σ_e, and q the number of coefficients in the least-squares equation.

For pure $SnBr_2$, a graph of $\log \sigma$ against $1/T$ showed a marked curvature above 693 K (Fig. 2). Therefore, the data for the higher temperature range were fitted to a quadratic function of temperature

$$\sigma = -85.087 + 0.32477T - 4.8774 \times 10^{-5}T^2$$

$$SnBr_2 \text{ (liquid, 693 to 853 K)}, \; n = 19, \; s = 0.51 \qquad (4)$$

4. Discussion

From the data presented in Fig. 2 it appears that there is a close resemblance between $SnBr_2$ and $CuSn_5Br_{11}$ in the molten state and a dissimilarity in the solid state. Just after freezing, the specific conductance of $CuSn_5Br_{11}$ is by one order of magnitude greater than that of $SnBr_2$ and declines much more slowly with decreasing temperature.

On the other hand, in the solid state the behaviour of $CuSn_5Br_{11}$ and $CuPb_3Br_7$ mentioned earlier [2, 3] are similar. They have identical activation energies of 0.34 eV as found from Table I and the data of Verma *et al.* [3]. Specific conductances of both compounds are approximate in value, too. For instance at 475 K, $\sigma\,(CuSn_5Br_{11}) = 0.64\,\Omega^{-1}\,m^{-1}$, while from the data of Verma *et al.* [3] we obtain $\sigma\,(CuPb_3Br_7) = 0.58\,\Omega^{-1}\,m^{-1}$. Based on these comparisons it may be supposed that the compound under study is also a superionic conductor. What is more, unlike $CuPb_3Br_7$, which on cooling undergoes resolution into CuBr and $PbBr_2$, followed by an abrupt drop in conductivity, it seems that $CuSn_5Br_{11}$ can be cooled to room temperature without decomposition, because the electrical conductivity changes smoothly, and below 435 K it is higher than in the CuBr–$PbBr_2$ system, e.g. by three orders of magnitude at 376 K.

Probably the copper ions are the predominant charge carrier in $CuSn_5Br_{11}$ as in $CuPb_3Br_7$ [2]. The Cu^+ ion must be more mobile than Sn^{2+} or Br^- ions due to its smaller size [1]. It is hardly probable for Sn^{2+} to be a mobile ion because the polyvalent cations interact more intensely with the surroundings. The diffusion coefficient of the Sn^{2+} ion in the solid stannous chloride at 373 K is only $1.0 \times 10^{-12}\,cm^2\,sec^{-1}$

TABLE I Arrhenius temperature dependence (Equation 2) for the specific conductance of $CuSn_5Br_{11}$ and $SnBr_2$ in solid and molten states

Compound	Temperature range (K)	$\log A$, [$\log (\Omega^{-1}\,m^{-1})$]	E_a (eV)	n	s (log units)
$CuSn_5Br_{11}$ (solid)	346–485	3.457	0.344	53	0.025
$CuSn_5Br_{11}$ (liquid)	502–594	3.4264	0.175	57	0.0023
$SnBr_2$ (solid)	464–496	14.856	1.55	14	0.024
$SnBr_2$ (liquid)	512–693	3.1956	0.155	32	0.0019

[30] when determined by radioactive tracer diffusion experiments. Therefore this salt is considered to be a chloride ion conductor [30, 31]. Similarly, the solid stannous iodide is an iodide ion conductor [32]. Thus it can be assumed that the solid stannous bromide is also an anion conductor.

Stannous bromide has a complex crystal structure [33] whose main features are the trigonal pyramids formed by the tin atom and its three nearest neighbour bromine atoms. The trigonal pyramids share two corners to form polymeric chains involving bromine bridges. The addition of cuprous bromide probably results in a partial depolymerization with the formation of complex ions. It is thought that they may form a rigid network, within which interstices are occupied by the mobile Cu^+ ions.

Destruction of the long-range order by fusion disturbs the conductivity paths, thus the cuprous ions can essentially no longer contribute to the electrical conductivity of $CuSn_5Br_{11}$ after fusion. If the molten $CuSn_5Br_{11}$ is regarded as a mixture of $SnBr_2$ to which a rather low content of CuBr has been added, the small effect of CuBr on the electrical conductivity of the molten $SnBr_2$ is compatible with a general picture of dopant influence on the electrical conductivity of fused salts [34]. The conductivity decreases markedly when a small ion is replaced by a larger one, but the conductivity remains nearly constant when a large ion, independently from its charge, is replaced by a small one.

In the molten state the specific conductivity as well as the activation energy of $CuSn_5Br_{11}$ are near those of $SnBr_2$ (Fig. 2, Table I). So it may be assumed that the structure of the molten $SnBr_2$ has not been affected substantially by introducing the Cu^+ ion in a quantity corresponding to the $CuSn_5Br_{11}$ formula. Raman spectra investigations of the solid and molten stannous bromide show [35] that on passing from the solid to the molten state, primary structure units have subsisted. The probability of the existence of chains, differentiated with respect to their length, is connected with an appropriate dynamic equilibrium

$$(SnBr_2)_{m+n} \rightleftarrows (Sn_mBr_{2m-1})^+ + (Sn_nBr_{2n+1})^- \quad (5)$$

where m and n each have to be as high as 3 at least. Molten stannous chloride has a similar structure [36]. Therefore, most probably the molten $SnBr_2$, like the molten $SnCl_2$ [37], should be an anionic conductor. A mixture formed after melting of the $CuSn_5Br_{11}$ has a minimally lower conductivity than that of the pure $SnBr_2$, maybe because the Cu^+ ions make the motion of the Br^- ions somewhat more difficult due to the formation of transient associates with them. The existence of the molecular species or other non-ionic structures in the molten cuprous halides must come into consideration [35, 38].

