JOURNAL OF MATERIALS SCIENCE 31 (1996) 2425–2428

Alternating current conductivity of solid and liquid phases in the tin diiodide–silver diiodide system

A. WOJAKOWSKA, E. KUNDYS, J. JOSIAK
Department of Inorganic Chemistry, Wrocław's University of Medicine, ul. Szewska 38, 50139 Wrocław, Poland

Electrical conductivity was measured in the solid and molten SnI_2–AgI system between 70 and 85 mol % AgI. High conductivity and a broad region of solid solubility, placed between 80 mol %, 75 mol % and about 40 mol % AgI and 635.8, 380 and 559.8 K, respectively, was confirmed. The addition of the SnI_2 to the molten AgI is accompanied by a decrease in the electrical conductivity and an increase in the activation energy. Temperature dependences of the specific conductivity indicate a similarity between molten mixtures and solid superionic phases.

1. Introduction

High electrical conductivity of Ag^+ ion in α-AgI, α-$RbAg_4I_5$ and many other silver complex compounds stimulate the search for new solid electrolytes in the systems involving silver salts. We have discovered in the SnI_2–AgI system [1] a new phase of proposed formula Ag_4SnI_6. We have also published a brief statement [2] about electrical conductivity in this phase.

Results of the conductivity measurements presented here confirmed the occurrence of the above superionic phase and indicated a solid solubility region towards a higher content of SnI_2 as well as defining the range of temperature stability.

It is well known that a high conductivity of α-AgI is due to a high degree of disorder in the Ag^+ sublattice. This last is often qualified as "molten" [3–7]. During a real melting an extraordinary event is observed [8] i.e. the decrease (by about 12%) of the electrical conductivity [9, 10]. The temperature needs to be up to 180 K above the melting point to reach the value of the conductivity of the solid just before melting.

In this work we also present results of the conductivity measurements for molten mixtures. They show an influence of the addition of SnI_2 on the electrical conductivity of the molten AgI as well as a relation between molten and solid phases behaviour.

2. Experimental procedure

The AgI–SnI_2 mixtures were prepared by direct synthesis of high purity silver, tin and iodine, in evacuated and sealed quartz ampoules. The samples were fused and kept at 880 K for some hours.

The capillary type conductivity cells with platinum electrodes permitted measurement of the conductivity of liquids as well as of solids [11, 12]. They were calibrated with fused KNO_3 and then filled with a homogenized salt mixture and sealed under vacuum.

Resistances were measured for several heating and cooling cycles using an alternating current bridge and an audio-frequency generator with continuous frequency control. No frequency dependencies were observed between 1 and 20 kHz. The cell assembly and the experimental procedure were described in detail previously [2, 12].

3. Results

The specific conductances $\sigma(\Omega^{-1}\,m^{-1})$ of solid and liquid SnI_2–AgI mixtures were determined as functions of temperature T (K). In the temperature range where the Arrhenius representation could be used

$$\sigma = \sigma_0 \exp(-E_a/RT) \qquad (1)$$

where E_a is the activation energy and R is the gas constant, the logarithms of σ were fitted to the function of the reciprocal of the absolute temperature by the method of least squares.

Appropriate data are summarized in Table I, where the compositions, the ranges of temperature concerned, the coefficients $a = \log\sigma_0$ and $b = (E_a \log e)/R$, the activation energies as well as the standard error of estimate s and the number of experimental data points n were shown.

4. Discussion

4.1. Solid state

In view of Ag_4SnI_6 formula established before [1], compositions centred about 80 mol % AgI were studied. A composition of 80 mol % AgI is characteristic of a high temperature limit of the phase, where it melts incongruently at 635.8 K (Fig. 1).

