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Solubility and Raman spectra of Ta(v) in LiF–NaF–KF–Na_2O melts

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Raman spectroscopy and solubility measurements have been used to study Ta(v) complexes in the molten LiF–NaF–KF eutectic (FLiNaK). Na_2O(s) was added to melts containing a given amount of K_2TaF_7, and samples were withdrawn at different ratios of oxide to tantalum. The samples were analysed for oxygen and Ta, and studied by Raman spectroscopy using the windowless graphite cell technique. The solubility was studied at 700 °C. Solubility measurements in a FLiNaK melt containing 0.0956 mol kg^{-1} K_2TaF_7 indicated that all the added amounts of oxide and tantalum dissolved in melts with $n_O/n_{Ta} < 1.8$, and precipitation of solid $AlkTaO_3$, which may be a compound with Alk = Li, Na or K, was observed at higher ratios. A solubility minimum was observed at $n_O/n_{Ta} = 3$. From the Raman data, the existence of the TaF_7^{2-} (C_s) and $TaOF_5^{2-}$ (C_{4v}) species at ratios up to 2 was established. A dioxofluoro complex, probably $TaO_2F_4^{3-}$ (C_{2v}), was also present. At $n_O/n_{Ta} > 3$ the solubility data were consistent with a dissolution of the $AlkTaO_3$ solid, and formation of a $TaO_4F_x^{(x+3)-}$ species. The tantalum tetraoxofluoride complex was possibly $TaO_4F_2^{5-}$ (C_{2v}). The solubility data indicated precipitation of an oxide rich solid at $n_O/n_{Ta} > 4$. The Raman spectra supported the existence of $TaO_4F_2^{5-}$ (C_{2v}) species as well as $(TaO_5)_n$ or $(TaO_6)_n$ network structures in these melts.

Introduction

Due to elaborate production methods, niobium and tantalum are expensive metals. An effort has therefore been made to develop an electroplating process, where only a thin layer of the refractory metal covers and protects a low cost base material. Mellors and Senderoff[1] were the first to produce coherent coatings of tantalum from the molten eutectic LiF–NaF–KF (FLiNaK) solvent. Their article was the second in a series of publications from the same authors where they discussed the deposition of niobium,[2,3] zirconium[4] and molybdenum.[5] FLiNaK was found to be a convenient electrolyte for the electrodeposition, due to its relatively low melting point of 459 °C and its ability to form stable tantalum fluoride complexes. During the electrochemical plating, it was observed that the presence of oxide in the system caused the deposit to become hard and brittle. It is therefore important to understand the influence of oxide on the complex formation and reduction mechanisms in the melts.

Studies of Ta(v) in melts[6] and different room temperature HF solutions[7–9] have shown a rather complex chemistry, and TaF_6^-, TaF_7^{2-}, TaF_8^{3-} and TaF_9^{4-} were claimed to exist.

Agulyanskii[10] performed a systematic study of the influence of outer-sphere cations on Ta(v) complexes in fluoride melts. He found that the established equilibrium (1) in alkali fluoride

$$TaF_7^{2-} \rightleftharpoons TaF_6^- + F^- \qquad (1)$$

melts was shifted to the left when passing from sodium to caesium based electrolytes. TaF_6^- was the predominant species in Na_2TaF_7–NaF melts with TaF_7^{2-} concentrations up to 1 mol%, while TaF_7^{2-} was the major species in Rb_2TaF_7–RbF melts.

von Barner *et al.*[11] studied Ta(v) in molten FLiNaK by means of Raman spectroscopy, and identified the TaF_7^{2-} complex. Bjerrum *et al.*[12] studied Ta(v) in solidified FLiNaK with both infrared absorption and Raman spectroscopy. Their work supports the findings of von Barner *et al.*,[11] and questions the conclusions drawn by Fordyce and Baum[6] and furthermore excludes the presence of TaF_8^{3-}. Raman spectroscopy of Ta(v) in solidified FLiNaK was also performed by Robert *et al.*,[13] and the TaF_7^{2-} ion was identified in agreement with von Barner *et al.* and Bjerrum *et al.*

von Barner *et al.*[14] used Raman spectroscopy to determine the structure of Nb(v) oxofluoro complexes in molten FLiNaK. By adding Na_2O and K_2NbF_7 to the melt, they studied complexes at different ratios of oxygen to niobium, n_O/n_{Nb}. The NbF_7^{2-} ion in the pure melts was found to react with the oxide according to the reaction:

$$NbF_7^{2-} + O^{2-} \rightleftharpoons NbOF_5^{2-} + 2F^- \qquad (2)$$

This equilibrium shifted to the left with increasing temperature. As eqn. (2) indicates, the niobium monooxofluoride was identified as $NbOF_5^{2-}$, but von Barner *et al.* emphasise that the ion might also be $NbOF_6^{3-}$. The monooxofluoride complex was dominating the Raman spectra at ratios of oxygen to niobium around 1. In melts with higher concentrations of oxide, a $NbO_2F_4^{3-}$ complex with the two oxygen atoms in *cis* positions was suggested to exist. The complex totally dominated the Raman spectra at ratios of oxygen to niobium around 2. When this ratio increased, a new species $NbO_3F_n^{(1+n)-}$ was probably formed. Furthermore, a degree of polymerisation was assumed to take place in these melts and the authors indicated the presence of edge sharing distorted NbO_6 octahedra. In a recent publication Andersen *et al.*[15] performed IR and Raman spectroscopy on molten and solidified samples of Nb(v) in FLiNaK at various temperatures and ratios of oxygen to niobium. They found that $NbOF_5^{2-}$ was the dominant species in melts with $n_O/n_{Nb} \approx 1$, while both $NbOF_5^{2-}$ and $NbOF_6^{3-}$ existed when the sample was solidified. Matthiesen *et al.*[16] studied oxofluoro complexes of niobium(IV,V) in liquid

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FLiNaK at 700 °C with varying oxide to niobium ratios. SrO was added to FLiNaK containing 0.22 mol kg^{-1} K_2NbF_7 and the following observations were recorded: $n_O/n_{Nb} < 2$; all the Nb(v) was dissolved; $n_O/n_{Nb} > 2$; a solid of the type $AlkNbO_3$ was formed; $n_O/n_{Nb} = 3$; a minimum of Nb(v) and O^{2-} solubilities were observed; $3 < n_O/n_{Nb} < 4$; the $AlkNbO_3$ previously formed dissolved, and a complex ion of the type $NbO_4F_x^{(3+x)-}$ was most probably formed; $n_O/n_{Nb} > 4$; no further dissolution took place.

Na_2O was used as an oxide source in the experiments with Nb(IV) since the lack of SrO solubility observed in these melts could be due to the stronger oxoacidic character of SrO relative to Na_2O. The experiments with four valent niobium showed a similar trend as for the experiment with Nb(v), with one important exception. With Nb(IV) there seemed to be a partial precipitation of a solid upon addition of oxide to melts with $1 < n_O/n_{Nb} < 2.2$. This was attributed to precipitation of $NbOF_2$(s).

