

SUPER IONIC CONDUCTION IN ALKALI METAL HEXACHLORO NIOBATES AND TANTALATES

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ac-conductivity, DSC, and neutron diffraction studies of the ionic conductors KNbCl_6 and KTaCl_6 are presented. The first order phase transitions to the super ionic state occur at temperatures in the range 299–334°C. Conductivities up to 0.35 S/cm are observed. The lowest transition is from a hexagonal to a cubic fcc structure, whereas no definite conclusions could be drawn concerning the structure of the super ionic phases, since only three diffraction peaks were observed in the diffractograms.

1. Introduction

The solid alkali metal hexachloro niobates and tantalates, of the type KNbCl_6 , have been studied by Palkin and Chikanov [1], Huber et al. [2] and recently by Sadoway [3]. These studies focused on phase diagram studies and vapor pressure measurements. Single frequency conductivity measurements (amplitude 6 V!) indicated extremely high conductivities at high temperature, after the samples had undergone 1 or 2 first order phase transitions [1]. The complex octahedral anions, NbCl_6^- and TaCl_6^- are stable at high temperature even in the molten alkali metal hexachloro metallates, as has been demonstrated by Raman spectroscopy [4]. It is in the light of these facts that we initiated a study of these materials as possible cation conductors.

2. Experimental

2.1. Synthesis

NbCl_5 (Cerac, 99.95%) was vacuum sublimed and then further purified by zone melting in a pyrex ampoule. TaCl_5 (Cerac, 99.95%) was vacuum sublimed. NaCl and KCl (analytical grade, Merck) were dried at 170°C in vacuum for 24 h and then melted in a quartz ampoule. The hexachloro compounds were made by two methods: equimolar mixtures were melted together at 440°C in sealed pyrex ampoules. It is essential that as little void volume as possible is present in the reaction ampoules since even small thermal gradients in the furnace will give rise to dissociation of the compound, e.g. pure pentachloride will condensate in the coldest part of the reaction vessel. One can also make the equimolar compounds by exposing the solid alkali metal chloride to the vapours of the pentachlorides [3]. The cubic form of KNbCl_6 was made this way [3]. All the samples were

handled in an argon filled glovebox with a water content of approximately 1–3 ppm.

2.2. Conductivity measurements

ac-impedance measurements were made by means of a Solartron 1174 frequency response analyser (10^{-4} Hz to 999.9 kHz) equipped with a preamplifier on the X-channel in order to increase the input impedance of the FRA from 1 M Ω to approximately 10^{12} Ω (and 30 pF versus ground). The impedance data were corrected for the phase shift of the preamplifier as well as for the influence of the capacity of the reference resistors and the Reed-relays, which were used to switch between different reference resistors for the current measurement (10 Ω –1 M Ω). The total voltage drop across the sample and the reference resistors never exceeded 50 mV. Samples for the low temperature measurements were 13 mm diameter discs pressed at 10 ton from finely pulverized material. 300 nm thick gold electrodes were evaporated onto the two circular sides of the discs using a PVD equipment installed in a glovebox. The typical geometrical factor, $1/A$, was approximately 0.1 cm^{-1} . High temperature conductivity measurements were made in sealed pyrex cells ($1\text{--}2 \text{ cm}^3$) with 2 W-wire electrodes. The geometrical factor of these cells were determined by measuring the resistance of the cells filled with standard aqueous KCl solution, and was typically 1 cm^{-1} . The sealed cells were heated to above the melting point of the hexachloro compound before the conductivity measurements were started. The salt was allowed to solidify around the W-electrodes.

2.3. Calorimetry

A Perkin-Elmer DSC 2C differential scanning calorimeter was used for the determination of transition temperatures and latent heats. The samples, 4–20 mg, were contained in sealed gold capsules.

2.4. Neutron diffraction

Finely ground powder of KNbCl₆ was contained in Pt tubes. The tubes were 7 cm long and 6 mm diameter with a 0.1 mm wall thickness. The sample tubes were closed in both ends by argon welding.

KTaCl₆ was held in a quartz tube of the same outer dimensions, but with a 0.5 mm wall thickness. The tubes were placed in a water cooled furnace of aluminum with a cylindrical heating element made of tantalum. The triple axis spectrometer TAS6 at the Risø DR3 reactor was used in the elastic mode for the experiments (wavelength 2.3–2.6 Å).

3. General properties

The ten compounds of the general formula, $M(\text{Nb/Ta})\text{Cl}_6$ (where $M=\text{Li, Na, K, Rb}$ and Cs) are very hygroscopic. They can easily be reduced and chloride is lost by partial hydrolysis with formation of ill-defined oxychloride compounds as the result. Furthermore, the conductivity measurements are difficult, firstly because the conductivity changes over so many decades, and secondly because the samples have a tendency to crumble/crack when passing through the solid–solid phase transitions.

The stability of the compounds of this family generally increases going from Li to the Cs-analogue: the Li and Na compounds are incongruently melting and have excessive MCl_5 dissociation pressures: e.g. at 350°C the NbCl_5 pressure above NaNbCl_6 and KNbCl_6 amount to 1.9 bar and 0.018 bar, respectively [3]. All compounds exhibit two or three polymorphs between room temperature and the melting points.