Below this temperature, an extension towards lower AgI content could be supposed (even to 40 mol % AgI at the eutectic temperature 559.8 K) based on disappearance of the eutectic temperature in this region as

TABLE I Specific conductance $\sigma(\Omega^{-1}\,\mathrm{m}^{-1})$ of solid and liquid SnI_2–AgI mixtures

Composition (mol% AgI)	Temperature range (K)	*a*	*b*	*n*	log*s*	E_a (kJ mol^{-1})
Solid mixtures						
85	461–597	2.964	629.1	25	0.004	12.04 ± 0.09
80	472–585	2.825	554.4	68	0.005	10.61 ± 0.08
78	456–605	2.822	564.9	50	0.005	10.81 ± 0.09
	391–426	3.940	1054	26	0.002	20.18 ± 0.15
70	422–581	3.104	795.2	44	0.008	15.22 ± 0.11
Liquid mixtures						
85	716–780	2.4935	216.5	14	0.0008	4.14 ± 0.11
80	673–873	2.5448	272.1	85	0.0009	5.21 ± 0.05
78	653–728	2.5157	333.9	77	0.0011	6.39 ± 0.05
70	624–683	2.6110	373.4	64	0.0021	7.15 ± 0.13

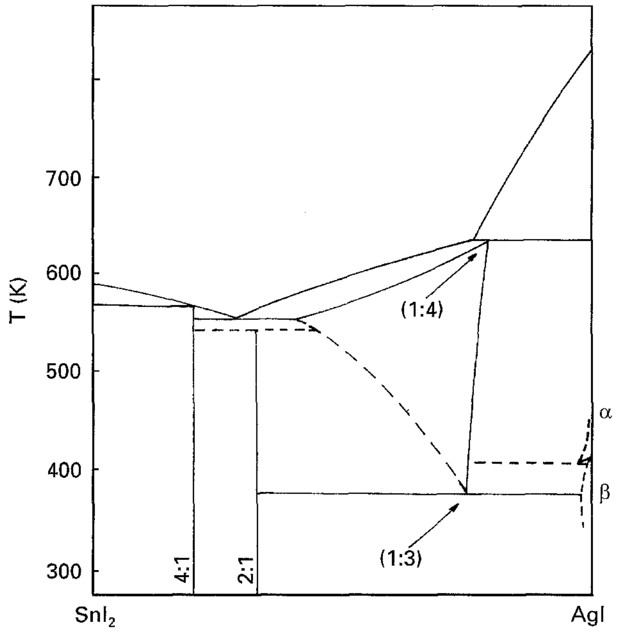

Figure 1 Phase diagram of the SnI_2–AgI system [1, 2, 13].

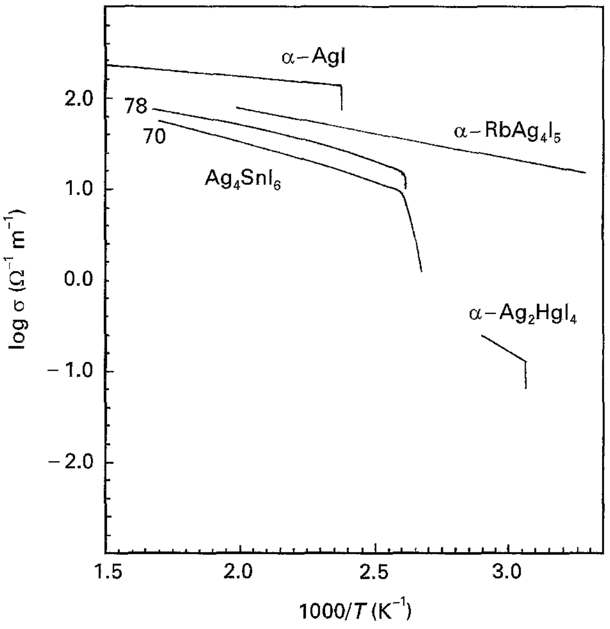

Figure 2 Arrhenius dependence for some solid ionics: α-AgI [9], α-$RbAg_4I_5$ [14], Ag_4SnI_6 78 and 70 mol% AgI (this work), Ag_2HgI_4 [15].

well on a flat course of the respective part of the liquidus curve (Fig. 1).