In a recent publication, Vik *et al.*[17] combined solubility measurements and Raman spectroscopy to study Nb(v) complexes in molten FLiNaK. Na_2O was added to a melt containing a given amount of K_2NbF_7, and samples were withdrawn at different ratios of oxide to niobium. The samples were analysed for oxygen and niobium, and studied by Raman spectroscopy using the windowless graphite cell technique. Solubility measurements in a FLiNaK melt containing 0.22 mol kg^{-1} K_2NbF_7 indicated that all the oxide and Nb(v) dissolved for $n_O/n_{Nb} < 2$. Further addition of Na_2O led to precipitation of a solid compound $AlkNbO_3$, and a solubility minimum was observed at $n_O/n_{Nb} = 3$. From the Raman data, the existence of NbF_7^{2-} (C_s), $NbOF_5^{2-}$ (C_{4v}) and $NbO_2F_4^{3-}$ (C_{2v}) at n_O/n_{Nb} ratios up to 2 was established. The spectral features indicated that a niobium trioxofluoride complex was present in melts with $n_O/n_{Nb} \approx 3$. The complex was possibly $NbO_3F_3^{4-}$. At $n_O/n_{Nb} > 3$ the solubility data were consistent with a dissolution of the $AlkNbO_3$ solid, and formation of a $NbO_4F_x^{(x+3)-}$ species. At $n_O/n_{Nb} > 4$ an oxygen rich solid seemed to precipitate. The Raman spectra indicated the existence of $NbO_4F_2^{5-}$ species as well as $(NbO_6)_n$ network structures in these melts.

A Raman spectroscopic study of Ta(v)–oxofluoro complexes in molten FLiNaK has also been reported by von Barner *et al.*[11] This work was less systematic than the parallel work on niobium,[14] but the spectra showed the formation of monooxo- and dioxo-fluoro complexes as Na_2O was added to the K_2TaF_7–FLiNaK melt. The authors indicated that the complexes could be $TaOF_5^{2-}$ and $TaO_2F_4^{3-}$. Apart from the work by von Barner *et al.*,[11] no spectroscopic work on tantalum in molten fluoride melts was found in the literature. There has, however, been an IR-Raman spectroscopic work on solidified K_2TaF_7–Na_2O–FLiNaK melt samples.[12] In this work the oxide content of alkali metal fluoride melts were measured spectroscopically and the presence of $TaOF_x^{(x-3)-}$ and a dimeric ion containing a Ta–O–Ta oxygen bridge was identified. Robert *et al.*[13] studied solidified melts in the same system by means of Raman spectroscopy. They proposed the existence of three complexes when $n_O/n_{Ta} < 0.5$: K_2TaF_7, $K_xTa_2OF_{8+x}$ and K_2TaOF_5. Furthermore they performed a systematic study on how the concentration of these species varied with the ratio n_O/n_{Ta}, and isolated the Raman spectra of each of the Ta-containing species.

The current paper deals with solubility and Raman spectroscopic measurements of Ta(v) complexes in molten FLiNaK. The results are interpreted and discussed in terms of the structural properties of the species found.

Experimental

Chemicals and materials

K_2TaF_7 from Alfa Aesar, was used without further purification.

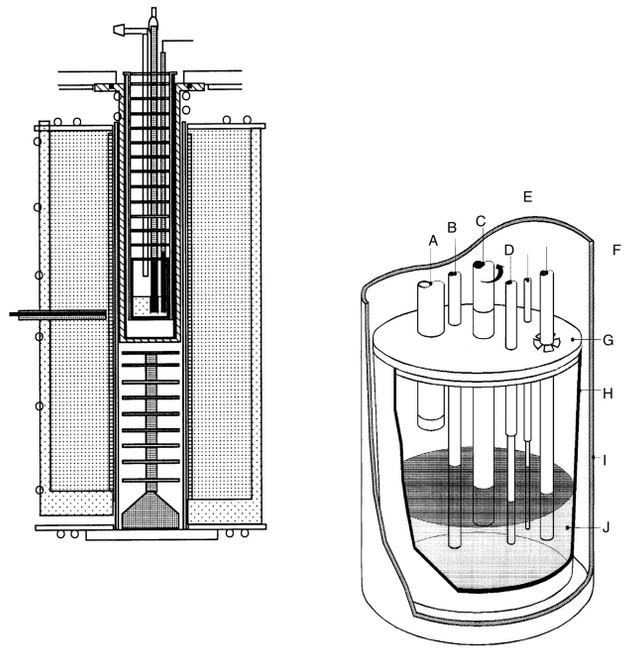

Fig. 1 Experimental cell and furnace mounted to a glove box: (A) quartz sampling tube; (B) electrode, not in use; (C) stirrer; (D) electrode, not in use; (E) electrode, not in use; (F) thermocouple; (G) graphite lid; (H) glassy carbon crucible; (I) quartz container; (J) melt.

Na_2O was made by decomposing Na_2O_2 from Merck KGaA in an Al_2O_3 crucible at 600 °C under a vacuum of 10^{-3} mbar for 12 hours. The product, a hard lump with a slight green colour, was transferred immediately to a glove-box where it was mortared to a fine powder. The decomposition procedure was repeated twice, and the compound was used within a few days. The oxide reacts quickly with air (with oxygen to form Na_2O_2, and water to form NaOH), and could not be stored (even in a very good glove-box having < 1 ppm H_2O and < 3 ppm O_2) for longer periods of time unless kept in a sealed evacuated glass ampoule. By dissolving the oxide in water and titrating with HCl, it was possible to find the purity of the compound. Assuming the reaction $Na_2O + H_2O \rightleftharpoons 2\ NaOH$ to take place upon contact with water, the solution was titrated until neutrality. A typical result after double decomposition showed a purity of 98.5% Na_2O. The analytical grade Ta_2O_5 (Cerac, USA 99.95%) was dried under vacuum in a glassy carbon crucible at 150 °C for 24 h before use. LiF (Alfa, Germany 99.5%), NaF (Merck, Germany 99%) and KF (Merck, Germany) were re-crystallised twice from their melts by slow cooling (3 °C h^{-1}) in a platinum crucible under Ar(g). All graphite and glassy carbon materials (Carbone-Loraine) were heated to 840 °C for 16 h at 10^{-3} mbar before use.

Procedures

The equilibrium studies at different oxide to tantalum ratios were carried out in a furnace mounted vertically under an argon filled glove box, making it possible to access the experimental cell from inside without introducing moisture to the cell. The water and oxygen content in the box were 1 and 3 ppm respectively. All handling of purified salts and samples were performed in the box. The cell and furnace assembly is shown in Fig. 1. A graphite lid was put on top of a glassy carbon crucible, and 12 graphite radiation shields were mounted on the top of the lid at a regular distance to decrease the vertical temperature gradient in the cell. A glassy carbon tube surrounded the radiation shields to reduce the corrosive action of fluorides on the quartz cell. The lid and the shields had holes for sample extraction and feeding of salts, stirring unit and thermocouple. Melt samples for chemical analysis were extracted from the melt using graphite ladles, while stirring was performed with a graphite

blade connected to an electrical motor *via* a steel rod. The experimental cell was inside a quartz tube, immersed in a Kanthal tube mounted inside the furnace to separate it from the glove-box. A brass lid, with holes similar to those in the graphite lid, was positioned on top of the quartz tube to prevent impurities from falling into the cell. The cell was kept in the glove-box furnace at 500 °C for 24 h in order to remove adsorbed water, before LiF, NaF, KF and K_2TaF_7 in given amounts were added to the glassy carbon crucible. Total amount of fluorides was about 100 g.

Equilibrium was established at 700 °C by carefully stirring the melt. A sample was then extracted and pellets of Na_2O were added to obtain a given n_O/n_{Ta} ratio. This was repeated in order to cover the range of oxygen to tantalum ratios from 0 to 6.1. The dissolution experiment with Ta_2O_5 was performed at 700 °C, by adding small amounts of the solid to FLiNaK. Stirring was applied, and samples were withdrawn from the melt. The oxide content of the extracted samples was determined by a carbothermal method using LECO TC-436, as described by Mediaas *et al.*[18,19]

Four parallels were analysed for each composition, and results are given as a mean value using a standard deviation based on a normal distribution. The four parallels were chosen from different parts of the solidified samples, to avoid any systematic error due to inhomogeneity in the quenched melts. Tantalum analyses of the extracted samples were performed by Inductive Coupled Plasma emission spectroscopy (ICP). The samples, 0.2 g each, were dissolved in 10 ml HF (40%) and 1 ml HNO_3 (68%), and distilled water was added to a volume of 100 ml. In order to dissolve the samples completely, it was necessary to keep the solutions at 50 °C, and this temperature was also used during injection of the solution during analysis to avoid precipitation.

