The Electrical Conductivity of Solid and Molten Lithium Tungstate

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The electrical conductivity of lithium tungstate has been measured on both sides of the melting point 738 °C. It was found that lithium tungstate probably forms a high temperature modification with cubic or pseudo-cubic structure from 684 to 738 °C.

Several sulphates form high temperature modifications which are characterized by higher mobilities of the cations than in ordinary solids. Especially high is the electrical conductivity of the cubic modifications of Li_2SO_4 (f.c.c) [1, 2] and $(Li, Ag)_2SO_4$ (b.c.c) [3], while that of the hexagonal high temperature modifications of Ag_2SO_4 and K_2SO_4 is about ten times lower [3–5].

It was to be expected that the situation is similar for salts like Li_2MoO_4 and Li_2WO_4. The authors have however found [6] that there is no high-conducting phase in solid Li_2MoO_4. In Li_2WO_4 with 14.5% Li_2SO_4 KISLOWA, POSYPAJKO, and BERGMAN [7] have found a polymorph transition at about 660 °C.

The electrical conductivity of molten lithium tungstate from 762 to 903 °C has recently been published by MORRIS and ROBINSON [8], but they have not measured the conductivity below the melting point 738 °C (l. c. [7]).

Our experimental technique is described elsewhere in detail [9]. The measurements were performed in argon atmosphere in quartz capillary cells. The lithium tungstate (Hopkin & Williams), containing less than 0.3% impurities, was dried for at least one day at 180 °C before use. The corrosion of pure quartz was found to be very small whereas preliminary experiments showed that Vycor glass is corroded considerably. Some measurements were also performed in air with Alsint cells [1].

Results and Discussion

It is seen from Fig. 1 that the electrical conductivity of lithium tungstate is almost the same above and below the melting point 738 °C. The slope of the curve changes at this temperature.

The specific electrical conductivity of a solid or molten salt is often written as an ARRHENIUS equation

$$\varkappa = \varkappa_0 \, e^{-Q/RT}$$

where $R = 1.9869$ cal/mole, degr., T = degrees Kelvin, and $\varkappa_0$ and Q are constants.

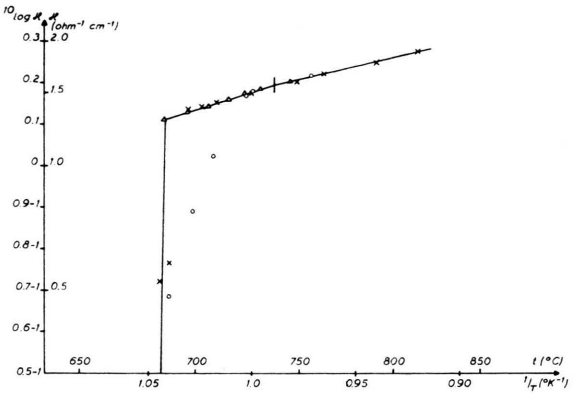

Fig. 1. Temperature dependence of the electrical conductivity of lithium tungstate. × and △: decreasing temperature; ○: increasing temperature.

Above 738 °C $\varkappa_0 = 23.6\ \Omega^{-1}\ cm^{-1}$ and $Q_0 = 5460$ cal/mole, but in the temperature region below 738 °C $\varkappa_0 = 104.2\ \Omega^{-1}\ cm^{-1}$ and $Q = 8410$ cal/mole.

The change of the ARRHENIUS coefficient Q at 738 °C is thus appreciable, and there are reasons to believe that lithium tungstate forms a high temperature modification between 684 and 738 °C.

The results obtained with quartz and Alsint cells are in good agreement and agree also with the equation given by MORRIS and ROBINSON [8], in spite of discrepances between their results [10] and ours [6] for molten lithium molybdate.

In order to check the lower transition point and to exclude supercooling and decomposition of the salt upon melting, we also pressed slabs from the salt and placed a slab, which was about 20 mm high and 10 mm in diameter, between two platinum discs. The salt was heated very slowly and a sudden increase of the conductivity was found at 684 °C, but the salt did not melt until at a higher temperature.