Results of electrical conductivity measurements give support to this suggestion. The Arrhenius law is valid for temperature ranges including the eutectic temperature, where no abrupt change of the conductance is observed (Table I).

The low temperature limit of the resistance measurements was that of 382 K where the phase Ag_4SnI_6 decomposed. This was accompanied by a substantial increase in volume followed by the cracking of conductance cells.

A broad region of solid solubility as well as the decomposition of the phase on cooling were observed also by Blachnik and Stöter [13] on the grounds of differential thermal analysis (DTA) results. They ascribed the formula Ag_3SnI_5 to the phase at its low temperature limit.

Fig. 2 shows log $\sigma(1000/T)$ plots for samples of 70 and 78 mol% AgI and, for comparison, those for α-AgI [9], α-$RbAg_4I_5$ [14] and α-Ag_2HgI_4 [15]. The electrical conductivity of Ag_4SnI_6 is very high, close to that of α-$RbAg_4I_5$. As is α-AgI and many of its derivatives, the phase Ag_4SnI_6 is not stable at room temperature. Nevertheless, a lower limit for its existence is about 40 K below that for α-AgI at normal pressures (Fig. 2).

An abrupt expansion on cooling observed at 382 K is simultaneously a sign of the diminution of the molar volume accompanying the formation of the Ag_4SnI_6 at the same temperature. It is similar to the formation of α-AgI from β-AgI [16]. A decrease of the molar volume when α-AgI is formed was ascribed by Phillips [17] to melting of the cationic sublattice and it was compared to the reduction of the molar volume during melting of tetrahedrally co-ordinated compounds of the $A^N B^{8-N}$ type with partial covalent bonding.

According to the spectroscopic theory of ionicity by Van Vechten and Phillips [18–20] and many later publications referring to it, the tetrahedral or octahedral co-ordination of anions around the cation in the crystal results from a dominance of the covalent or ionic bonding, respectively. A difference of the energy value between the tetrahedral and octahedral co-ordination in AgI is only about 2 kJ mol^{-1} [17]. Another cation added could stabilize the first or the second co-ordination. However, the relation of these new structures with that of α-AgI is doubtful because they are often complex and non-typical. Surely, foreign ions will cause an increase of sharing co-ordination polyhedra via common sides and the network of iodide ions will be strengthened. Inherent foreign cations co-ordinated by six ions of I^- reduce distortion, inevitable in case of the space filling only by the regular tetrahedra [21].

Ag_4SnI_6 has a regular structure [13, 22]. Since some of the tin in SnI_2 itself is octahedrally co-ordinated [23], one can expect Sn^{2+} ions to occupy parallel sites in the Ag_4SnI_6 structure, as Rb^+ ions do in the $RbAg_4I_5$ structure [24, 25]. The Ag_4SnI_6 phase extends towards SnI_2 within the range of about 40 mol %. X-ray diffraction data for samples of different compositions i.e. 75 [13] and 67 [22] mol % AgI and at different temperatures: 430 [13] and 523 K [22], respectively, are identical. The lattice constant is the same: 0.63 nm. It is possible that the size of the elementary cell is determined by the rigid network of the iodide ions. The concentration of the iodide ions as common ions is not changed within the phase. On the other hand, the electrical conductivity as well as activation energy are changed visibly. At 540 K, for example, the electrical conductivity decreases from $60\,\Omega^{-1}\,m^{-1}$ for 78 mol % AgI to $43\,\Omega^{-1}\,m^{-1}$ for 70 mol % AgI. Activation energy increases from $10.81\,kJ\,mol^{-1}$ to $15.22\,kJ\,mol^{-1}$, respectively (Table I). This could result from a decreased concentration of the conducting Ag^+ ions as well as from obstacles to their motion arising e.g. from an increase of the repulsive forces between positive ions Ag^+ and Sn^{2+} or from the increasing occupancy of the octahedral sites when increasing concentration of Sn^{2+} ions.