Raman analysis

The 488 nm line of an argon ion laser (Spectra Physics, Model 2017, Power: 600 mW) was used for exciting the spectra. For analysing and collecting the spectra the T-64000 (Jobin Yvon) Raman system, equipped with a Spectraview-20 2D™ liquid N_2-cooled CCD detector was used, in the triple configuration. The spectral resolution was 5–6 cm^{-1} and the integration time was 20 s. The spectral window centred at 450 and 850 cm^{-1} in the Stokes region in order to record a spectrum from 50 up to 1200 cm^{-1}. Before each experiment two liquid samples were used for adjusting the optics and the polarisation characteristics of the spectra; CCl_4 at room temperature and a mixture of 0.3 $ZnCl_2$–0.7 CsCl at 800 °C. The system was interfaced with a personal computer and the spectra were saved in digital form. Two different polarisation directions were used for recording the spectra namely VV and HV. Due to the highly corrosive nature of FLiNaK melts, the windowless graphite cell technique was used for recording the spectra. The cell design was described by Gilbert *et al.*[20,21] and the high temperature furnace was described by Dracopoulos and Papatheodorou.[22] The cells were degassed at 1000 °C for ten hours before use.

Results and discussion

Solubility of Ta^{5+}–O^{2-}–F^- in FLiNaK with variations in the O^{2-} content

The influence of Na_2O concentration on the Ta(v)–F–O complexation and solubility in FLiNaK melts containing a given amount of K_2TaF_7, was studied as a function of the n_O/n_{Ta} molar ratio at 700 °C. The tantalum and oxide concentrations in the melt are plotted *versus* n_O/n_{Ta} in Fig. 2, where the content of oxygen and tantalum in both the melt and in the possible solid Ta–O-containing compounds are included in the n_O/n_{Ta} ratio. The dotted line indicates the total concentration of oxide in the system. This line gives the theoretical value of O^{2-} expected if all the added Na_2O went into solution. The measured oxide content in samples with $n_O/n_{Ta} > 4$ has a rather high standard deviation, and this is probably due to inhomogeneity of the quenched samples. The mean value of the analysed data will, however, be fairly accurate, since most of the sample was used for analysis or the samples for analysis were taken from representative parts of the quenched melt in order to compensate for the gradient in concentration through the salt. It is possible to give an evaluation of the stoichiometry of the precipitating species as well as the complexes formed from the data below. The n_O/n_{Ta} data are based on added amounts of Na_2O and K_2TaF_7 (0.0956 mol kg^{-1} melt). Corrections are made for the measured tantalum and oxygen content in the salt due to samples withdrawn for analysis.

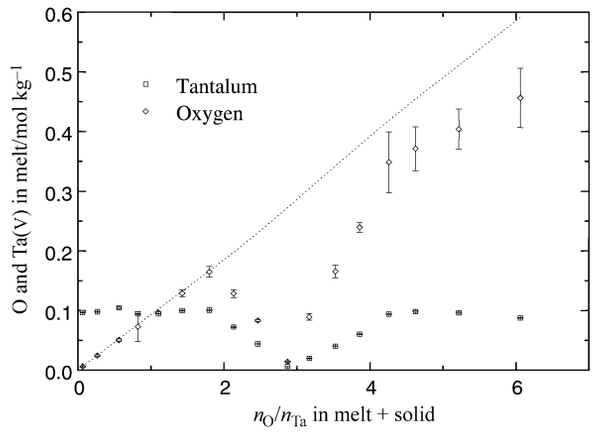

Fig. 2 Oxide (Na_2O) and Ta(v) concentrations in the liquid LiF–NaF–KF eutectic at 700 °C *versus* the molar ratio, n_O/n_{Ta}, in the melt and in the solid phases.

$0 < n_O/n_{Ta} < 2$. The tantalum concentration in the melt is constant, and the oxygen concentration increases linearly as the ratio n_O/n_{Ta} increases. All the added oxide goes into solution. The results are consistent with reaction (3):

$$yO^{2-} + zTaF_7^{2-} \rightleftharpoons Ta_zO_yF_x^{(2y+x-5z)-} + (7z - x)F^- \quad (3)$$

The formation of possible species of the type $TaOF_5^{2-}$ and $TaO_2F_4^{3-}$ as suggested by von Barner *et al.*[11] and Robert *et al.*[13] may therefore be reasonable. It should be noted that the oxygen concentration is, within the experimental errors, equal to the added amount of oxide. Fig. 2 indicates that a decrease of both concentrations occur at $n_O/n_{Ta} \approx 1.8$. This could mean that precipitation of a solid compound starts before a total conversion of tantalum monooxide to tantalum dioxo complexes has occurred. In the related niobium system (see Vik *et al.*[17]), such precipitation started at around $n_O/n_{Nb} \approx 2.2$.

$2 < n_O/n_{Ta} < 3$. As shown in Fig. 2, both the tantalum and the oxygen content of the melt decreases linearly as n_O/n_{Ta} increases. A minimum in solubility is reached at $n_O/n_{Ta} = 3$. Precipitation of a solid compound $AlkTaO_3$ seems to occur as indicated by reaction (4):

$$TaO_2F_4^{3-} + O^{2-} + Alk^+ \rightleftharpoons AlkTaO_3(s) + 4F^- \quad (4)$$

According to reaction (4), the slopes of the lines for the decreasing concentrations of Ta(v) and O^{2-} should be close to −1 and −2, respectively. The lines in Fig. 2 show slopes of about −0.9 and −1.8 mol kg^{-1}. This small deviation from the theoretical values might be due to the presence of Na_2O_2 as was discussed for niobium by Vik *et al.*,[17] or to difficulties in measuring the slope correctly. As can be seen from Fig. 2, the solubility of oxygen and tantalum is very low at $n_O/n_{Ta} \approx 3$. It is therefore possible that precipitation of $AlkTaO_3$ according

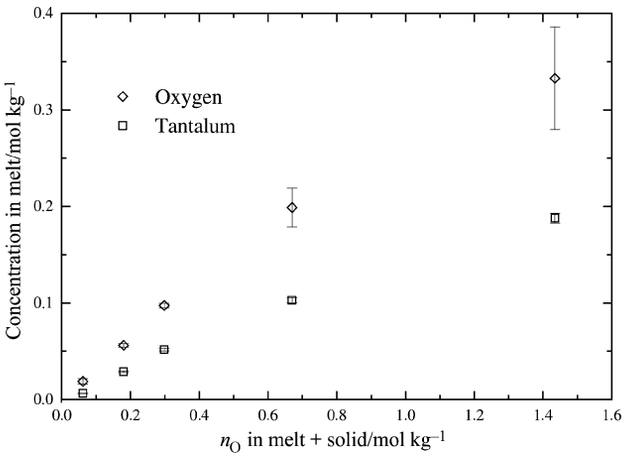

Fig. 3 Oxide and Ta(v) concentrations in the liquid LiF–NaF–KF eutectic at 700 °C *versus* added amounts of O coming from Ta_2O_5.

to reaction (4) starts before $n_O/n_{Ta} = 2$; before all the tantalum containing species are converted to a tantalum dioxofluoride complex. To verify this, it is necessary to know the equilibrium constant not only of reaction (4), but also all the equilibrium constants of possible reactions in eqn. (3). This is not possible based on the present data only. The minimum in solubility was measured at $n_O/n_{Ta} = 2.9$ where the concentrations of oxygen and tantalum were 0.014 mol kg^{-1} melt and 0.0062 mol kg^{-1} melt respectively. This means that the solubility of the solid compound $AlkTaO_3$ is equal to or lower than 0.0062 mol kg^{-1} at $n_O/n_{Ta} = 3$ and 700 °C. Compared with the measured solubility of $AlkNbO_3$ of 0.045 mol kg^{-1} at 700 °C (see Vik *et al.*[17]), it is apparent that $AlkTaO_3$ is a lot less soluble in molten FLiNaK at this temperature than the Nb-compound. No previous measurements of solubility of $AlkTaO_3$ in molten alkali fluoride have been found in the literature.