These experimental difficulties led us to concentrate our study on the relatively stable potassium compounds, although some conductivity data were initially obtained for NaTaCl_6 .

4. Results from calorimetry

Several reports of the transition temperatures are given in the literature [1–3], but no latent heats have been reported so far. From visual observations and the diffraction studies we know that the endothermic reaction at the highest temperature corresponds to melting. The two lower ones are thus solid–solid transitions. Transition temperatures ($\pm 5^\circ\text{C}$) and enthalpies of transition are given in table 1. As is often observed for phase transitions to a highly conductive state, the heat of transition is comparable

Table 1
Phase transition temperatures ($^{\circ}\text{C}$) and enthalpies of KNbCl_6 and KTaCl_6 observed by DSC and ionic conductivity.

DSC	$\gamma \rightarrow \beta$	$\beta \rightarrow \alpha$	$\alpha \rightarrow \text{liq.}$	Ref.
KNbCl_6	175	328	395	this study
	160	321	396	[1]
	1915 cal/mole	792 cal/mole	1226 cal/mole	
KTaCl_6	180 (267)	324	392	this study
	160	312	410	[1]
	1927 cal/mole	940 cal/mole	too broad	
Transition temperature ($^{\circ}\text{C}$) from ionic conductivity				
Both salts	125–170	300–310	no discontinuity	this study

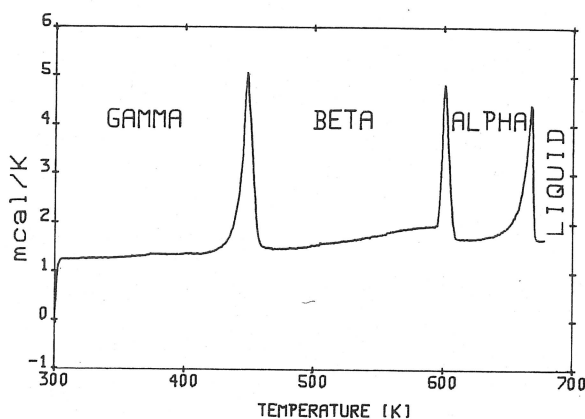


Fig. 1. Specific heat of 6.9 mg KNbCl_6 in a sealed gold pan. Heating rate: 10 K/min.

with (or higher than) the heat of fusion. The behaviour of KTaCl_6 is qualitatively the same as that of KNbCl_6 , but a rather strong thermal event often appeared around 260–270 $^{\circ}\text{C}$. We have not found any reports of thermal events for KTaCl_6 in this temperature range. The phenomenon remains unexplained. Supercooling of the phases were also observed (10–15 $^{\circ}\text{C}$ for solidification; 25–75 $^{\circ}\text{C}$ for the solid–solid transitions). The specific heat of KNbCl_6 (8 atoms/“molecule”) at 300 K was found to be 48.17 cal/mole K, which is very close to the expected value $3 \times 8 \times R$ (assuming a harmonic oscillator approximation).

5. Results from conductivity measurements

The admittance data could be interpreted on basis of a conventional equivalent circuit for an ionic con-

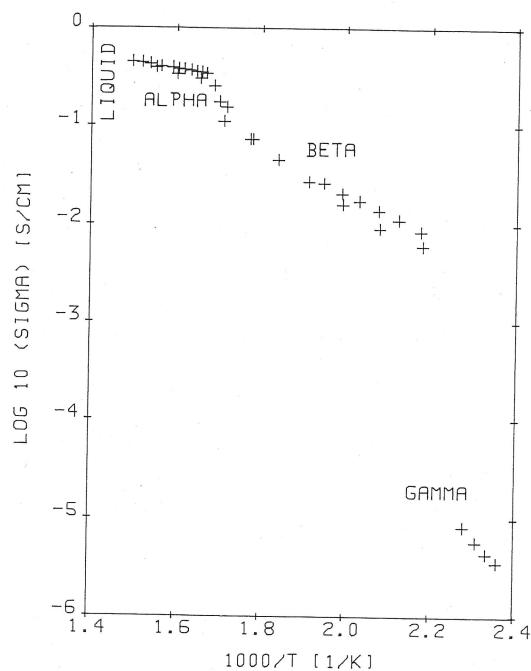


Fig. 2. Arrhenius plot of the specific conductivity of KNbCl_6 measured with blocking W-electrodes.

ductor between two blocking electrodes. An Arrhenius plot is shown in fig. 2; in table 2 are given the fitted constants in the Arrhenius expression. The two potassium compounds have similar conductivities although the hysteresis around the gamma–beta transition makes the fitted Arrhenius function quite uncertain for the gamma phases. The conductivity of NaTaCl_6 is roughly a factor 1.5–2 higher than for KNbCl_6 , but it could not be measured reproducibly above 175 $^{\circ}\text{C}$. There is no discontinuity in the conductivity when the compounds melt, however the

Table 2
Fitted parameters in Arrhenius expression for specific ionic conductivity of KNbCl₆ and KTaCl₆.