It is difficult to say now, if Ag^+ ions pass through the shared faces from one tetrahedron to another, as in bcc iodine lattice (α-AgI) [26], or from tetrahedron to an octahedron and vice versa, as in fcc iodine lattice (α-CuI) [26]. This last could be expected for Ag_4SnI_6 for the reasons that (a) existing X-ray data qualify the structure as regular face centred [13], and (b) extension of the composition towards SnI_2 and a decrease in electric conductivity in this direction can indicate a similarity to α-Ag_2HgI_4 (Fig. 2), having fcc iodine sublattice and high electric conductivity [15, 27]. This is, however, lower than that of other compounds derived from AgI, probably due to a high energy barrier for conduction through the octahedra [28].

Considering the general expression for conductivity

$$\sigma = nZe\mu \qquad (2)$$

where n is the concentration of charge carriers, Ze is their charge and μ is their mobility. Taking the concentration of the mobile species as the total concentration of Ag^+, calculated from X-ray density data for Ag_4SnI_6 ($d = 5.56\,g\,cm^{-1}$ [22]), the mobility of charge carriers can be obtained. At 475 K μ is equal to $3.5 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$. This number is the same magnitude as mobilities of Ag^+ in α-AgI or in α-$RbAg_4I_5$ [29]. So the above value, together with high conductivities and low activation energies, allows this phase to be included among superionic conductors.

4.2. Liquid state

In the range of temperatures not too far removed from the melting point, the conductivity of molten salts often obeys the Arrhenius law (Equation 1). However, in contrast to ionic solids, where electrical conductivity is often due to one type of carrier, in molten salts many species are mobile. Their movement generally has a co-operative character. Consequently, electrical conductivity of liquids is not very susceptible to structural changes.

First measurements of the electrical conductivity of molten AgI were made by Kohlrausch [8], who was followed by some research workers in the first quarter of the twentieth century. These investigations, critically examined, are still recommended [30–32] in the publications which appeared under auspices of the National Bureau of Standards and Molten Salt Data Center, Rensselaer Polytechnic Institute (USA). Activation energy, evaluated from the temperature-dependent equation for specific conductivity of molten AgI in the temperature range from 830 to 1073 K [32], is $4.79\,kJ\,mol^{-1}$.

The phenomenon of diminishing the electrical conductivity on melting was reported by Tubandt and Lorenz [9] who also discovered the extraordinarily high electrical conductivity of the high temperature polymorphic modification of the silver iodide (α-AgI). Kvist and Josefson [10] made a thorough study of the electrical conductivity variation during melting of α-AgI and the drop in conductivity was estimated to be about 12%. The activation energy $2.15\,kJ\,mol^{-1}$ obtained from the equation (1), according to the Kvist and Josefson data is about half of that derived from Janz's compilation [32]. Our values for activation energies of SnI_2–AgI molten mixtures (Table I), decreasing with the AgI content, seem to support the value of $2.15\,kJ\,mol^{-1}$ for the pure molten silver iodide. A similar value of $2.57\,kJ\,mol^{-1}$ arises from Richter's group's determinations [33].

When SnI_2 was added to the molten AgI, the electrical conductivity was reduced and the activation energy was increased (Fig. 3). Such a tendency was also observed in solutions of alkali metal iodides [33], PbI_2 [34], CdI_2 or SrI_2 [35] in molten AgI. So the molten silver iodide shows a typical molten salt behaviour where electrical conductivity depends mainly on the radius of the added cation and less on its charge [36] and where faster ions Ag^+ are hampered by slower ions e.g. K^+ or Cd^{2+} (drag effect [37, 38]). Our results indicate this effect to be present also in SnI_2–AgI molten mixtures.

The same is again valid for SnI_2–CuI molten mixtures, which we had studied previously [39]. But they have lower conductivities and higher activation energies than respective SnI_2–AgI mixtures (Fig. 3).