$3 < n_O/n_{Ta} < 6.5$. Dissolution of the solid $AlkTaO_3$ compound occurs, and the concentration of tantalum and oxygen increases linearly up to a value of $n_O/n_{Ta} > 4$. The slopes of the increasing concentrations are 0.66 and 2.52 mol kg^{-1} for tantalum and oxygen respectively. This indicates that about two thirds of the solid $AlkTaO_3$ dissolves, or that another solid tantalum oxide is formed upon addition of Na_2O. At $n_O/n_{Ta} > 4$ there is again a change in the slopes of the increasing concentrations *versus* n_O/n_{Ta} plots. The formation of a tantalum tetraoxyfluoride as indicated in reaction (5) is likely.

$$AlkTaO_3(s) + O^{2-} + xF^- \rightleftharpoons TaO_4F_x^{(3+x)-} + Alk^+ \quad (5)$$

The oxygen content continues to increase linearly when n_O/n_{Ta} increases further, but with a different slope than below $n_O/n_{Ta} = 4$. The increase is less than would have been expected if all the added oxide dissolved completely. The tantalum concentration is slightly decreased indicating a possible formation of another solid compound. Something similar has been proposed for the related niobium system by Vik *et al.*[17] It is impossible, however, to identify the composition of the solid from the present data.

Solubility of Ta_2O_5 in FLiNaK

Small amounts of Ta_2O_5 were added stepwise to molten FLiNaK at 700 °C, and the concentrations of oxygen and tantalum measured. Data are given in Fig. 3. The initial oxide concentration in the purified melt was 0.0071 mol kg^{-1} melt. It can be seen that for small additions of Ta_2O_5, the oxygen and the tantalum concentrations increase linearly with the added amounts. The concentrations of O^{2-} and Ta(v) are, however, smaller than those given by the added Ta_2O_5. The dissolution process is clearly accompanied by a precipitation. Matthiesen *et al.*[16] performed a similar experiment with Nb_2O_5 in FLiNaK at 700 °C, and found that precipitation of $AlkNbO_3$(s) occurred. By adding 1 mol of Nb_2O_5(s), only 1 mol (50%) niobium and 2 mol (40%) oxygen dissolved. From the present results it can be seen that the precipitation is even larger. Addition of 1 mol Ta_2O_5(s) increases the tantalum and oxygen content by approximately 0.96 ± 0.03 (48 ± 3 mol%) and 1.66 ± 0.11 mol (33 ± 7 mol%) respectively. 1.04 ± 0.03 and 3.34 ± 0.11 mols of tantalum and oxygen, respectively, precipitated. The first three measurements in Fig. 3 were used to calculate these numbers.

The data in Fig. 2 show a clear minimum in solubility at $n_O/n_{Ta} \approx 3$, and suggest that the precipitating solid is $AlkTaO_3$. The 1.04 ± 0.03 mol tantalum and 3.34 ± 0.11 mol oxygen precipitating when Ta_2O_5 is dissolving in FLiNaK strongly indicates precipitation of $AlkTaO_3$. The oxygen to tantalum ratio in the melt is clearly below 2 when Ta_2O_5 dissolves in FLiNaK. This fits well with the solubility experiment presented in Fig. 2. For the sample at $n_O/n_{Ta} = 2.46$ it is found that the oxygen to tantalum ratio in the melt is 1.9. This indicates a co-formation of $TaOF_x^{(x-3)-}$ and $TaO_2F_x^{(1-x)-}$ complexes. The data in Fig. 2 also indicate precipitation of $AlkTaO_3$ before $n_O/n_{Ta} = 2$. A continuation of the Ta_2O_5 additions did not result in saturation. Both the oxide and the tantalum concentration increased, but less than for previous additions, and both concentrations increased with increasing temperature. Data are, however, not presented since this work was not completed.

Raman spectroscopic analysis of Ta(v)–O–F complexes in FLiNaK with varying n_O/n_{Ta} ratios

Table 1 lists the main observed frequencies from the Raman spectra of Ta(v) in FLiNaK–K_2TaF_7–Na_2O mixtures at different temperatures and compositions. The fluorescence background in the measured spectra was negligible. A large number of spectra were recorded and only some are presented to give an overall structural picture of the liquid system. Figs. 4–7 show representative Raman spectra obtained for a series of FLiNaK–K_2TaF_7–Na_2O liquid mixtures at different n_O/n_{Ta} ratios. These are spectra of the melt samples presented in Fig. 2. The following general observations can be made.

$0 < n_O/n_{Ta} < 3$. At $n_O/n_{Ta} \approx 0.06$ (Fig. 4), at least four main bands dominate the spectra; three polarised (p) at 906, 640 and 600 cm^{-1} and one broad depolarised (dp) at 314 cm^{-1}. As the oxide concentration increases, the intensity of the band at 640 cm^{-1} decreases, and almost vanishes at $n_O/n_{Ta} > 0.56$, while the band at 600 cm^{-1} increases. At the same time, a broad polarised band centred at ≈ 520 cm^{-1} appears and reaches its maximum intensity at $n_O/n_{Ta} = 0.82$ (Fig. 4). By further increasing the n_O/n_{Ta} ratio the depolarised band at 314 cm^{-1} is replaced by two new depolarised bands at 302 and 360 cm^{-1} (shoulder) (Fig. 5). In the high frequency region two new bands appear, one depolarised at 790 (dp) and one polarised at 870 (p) cm^{-1}. The last four bands dominate the spectra for n_O/n_{Ta} ratios up to 2.46. The band at 600 cm^{-1} is present at $n_O/n_{Ta} = 1.10$ (and possibly at $n_O/n_{Ta} = 1.43$) (Fig. 5) but disappears at higher n_O/n_{Ta} ratios.

The relative intensities of the bands in Figs. 4 and 5 need to be commented upon. The spectrum of the melt with the ratio $n_O/n_{Ta} = 1.80$ appears to be less noisy than the spectra of less oxide rich melts. This is because the absolute intensity of the $n_O/n_{Ta} = 1.80$ spectrum is higher than, for example, the spectrum of the melt at $n_O/n_{Ta} = 0.82$. The bands at 790 (dp) and 870 (p) cm^{-1} are more intense in nature than the band at 906 cm^{-1}. This is why the high frequency region of the spectrum of the $n_O/n_{Ta} = 1.10$ melt is dominated by the two former bands. The same is true for the spectra of melts with $n_O/n_{Ta} < 1$. At first glance, the band at 906 cm^{-1} in the spectrum of the $n_O/n_{Ta} = 0.26$ melt seems to be much too intense compared to the band at 640 cm^{-1}. This phenomenon will, however, occur since the vibration