We have compared the electrical conductivity of lithium tungstate with some other salts which also form high temperature modifications (Fig. 2). The temperature dependence of $\log \varkappa$ is rather similar to that of lithium sulphate, but the change of the conductivity at the melting point is much bigger in Li_2SO_4.

If it is assumed that the transference number of the sulphate ions equals zero both in molten lithium sulphate and in the solid high temperature modification, the jump in the conductivity at the melting point might be explained by assuming that there is only a change of the coupling mechanism of the lithium ions. It has been found that the number of ions taking part

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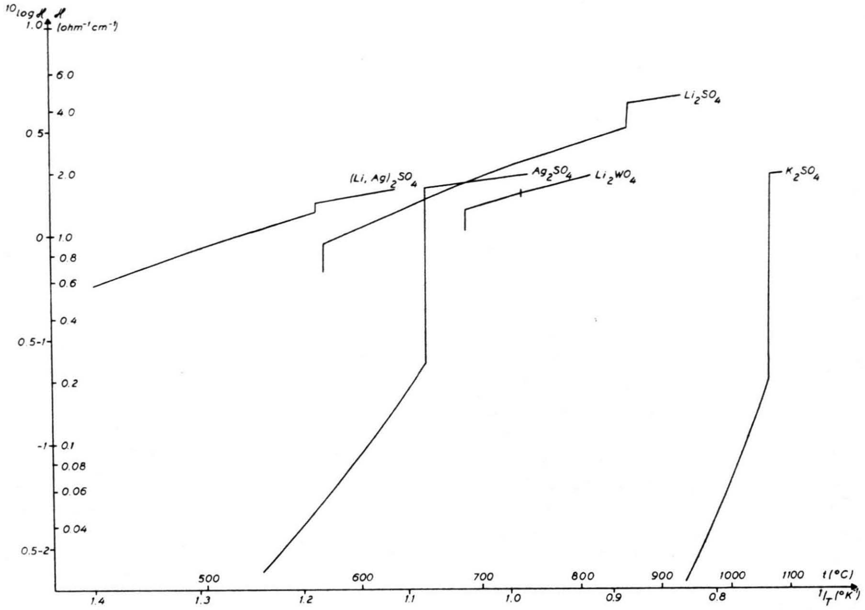

Fig. 2. The temperature dependence of the conductivity of some salts with high temperature modifications.

in a cooperative motion is 2.0 in the solid[2] and 2.7 in the melt[11] and the quotient between the electrical conductivity of the melt and the solid at the melting point is also about 1.3 (l. c.[1]). The radius of the sulphate ion (2.9 Å) is smaller than that of the tungstate ion (3.6 Å)[7] and it is probable that if the size of the anion is increased, the change in the mechanism of transport will be still smaller and also the jump in the conductivity.

The transition point 660 °C in Li_2WO_4 with 14.5% Li_2WO_4 seems to be in good agreement with the transition point found by us in the pure salt.

It is thus probable that lithium tungstate forms a cubic or pseudo-cubic high temperature modification from 684 to 738 °C.

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The Isotope Effect for Electromigration of Rubidium Ions in Molten Rubidium Nitrate

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The relative difference between the electromigration mobilities of the two rubidium isotopes was found to be 0.0008 in molten rubidium nitrate at 350 °C, corresponding to a mass effect of 0.035. A comparison is made with new results for $LiNO_3$ and $RbNO_3$.

The isotope effect of cation electromigration in pure molten nitrates has been studied previously in lithium nitrate[1–3] and in potassium nitrate[4]. This investigation has now been extended to pure rubidium nitrate. The experimental arrangement is essentially the same as described before[4, 5], except that a U-shaped cell was used. With this cell the required amount of salt was about 15 g, instead of 100 g in the old type of cell[2, 4]. In the old cell the large cathode compartment formed a bath surrounding the separation tube, which was thus kept at the temperature of the cells, while in the new cell the separation tube becomes hotter than the two electrode compartments. The temperature of the sepa-

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[5] In the previous experiments washbottles containing an oil were used to indicate the gas flow. We now used nitric acid instead which is preferable.