Pure molten CuI as well as high temperature superionic α-CuI also have lower conductivities and higher activation energies than pure molten AgI and superionic α-AgI, respectively. The fraction of ionic character on the Phillips scale [19] is higher for the Ag-I bond than for the Cu-I bond: 0.770 and 0.692, respectively. Hence, a higher concentration of ionic current carriers, e.g. in molten AgI, as compared with

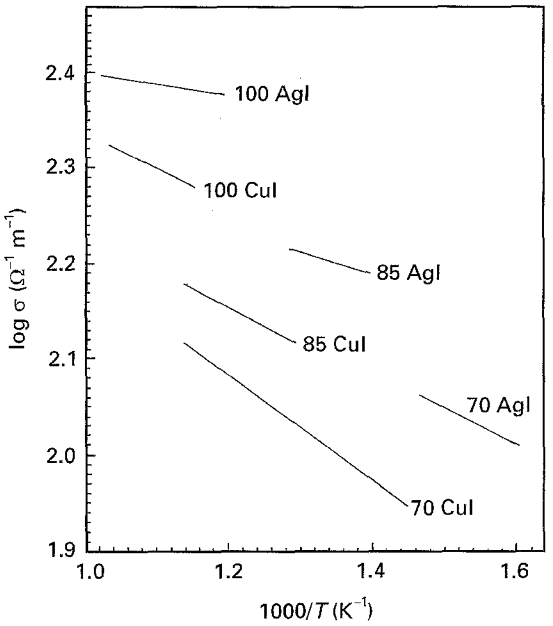

Figure 3 Temperature dependence of the specific conductivity for molten AgI [10], molten CuI [39] and their molten mixtures with SnI_2 (85 and 70 mol % AgI or CuI) (this work) [39].

that in molten CuI, can be expected. This could be the reason for a superior conductivity of molten AgI in spite of a larger cation.

In the 1970s and 1980s, very intensive studies of superionic conductors, for which α-AgI is an archetype and still the most representative example, did not cause any significant interest in the molten silver iodide investigations. Recently, studies of the molten AgI have been taken up more frequently, also in view of searching structural correlations between the liquid and solid phases [40–42].

5. Summary

A very high electrical conductivity (e.g. 60 $\Omega^{-1}\,m^{-1}$ at 540 K) and estimated charge carrier mobility ($3.5 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$) together with a small activation energy for conduction (10.8 kJ mol^{-1}) allows us to include Ag_4SnI_6 among the superionic phases. It is formed at 382 K and melts incongruently at 635.8 K. Formation in the solid state is accompanied by a considerable decrease in molar volume. The phase shows a broad region of solid solubility (about 40 mol %) towards higher SnI_2 contents.

The addition of the SnI_2 to the molten AgI brings about reducing the electrical conductivity and increasing the activation energy. The migration of the fast Ag^+ ions is restrained by the slow Sn^{2+} ions probably due to the interatomic drag effect.

A comparison between the electrical conductivity of the SnI_2–AgI molten mixtures and that of the SnI_2–CuI molten mixtures, between that of the pure molten AgI and CuI and between that of the solid α-AgI and α-CuI indicates a similarity between molten mixtures and solid superionic phases.