Table 1 Observed Raman bands in melts with an initial concentration of tantalum 0.0956 mol kg^{-1} melt at different n_O/n_{Ta} ratios and temperatures. Numbers in parentheses indicate bands and frequencies with an estimated error of 5 cm^{-1}. Other frequencies have an estimated error of 1 cm^{-1}

n_O/n_{Ta}	T/°C	Main frequencies/cm^{-1}								
0.06	750		314	(380)	(600)	640			906	
0.26	750		314	(520)	600	640			906	
0.56	750		314		600	640	790	(870)	906	
0.82	750	306	(360)	520	600	(640)	792	870	906	
1.10	750	306	(360)		600	(640)	790	870	(906)	
1.43	750	306	360		600		790	870	(906)	
1.80	850	306	360		(600)		790	870		
2.46	840	(306)	(360)				790	870		
2.87	940						865			980
3.17	930						850			
3.53	940						845			
3.86	940		(300)				843			
4.26	920		(300)			(740)	840			
4.63	940		(320)			740	840		1050	
5.22	850		320			740	840		1050	
6.06	900		320			740	840		1050	

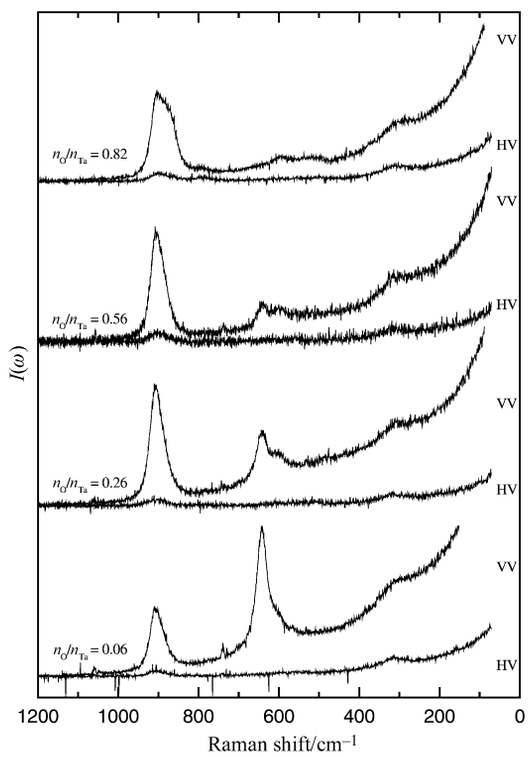

Fig. 4 Raman spectra of Ta(v) complexes in FLiNaK melts. 0.06 < n_O/n_{Ta} < 0.82. The melt with n_O/n_{Ta} = 0.06 may have had a higher oxide content during the Raman study due to an increase in the 906 cm^{-1} band during the first part of the recording of the spectrum. Added K_2TaF_7 = 0.0956 mol kg^{-1}. T = 750 °C.

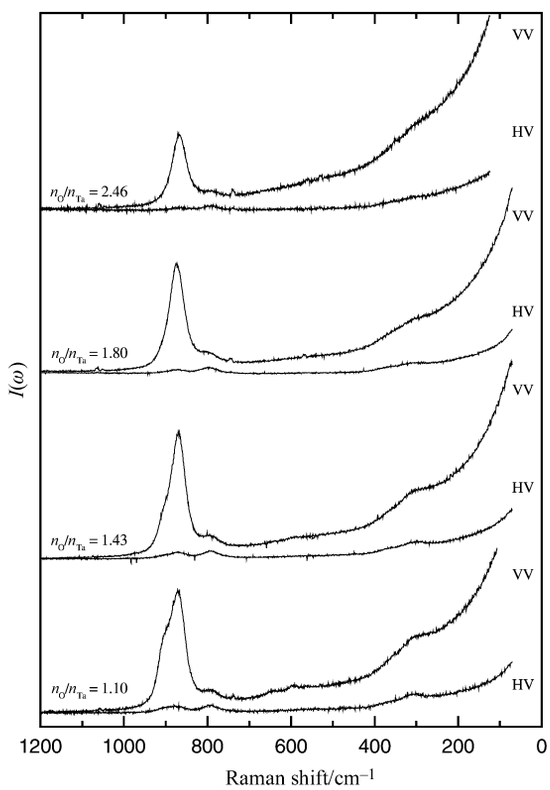

Fig. 5 Raman spectra of Ta(v) complexes in FLiNaK melts. 1.10 < n_O/n_{Ta} < 2.46. Added K_2TaF_7 = 0.0956 mol kg^{-1}. T = 750 °C for n_O/n_{Ta} = 1.10 and 1.43, T = 850 °C for n_O/n_{Ta} = 1.80 and T = 840 °C for n_O/n_{Ta} = 2.46.

at 906 cm^{-1} gives a more intense band than the vibrations at 640 or 600 cm^{-1}. By comparing the intensities of the bands at 640 and 600 cm^{-1} (even though these are quite noisy) it becomes apparent that the spectra are representative for the given melt compositions.

However, by comparing the general intensities of the present work with those measured by von Barner *et al.* on tantalum-[11] and niobium-complexes,[14] there seems to be an obvious discrepancy. For a FLiNaK melt with n_O/n_{Ta} = 0.5 the intensity ratio of the Ta–oxofluoride peak at 900 cm^{-1} to the Ta–fluoride peak at 640 cm^{-1} seemed to be 1/1 within experimental errors. A similar trend was reported in their parallel work on niobium fluoride and oxofluoride complexes. There are two important differences between the present work and the work by von Barner *et al.* They used melts that were more concentrated with Nb(v) or Ta(v), and they did not measure the actual oxide and refractory metal concentrations in the melt. Through the solubility measurements presented here, it has been possible to obtain the concentrations of Nb(v), Ta(v) and O^{2-} in the liquid samples withdrawn from the different melts. von Barner *et al.* seem to have trusted that their addition of purified chemicals would give correct concentrations in the melt. The spectrum of a FLiNaK melt with 2.7 mol% Nb(v) and no additions of oxide [14] is reported to have n_O/n_{Nb} = 0.26. It is not explained how this value was obtained. If the observed intensity of the oxide band was used as a basis to calculate the oxide concentration, the result would be uncertain due to differences in Raman intensities between different runs. We do, however, acknowledge that our samples could have absorbed oxide during the Raman experiment itself, and such absorption would have changed the relative oxide concentrations significantly in the low oxide containing melts. This problem was observed at n_O/n_{Ta} = 0.06.

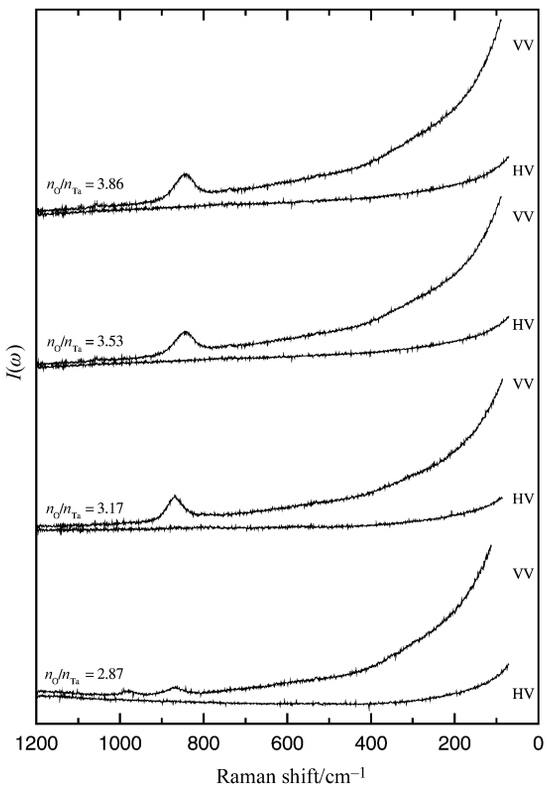

Fig. 6 Raman spectra of Ta(v) complexes in FLiNaK melts. $2.87 < n_O/n_{Ta} < 3.86$. Added $K_2TaF_7 = 0.0956$ mol kg^{-1}. $T = 940$ °C for $n_O/n_{Ta} = 2.87$, $n_O/n_{Ta} = 3.53$ and $n_O/n_{Ta} = 3.86$. $T = 930$ °C for $n_O/n_{Ta} = 3.17$.