Phase	Activation energy (eV)	Preexponential S·K/cm	Temperature range (°C) for fit
KNbCl ₆			
γ	0.94	2.44 × 10 ⁸	40–164
β	0.57	5.58 × 10 ⁶	185–311
α	0.21	1.14 × 10 ⁴	336–386
KTaCl ₆			
γ	0.72	2.33 × 10 ⁶	41–155
β	0.58	5.24 × 10 ⁶	182–299
α	0.17	4.5 × 10 ³	310–409

solid–solid phase transition observed by DSC are fairly well revealed by the conductivity method as well. The present investigation thus confirms the high conductivities reported by Palkin and Chikanov [1], who found 5×10^{-3} S/cm just above the gamma–beta transition and 0.2 S/cm near the melting point.

6. Structural findings

No single crystal structure determinations or high temperature studies of the present hexachloro metallates are described in literature. The following crystal symmetries at room temperature (as determined from X-ray powder diffractograms) have been suggested: NaNbCl₆ is tetragonal [3]; KNbCl₆ is cubic fcc [3,5] and K-, Rb-, and CsTaCl₆ are hexagonal [3,6]. Smirnova and Tsintsius [7] furthermore describes Rb- and CsNbCl₆ as crystallising in the tetragonal system, however the diffraction patterns appear to be more complex, and not indexable as tetragonal [3].

The quality of our diffraction patterns and the small number of observed reflections did not allow a structure analysis of any of the three polymorphs by fitting to the total profile of the diffractogram. The obtained results are summarised in table 3.

6.1. Gamma phase

The hexagonal structure of KTaCl₆ was confirmed. The room temperature structure of KNbCl₆

Table 3
Crystal symmetries of KNbCl₆ and KTaCl₆ at different temperatures determined by neutron diffraction.

Phase	KNbCl ₆	KTaCl ₆
γ	hexagonal, $a = 11.62 \text{ \AA}$, $c = 10.97 \text{ \AA}$ 7 peaks, 7 ^{a)} 20°C ^{b)}	hexagonal, $a = 11.62 \text{ \AA}$, $c = 10.97 \text{ \AA}$ 19 peaks, 18 20°C
β	fcc, $a = 10.00 \text{ \AA}$ 9 peaks, 9 230°C	fcc, $a = 10.09 \text{ \AA}$ 11 peaks, 11 250°C
α	1 peak, 0 377°C	3 peaks, 0 343°C

^{a)} Number of observed and indexed diffraction peaks for each phase.

^{b)} Temperature of diffraction experiment.

made by melting the two constituents together gave complex patterns, which indicated that KNbCl₆ was present both as supercooled cubic beta phase and as a new hexagonal modification, with reflections at almost exactly the same d -spacings as for the hexagonal KTaCl₆. KNbCl₆ made by the solid–vapor process at MIT (3) was cubic fcc even at room temperature. The reason for this stabilisation is unresolved. A few extra diffraction lines were also observed in this sample. The DDSC-trace of this sample only showed the beta–alpha transition temperature (314°C) and no clear peak for melting could be determined.

6.2. Beta phase

The fcc-structure of the beta phases is most likely a disordered phase with the M(V)Cl₆[−] octahedra at the fcc-positions as proposed in 1968 by Kozhina et al. [5]. We find a reasonable agreement between observed and calculated structure factors for a model, where the M(V)-Cl bonds are along the $\langle 100 \rangle$ directions.

None of the investigated guesses on structures could reproduce the measured intensities exactly. The best results were obtained for a Nb–Cl bond length equal to 2.5 Å, which is actually the sum of the classical ionic radii (Nb(+5): 0.69 Å and Cl(−1): 1.81 Å). Various distributions of the potassium ions were tried, but the general conclusion concerning the ori-

entation of the MCl_6 octahedra was not influenced hereby.

There is only room enough for the alkali metal ions at the tetrahedral positions in the fcc structure, of which only half should be occupied on average according to simple stoichiometric considerations (a fluorite structure with half filled cation lattice).

6.3. Alpha phase

We observe three reflections for the alpha phase of $KTaCl_6$ ($d=5.75, 3.34$ and 2.34 Å, respectively) and only one for $KNbCl_6$ ($d=5.73$ Å). None of these reflections were due to KCl. Significant dissociation of the hexachloro complexes can therefore be excluded. The alpha phases are likely to be cubic also, but a test for simple cubic or body-centered cubic symmetry cannot be carried out on basis of 3 reflections only. The alpha phases may contain rotating MCl_6 octahedra, similar to the rotating sulphate groups in the cubic high temperature phase of Li_2SO_4 -type crystals [8].

7. Conclusions

The alkali metal hexachloro niobates/tantalates form a new family of superionic compounds with presumably relatively simple structures. The compounds are extremely difficult to handle i.e. they are

hygroscopic and easily reduced. The scatter in the reported solid-solid and melt transition temperatures is likely to be due to deviations in stoichiometry due to loss of some pentachloride at higher temperatures.

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