References

1. A. WOJAKOWSKA and J. TERPILOWSKI, *Polish J. Chem.* **59** (1985) 115.
2. A. WOJAKOWSKA and E. KUNDYS, *Phys. Status. Solidi A* **101** (1987) K153.
3. L. W. STROCK, *Z. Phys. Chem. B* **25** (1934) 441.
4. M. O'KEEFE and B. G. HYDE, *Phil. Mag.* **33** (1976) 219.
5. M. O'KEEFE, *Comments Sol. State Phys.* 7 (1977) 163.
6. S. USHIODA and M. J. DELANEY, *Solid State Commun.* **32** (1979) 67.
7. M. A. HOWE, R. L. McGREEVY and E. W. J. MITCHELL, *Z. Phys. B – Condensed Matter* **62** (1985) 15.
8. W. G. KOHLRAUSH, *Wied. Ann.* **17** (1882) 642.
9. C. TUBANDT and E. LORENZ, *Z. Phys. Chem.* **87** (1914) 513.
10. A. KVIST and A. -M. JOSEFSON, *Z. Naturforsch A* **23** (1968) 625.
11. Y. FOUQUE, M. GAUNE-ESCARD, W. SZCZEPANIAK and A. BOGACZ, *J. Chim. Phys. Phys., Chim. Biol.* **75** (1978) 361.
12. A. WOJAKOWSKA and E. KUNDYS, *J. Mater. Sci.* **25** (1990) 3780.
13. R. BLACHNIK and U. STÖTER, *Thermochimica Acta* **112** (1987) 47.
14. J. N. BRADLEY and P. D. GREENE, *Trans. Faraday Soc.* **63** (1967) 424.
15. K. W. BROWALL and J. S. KASPER, *J. Solid State Chem.* **15** (1975) 54.
16. E. COHEN and W. J. D. VAN DOBLENBURGH, *Z. Phys. Chem. A* **137** (1928) 289.
17. J. C. PHILLIPS, *J. Electrochem. Soc.* **123** (1976) 934.
18. *Idem., Phys. Rev. Letters* **20** (1968) 550.
19. J. A. VAN VECHTEN, *Phys. Rev.* **187** (1969) 1007.
20. J. C. PHILLIPS, *Rev. Mod. Phys.* **42** (1970) 317.
21. D. O. RALEIGH, *J. Electrochem. Soc.* **124** (1977) 1157.
22. C. OLIVES-DOMANGE, Thesis (University René Descartes, Paris 1971).
23. R. A. HOWIE, W. MOSER and C. TREVENA, *Acta Crystallogr. B* **28** (1972) 2965.
24. S. GELLER, *Science* **157** (1967) 310.
25. J. N. BRADLEY and P. D. GREENE, *Trans. Faraday Soc.* **63** (1967) 2516.
26. J. B. BOYCE, T. M. HAYES and J. C. MIKKELSEN, *Phys. Rev. B* **23** (1981) 2876.
27. J. A. A. KETELAAR, *Trans. Faraday Soc.* **34** (1938) 874.
28. T. WONG, M. BRODWIN, J. I. McOMBER and D. F. SHRIVER, *Solid State Commun.* **35** (1980) 591.
29. R. R. ARMSTRONG, R. S. BULMER and T. DICKINSON, *J. Solid State Chem.* **8** (1973) 219.
30. 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", National Standards Reference Data, Ser. **15** (1968), NBS (US); Russian translation (Khimiya, Leningrad 1971).
31. G. JANZ, R. P. T. TOMKINS, C. B. ALLEN, J. R. DOWNEY, Jr. and S. K. SINGER, *J. Phys. Chem. Ref. Data* **6** (1977) 409.
32. G. JANZ, "Properties of molten salts database", National Institute of Standards and Technology, Standard Reference Database **27** (1992).
33. H. P. BOSSMAN, A. HILDEBRANDT and J. RICHTER, *Z. Naturforsch. A.* **41** (1986) 1129.
34. H. G. DAMLE and S. S. KATTI, *Ind. J. Chem. A* **16** (1978) 679.
35. *Idem., ibid.* **19** (1980) 897.
36. G. G. W. GREENING and G. K. WEIL, *Z. Naturforsch. A* **42** (1987) 1283.
37. A. KLEMM, *ibid.* **39** (1984) 471.
38. M. CHEMLA and I. OKADA, *Electrochim. Acta* **35** (1990) 1761.
39. A. WOJAKOWSKA, *J. Chim. Phys. Phys. Chim. Biol.* **87** (1990) 367.
40. A. J. STAFFORD and M. SILBERT, *Z. Phys. B* **67** (1987) 31.
41. H. TAKAHASHI, S. TAKEDA, S. HARADA and S. TAMAKI, *J. Phys. Soc. Japan* **57** (1988) 538.
42. F. SHIMOJO and M. KOBAYASHI, *ibid.* **60** (1991) 3725.

Received 1 December 1994
and accepted 20 November 1995