During this run the Raman band at 906 cm^{-1} increased with time. The oxide concentration of this melt could therefore easily be significantly higher than indicated in Fig. 4.

The different intensities of the different tantalum oxofluoride complexes can explain why the peaks at 790 and 870 cm^{-1} are already present in the spectrum at $n_O/n_{Ta} = 0.82$. Three complexes, Ta fluoride, Ta monooxofluoride and Ta dioxofluoride, are probably present at this composition. The latter complex is present only in minor amounts, but seemingly enough is there to show up in the spectrum.

$3 < n_O/n_{Ta} < 6.06$. With increasing oxide content a polarised band at 850 cm^{-1} becomes the main feature in the spectra ($n_O/n_{Ta} = 3.17$) (Fig. 6). By further increasing the oxide concentration a red shift of the main polarised band is observed up to 840 cm^{-1}. The intensity of this band increases almost linearly with increasing n_O/n_{Ta} ratio. In melts with $n_O/n_{Ta} \approx 4$, two depolarised bands at 320 and 740 cm^{-1} appear, and at even higher ratios a high frequency polarised band at 1050 cm^{-1} is observed (Fig. 7). The intensity of the latter increases relative to the other three bands with increasing oxide content.

Ta_2O_5 dissolved in FLiNaK

Spectra are shown in Fig. 8, and are marked as samples 1, 2, 3 and 5, meaning samples from the same melts as shown in Fig. 3 from left to right. A polarised band at 870 cm^{-1} appears after the first addition of Ta_2O_5. Its intensity increases upon further additions of the oxide. At the same time, three depolarised bands at 306, 360 and 790 cm^{-1} become visible, and their intensity seems to be proportional to the intensity of the 870 cm^{-1} band for samples 2, 3 and 5. Furthermore sample 2 contains two polarised bands at 640 and 980 cm^{-1}. The latter is visible in the spectrum of sample 3 and possibly also in the spectrum of sample 5. While the intensity of the bands at 306, 360, 790 and 870 cm^{-1} increases upon addition of Ta_2O_5, the intensity of the 980 cm^{-1} either remains constant or decreases. The spectrum of

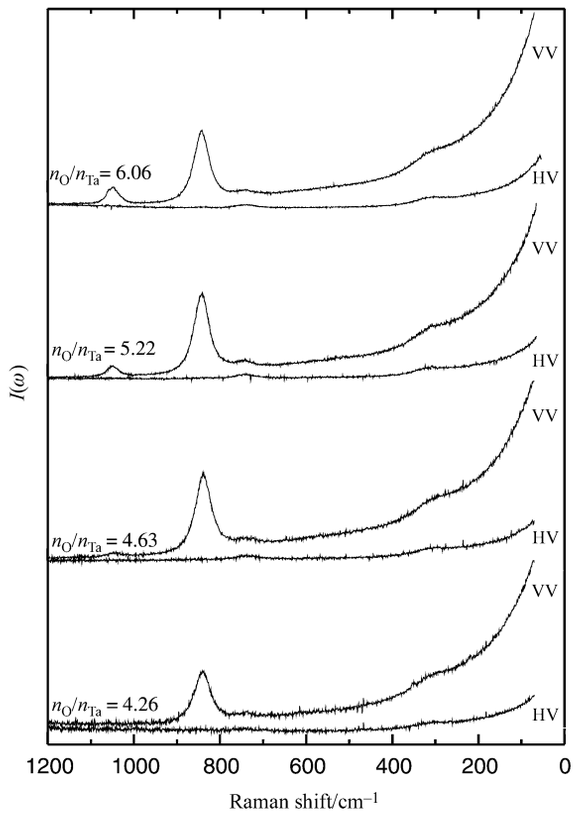

Fig. 7 Raman spectra of Ta(v) complexes in FLiNaK melts. $4.26 < n_O/n_{Ta} < 6.06$. Added $K_2TaF_7 = 0.0956$ mol kg^{-1}. $T = 920$ °C for $n_O/n_{Ta} = 4.26$, $T = 940$ °C for $n_O/n_{Ta} = 4.63$, $T = 850$ °C for $n_O/n_{Ta} = 5.22$ and $T = 900$ °C for $n_O/n_{Ta} = 6.06$.

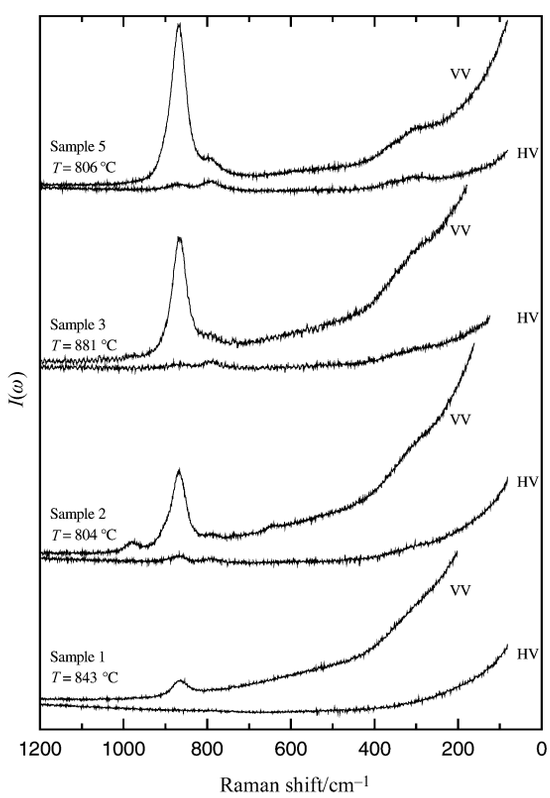

Fig. 8 Raman spectra of Ta_2O_5 dissolved in FLiNaK. Samples 1, 2, 3 and 5 correspond to increasing additions of oxide (see also Fig. 3). Sample 1: 0.061 mol O added, $n_O/n_{Ta} = 2.95$ in the melt. Sample 2: 0.180 mol O added, $n_O/n_{Ta} = 1.95$ in the melt. Sample 3: 0.298 mol O added, $n_O/n_{Ta} = 1.88$ in the melt. Sample 5: 1.435 mol O added, $n_O/n_{Ta} = 1.77$ in the melt.

Table 2 Raman bands for tantalum fluoride complexes in various solid, aqueous and molten salt media

Complex	Medium	Vibrations/cm^{-1}				Ref.
TaF_6^-	HF solution			585	696	7
TaF_6^-	$CsTaF_6$(s)		272	581	692	7
TaF_6^-	HF solution		282	595	711	8
TaF_6^-	$KTaF_6$(s)		280	590	710	8
TaF_6^-	HF solution				699	23
TaF_6^-	$CsTaF_6$(s)				685	24
TaF_7^{2-}	HF solution	280	380	645		7
TaF_7^{2-}	K_2TaF_7(s)	275	392	640		7
TaF_7^{2-}	K_2TaF_7(s)	290	400	645		8
TaF_7^{2-}	HF solution	280		645		23
TaF_7^{2-}	K_2TaF_7(s)		380	630		24
TaF_7^{2-}	FLiNaK(l)	276		640		11
TaF_7^{2-}	FLiNaK(s)		380	645		12
TaF_7^{2-}	FLiNaK(s)	290	380	645		13
TaF_7^{2-}	FLiNaK(l)		380	640		This work
TaF_8^{3-}	Na_3TaF_8(s)	371	411	461	614	7

sample 5 is totally dominated by these first four bands. A shoulder is possibly present at the high frequency side of the 870 cm^{-1} band, and is probably due to the polarised band at 906 cm^{-1} described in the previous section. The most important observation is the 980 cm^{-1} band. This band was not observed when Nb_2O_5 was dissolved in FLiNaK, and is a clear difference between the spectra of these otherwise very similar metals. The different Ta(v) fluoro and oxofluoro complexes that form in molten FLiNaK will be discussed in the next sections.