Acknowledgements

The authors thank Professor J. Terpiłowski for providing guidance for this work, Dr W. Szczepaniak for introducing us to the experimental techniques, R. Wojakowski and Ł. Wojakowski for computer programs. This work forms part of a programme of CPBP 01.15.

References

1. A. WOJAKOWSKA, *J. Therm. Anal.* **35** (1989) 91.
2. T. TAKAHASHI, O. YAMAMOTO and M. TAKAHASHI, *J. Solid State Chem.* **21** (1977) 37.
3. B. K. VERMA, O. P. SRIVASTAVA and H. B. LAL, *Phys. Status Solidi (a)* **64** (1981) 467.
4. G. J. JANZ, R. P. T. TOMKINS, C. B. ALLEN, J. R. DOWNEY Jr and S. K. SINGER, *J. Phys. Chem. Ref. Data* **6** (1977) 409.
5. G. JANDER and K. BRODERSEN, *Z. Anorg. Allg. Chem.* **264** (1951) 57.
6. G. J. JANZ, F. W. DAMPIER, G. R. LAKSHMINARAYANAN, P. K. LORENZ and R. P. T. TOMKINS, "Molten Salts", Vol. 1, "Electrical Conductance, Density, and Viscosity Data", Nat. Stand. Ref. Data Ser. No. 15 (National Bureau of Standards, USA, 1968) (Russian translation Izd. "Khimiya", Leningrad, 1971) p. 67.
7. C. TUBANDT, "Landolt-Börnstein", Erg.-Bd. II (Springer, Berlin, 1931) p. 1042.
8. J. GEILER, PhD thesis, University of Halle, Germany (1928).
9. C. TUBANDT, in "Handbuch der Experimentalphysik", Vol. 12 (Akademische Verlagsgesellschaft, Leipzig, 1933) Part 1.
10. J. B. WAGNER and C. WAGNER, *J. Chem. Phys.* **26** (1957) 1597.
11. A. GOLDMANN, *Phys. Status Solidi (b)* **81** (1977) 9.
12. J. N. BRADLEY and P. D. GREENE, *Trans. Faraday Soc.* **62** (1966) 2069.
13. *Idem, ibid.* **63** (1967) 424.
14. T. MATSUI and J. B. WAGNER Jr, *J. Electrochem. Soc.* **124** (1977) 937.
15. T. TAKAHASHI, O. YAMAMOTO, S. YAMADA and S. HAYASHI, *ibid.* **126** (1979) 1654.
16. R. KANNO, Y. TAKEDA, M. IMURA and O. YAMAMOTO, *J. Appl. Electrochem.* **12** (1982) 681.
17. T. MATSUI and J. B. WAGNER Jr, *J. Electrochem. Soc.* **124** (1977) 941.
18. R. KANNO, Y. TAKEDA, Y. MASKAYAMA, O. YAMAMOTO and T. TAKAHASHI, *Solid State Ionics* **11** (1983) 221.
19. V. F. VYBORNOV, V. S. SHVETSOV, V. V. IVANOV and A. N. KOLOMOETS, *Izv. Akad. Nauk. SSSR Neorg. Mater.* **20** (1984) 1413.
20. O. P. SRIVASTAVA, A. K. SRIVASTAVA and H. B. LAL, *J. Mater. Sci.* **20** (1985) 1763.
21. V. S. SHVETSOV, V. F. VYBORNOV and V. V. IVANOV, *Elektrokhimiya* **18** (1982) 986.
22. V. S. SHVETSOV and V. F. VYBORNOV, *ibid.* **19** (1983) 942.
23. T. TAKAHASHI, O. YAMAMOTO and A. SAWAI, *J. Appl. Electrochem.* **8** (1978) 161.
24. N. JOUINI, L. GUEN and M. TOURNOUX, *Rev. Chim. Mineral.* **21** (1984) 335.
25. G. HERRMANN, *Z. Anorg. Chem.* **71** (1911) 257.
26. M. G. ALEXANDER and B. RILEY, *Mater. Res. Bull.* **19** (1984) 1527.
27. P. H. FOURCROY, F. THEVET and J. RIVET, *Comp. Rend, Acad. Sci. Ser. II* **305** (1987) 1069.
28. E. P. MENSEL, *Ber. Deutsch. Chem. Ges.* **3** (1870) 123.
29. L. SUCHOW and G. R. POND, *J. Amer. Chem. Soc.* **75** (1953) 5242.
30. N. KIMURA, Y. NIIZEKI and O. TAKAGI, *Tohoku Kogyo Daigaku Kiyo* **1** (1984) 169.
31. N. KIMURA and Y. NIIZEKI, *Solid State Ionics* **3-4** (1981) 385.
32. T. A. KUKU, *ibid.* **20** (1986) 217.
33. J. ANDERSSON, *Acta Chem. Scand.* **A29** (1975) 956.
34. K. G. WEIL, *NATO ASI Ser. c* **130** (1984) 255.
35. W. BUES, M. SOMER and W. BROCHNER, *Z. Anorg. Allg. Chem.* **435** (1977) 119.

36. J. M. R. CLARKE and C. SOLOMONS, *J. Chem. Phys.* **47** (1967) 1823.
37. V. N. LYUBIMOV, V. A. FEDOROV, V. M. GRANKIN and P. P. SEMIANNIKOV, *Izv. Sib. Otd. Akad. Nauk SSSR* **12** (1970) 24.
38. J. G. POWLES, *J. Phys. C* **8** (1975) 895.

Received 13 April
and accepted 29 September 1989