The tantalum(v) fluoride complex

As for the case of the niobium fluoride complex in molten FLiNaK,[17] the Raman spectra of samples having very low oxygen to tantalum ratios were extremely difficult to measure. The spectrum representing a melt with $n_O/n_{Ta} = 0.06$ in Fig. 4 is rather noisy, and it is difficult to measure accurate frequencies for the bands below 400 cm^{-1}. We therefore ran a new set of experiments focusing mainly on the low frequency region. From these experiments it was clear that in addition to the 314 cm^{-1} depolarised band another depolarised band appeared at around 380 cm^{-1}.

The spectral behaviour of the bands at 640 and 380 cm^{-1} could be associated with the tantalum fluoride complex in FLiNaK since they are disappearing from the spectra with an increasing n_O/n_{Ta} ratio. The behaviour of the remaining bands in the spectrum as described above is ascribed to oxygen containing tantalum complexes. In the related niobium system,[17] the NbF_7^{2-} and the NbF_6^- species could be present since no other configurations had been reported. The tantalum system is more complex since the possible existence of TaF_6^-, TaF_7^{2-}, TaF_8^{3-} and TaF_9^{4-} has been reported in various molten salt and aqueous media.[6–14] To determine the symmetry of the tantalum(v) fluoride complex in molten FLiNaK, it is reasonable to compare the measured spectra and the identified bands with results obtained in related systems. Table 2 lists relevant studies of tantalum complexes in the solid, aqueous and molten states.

The findings of TaF_9^{4-} by Varga and Freund[9] in perchloric acid solutions containing Ta(v) and hydrofluoric acid were based on potential measurements rather than vibrational spectroscopy. The strongest Raman bands for the TaF_6^-, TaF_7^{2-} and TaF_8^{3-} complexes occur at 685–711 cm^{-1}, 630–645 cm^{-1} and 614 cm^{-1} respectively. Variations occur due to different media and experimental conditions. It is reasonable to first focus on this vibration, to find the symmetry for the tantalum fluoride complex in molten FLiNaK. As indicated in Table 2, the observed band at 640 cm^{-1} is ascribed to the presence of TaF_7^{2-} in molten FLiNaK. The band is very close to that which has been observed for the complex in solid K_2TaF_7 by Keller and Strode,[7] Matwiyoff *et al.*[8] and Babkin *et al.*[24] Furthermore it is very close to the measured band at 645 cm^{-1} that was associated with TaF_7^{2-} by Keller and Strode[7] and Tsikaeva *et al.*[23] in aqueous HF. The presence of TaF_7^{2-} in the melts with very low oxide content is further supported by the observation of the weak depolarised band at 380 cm^{-1}. This band was observed in an aqueous tantalum containing HF solution by Keller and Strode[7] and in solid K_2TaF_7 by Babkin *et al.*[24] It should be noted, however, that Keller and Strode[7] and Matwiyoff *et al.*[8] found this band at a slightly higher frequency in this solid. As mentioned earlier, Fordyce and Baum[6] studied Ta(v)–fluoride complexes in molten alkali fluorides by means of infrared-reflection spectroscopy. TaF_7^{2-} was found to be the only stable species in KF–LiF melts. In the less polarising NaF–LiF solvent both TaF_7^{2-} and TaF_6^- were observed. Their conclusion was that when KF was present in the system, TaF_6^- was no longer stable. This seems to be the case for molten FLiNaK as well. The six-coordinated complex would be expected to have a strong Raman band at around 700 cm^{-1}, and such a vibration is not present in Fig. 4. The existence of a TaF_8^{3-} complex would cause a band around 610 cm^{-1}, and the intensity of this vibration would decrease with increasing oxide concentration. The band at 600 cm^{-1} increases when oxide is added to the system, and cannot be due to an eight-coordinated tantalum fluoride complex. It is therefore concluded that TaF_7^{2-} is the major species in molten FLiNaK at 750 °C.

Hoard[25] determined the structure of both NbF_7^{2-} and TaF_7^{2-} by means of XRD measurements, and found both to be of C_{2v} symmetry. Brown and Walker[26] showed that this might be inaccurate or incorrect for the niobium species. They proposed C_s symmetry for the NbF_7^{2-} ion. A similar study to that of Brown and Walker has not been found in the literature for the tantalum complex. This means that the symmetry of TaF_7^{2-} is uncertain, and the bands at 640 and 380 cm^{-1} cannot be ascribed to specific vibrations for a given point group. The polarised nature of the 640 cm^{-1} band does, however, indicate that it is due to a symmetric Ta–F stretching vibration of the TaF_7^{2-} complex. Similarly for the depolarised 380 cm^{-1} band. It is probably due to an asymmetric bend or deformation mode in the same species. The presence of TaF_7^{2-} in molten FLiNaK is in agreement with the findings of Fordyce and Baum[6] in molten KF–LiF, von Barner *et al.*[11] in molten FLiNaK and by Bjerrum *et al.*[12] and Robert *et al.*[13] in solidified FLiNaK.

The tantalum(v) monooxofluoride complex

The band at 904 cm^{-1} is attributed to the tantalum monooxofluoride complex. The polarised band is visible in all melts with $n_O/n_{Ta} \leq 1.8$, and is due to a symmetric Ta=O stretching mode in the $TaOF_x^{(x-3)-}$ complex. This is similar to the 922 cm^{-1} band due to the Nb=O symmetric stretching mode in the $NbOF_5^{2-}$ complex. The band at 314 cm^{-1} is present in the spectra of melts with $n_O/n_{Ta} < 0.82$, and is replaced by the bands at 306 and 360 cm^{-1} at higher ratios of oxygen to tantalum. At the same time, the bands at 870 and 790 cm^{-1} appear in the high frequency region. The four new bands are therefore ascribed to a new species with an oxide content higher than 1, and the 314 cm^{-1} band must therefore be due to the $TaOF_x^{(x-3)-}$ complex. A similar assignment has been made by von Barner *et al.*[11] using molten FLiNaK and by Robert *et al.*[13] using solidified FLiNaK. They measured Raman shifts at 312 and 319 cm^{-1} respectively. von Barner *et al.*[11] ascribed their depolarised band at 312 cm^{-1} to a Ta–F vibration of the $TaOF_x^{(x-3)-}$ complex. A similar band at 304 cm^{-1} has been observed for the $NbOF_5^{2-}$ complex by Vik *et al.*[17] It was shown that the 304 cm^{-1} band might be due to a Nb–O–F (E)-bending mode of the species. Pausewang *et al.*[27] ascribed the band at 306 cm^{-1} in solid Cs_2NbOF_5 and the band at 310 cm^{-1} in solid Cs_2TaOF_5 to this type of vibration. It is therefore possible that the band at 312 cm^{-1} is due to a Ta–O–F bending mode, rather than a Ta–F vibration.[11]

The origin of the polarised bands at ≈ 600 cm^{-1} and ≈ 520 cm^{-1} is rather uncertain. von Barner *et al.*[11] assigned the former

band to the Ta–F symmetric stretching vibration in the $TaOF_5^{2-}$ complex anion. In contrast, Robert *et al.*[13] in their Raman spectra of solidified melts found two peaks at 600 cm^{-1} and 545 cm^{-1}, which were attributed to the Ta–F stretching frequencies of the $Ta_2OF_{x+8}^{x-}$ and $TaOF_5^{2-}$ species respectively. In an earlier Raman study of crystalline $(NH_4)_3TaOF_6$,[7] it has been found that the Ta–F stretching mode is at 540 cm^{-1}.

The systematics of the Raman spectra of several M–O–F (M = refractory metal) in both molten and solid phase indicates that a replacement of two fluorines by one oxygen atom leads to a decrease in the M–F stretching frequency of about 40 cm^{-1}. Replacement of one fluorine by one oxygen leads to a decrease of >85 cm^{-1}. This was discussed thoroughly by Vik *et al.*[17] The Ta–F stretching frequency was found at 595 cm^{-1} in crystalline Cs_2TaOF_5 by Pausewang *et al.*[27] This compound contains isolated $TaOF_5^{2-}$ species in the crystal lattice. If this complex anion is preserved in the liquid phase, then the Ta–F frequency is expected at ≈ 600 cm^{-1}. Thus it is more likely that the observed band at 600 cm^{-1} in the molten Ta–O–F system could be associated with the $TaOF_x^{(x-3)-}$ species.

The origin of the other broad polarised band at 520 cm^{-1} is more complicated. As we discussed above, a band at 540 cm^{-1} found in the Raman spectra of several solid compounds and solidified melts of the Ta–O–F system was assigned to the Ta–F stretching frequency of either $TaOF_6^{3-}$ or $TaOF_5^{2-}$ species. On the other hand, this band could be due to a bridging Ta–F–Ta vibration of a dimeric $Ta_2O_2F_{2x+1}^{(2x-1)-}$ species, since the bridging mode is expected between the 314 and 600 cm^{-1} bands. Thus the 520 cm^{-1} could be due to either $TaOF_6^{3-}$ and/or dimeric $Ta_2O_2F_{2x+1}^{(2x-1)-}$ and thus no definite conclusions can be made. Further experiments are therefore needed at elevated temperatures in both solid and liquid phase in order to elucidate the origin of this band.

The tantalum(v) dioxofluoride complex

As mentioned in the previous section, the four bands at 306 (dp), 360 (dp), 790 (dp) and 870 (p) cm^{-1} were ascribed to a tantalum oxofluoride complex with an oxide to tantalum ratio higher than 1. The bands first appear in the spectrum of a melt with $n_O/n_{Ta} = 0.8$ (Fig. 4), and their intensity continues to increase with increasing oxide contents as shown in Fig. 5. The spectral behaviour is very similar to that of the four bands at 290 (dp), 368 (dp), 816 (dp) and 880 (p) cm^{-1} for $NbO_2F_4^{3-}$.[17] The four bands that dominate the spectrum of the melt with $n_O/n_{Ta} = 1.80$ in Fig. 5 are therefore ascribed to the presence of a tantalum-dioxofluoride complex of the type $TaO_2F_x^{(x-1)-}$.

The spectrum of a melt with $n_O/n_{Ta} = 2.87$ indicates that the band at 980 cm^{-1} has a different origin. The spectrum is dominated by the 980 cm^{-1} band and a band at around 865 cm^{-1} that might be the weak remains of the polarised band at 870 cm^{-1}. The concentration of tantalum containing species is very low in this sample, and the Raman spectrum has low intensity. The very high frequency and the polarised property of the 980 cm^{-1} band indicates that it is due to a Ta=O symmetric vibration. The Ta–O bond is stronger than those in $TaOF_5^{2-}$ and $TaO_2F_4^{3-}$ which causes the symmetric vibration to occur at a significantly higher frequency. Apart from this, the band is difficult to assign. A detailed assignment of the four bands of $NbO_2F_4^{3-}$ in FLiNaK was given by Vik *et al.*[17] Due to the spectral similarities of the niobium- and the tantalum-dioxofluoro complex, the band assignments will be covered only briefly.

The polarised band at 870 cm^{-1} is assigned to a symmetric Ta–O vibration where the high frequency reflects the character of a strong double bond. The bond is weaker than the Ta–O bond in $TaOF_5^{2-}$, and the vibration of the dioxo complex occurs at a frequency about 34 cm^{-1} lower than for the monooxo complex. This decrease is slightly lower than for the case of niobium mono/dioxo complexes, where a red shift of about 45 cm^{-1} was observed when a fluorine atom was replaced with an oxygen atom. The depolarised band at 790 cm^{-1} is attributed to an asymmetric vibration of the TaO_2^+ entity. The band at 815 cm^{-1} observed for $NbO_2F_4^{3-}$ in FLiNaK was shown to be both IR and Raman active, and was used to exclude a centre of symmetry in the niobium species. IR spectra of the different tantalum complexes have not been recorded in the present work, but Bjerrum *et al.*[12] measured Raman and IR spectra of tantalum in solidified FLiNaK melts with $0 < n_O/n_{Ta} < 2$. The IR spectrum of a sample with $n_O/n_{Ta} = 2$ unfortunately had a very low intensity, and the different bands were difficult to resolve. Furthermore the Raman spectrum of the same sample is rather different from that recorded in the molten state.

In addition to the four bands in the present work, the spectrum of Bjerrum *et al.* contains two bands at 620 and 700 cm^{-1}. It is therefore impossible to exclude a centre of symmetry in the $TaO_2F_x^{(x-1)-}$ complex by using the mutual exclusion rule. This does not, however, mean that the complex necessarily has a symmetry centre. As pointed out by Griffith and Wickins,[28] the *cis* configuration is clearly preferred in d^0-complexes. This is the case for both Ta^{5+} and Nb^{5+}, and is an indication that $TaO_2F_x^{(x-1)-}$ does not have a centre of symmetry. In accordance with the assignment of the band at 290 cm^{-1} to an asymmetric Nb–O–F vibration in the $NbO_2F_4^{3-}$ complex,[17] the depolarised band at 306 cm^{-1} is assigned to an asymmetric Ta–O–F vibration in $TaO_2F_x^{(x-1)-}$. Compared with the depolarised Ta–O–F band of $TaOF_5^{2-}$, the frequency of the asymmetric vibration is reduced by 8 cm^{-1} (15 cm^{-1} reduction in the niobium case). A deformation, $\delta(MO_2)$, mode of the $NbO_2F_4^{3-}$ complex was an explanation for the origin of the band at 370 cm^{-1}.[17] It is assumed that the depolarised band at 360 cm^{-1} for $TaO_2F_x^{(x-1)-}$ has the same origin.

Determination of the number of fluorine atoms in the niobium dioxofluoride complex,[17] could be made by comparison with the IR bands of the $Rb_2KNbO_2F_4$ solid measured by Pausewang and Rudorf.[29] IR or Raman measurements of a similar tantalum solid have, however, not been found in the literature and the number of fluorine atoms in the $TaO_2F_x^{(x-1)-}$ complex must be determined using other data. Griffith and Wickins,[28] and Pausewang and Dehnicke[30] studied dioxohalide complexes of vanadium, molybdenum and tungsten in various alkali and ammonium solids. It was shown that the symmetric $\nu(MO_2)$ vibration occurred at 965, 948 and 946 cm^{-1} for $(NH_4)_2[Mo(V)O_2F_3](s)$, $(NH_4)_2[Mo(VI)O_2F_4](s)$ and $(NH_4)_3[Mo(VI)O_2F_5](s)$, respectively. As expected, the frequency decreased with increasing number of fluorine atoms, but the difference between the last two compounds was very small. $(NH_4)_2[Mo(V)O_2F_3](s)$ contained six-coordinated molybdenum atoms with bridging fluoride ligands, and was probably a dimeric species with two *cis*-dioxo groups. The fluoride bridge was, however, not visible in the Raman spectrum. A similar compound, $K_2VO_2F_3(s)$, was studied by Pausewang and Dehnicke[30] by means of IR spectroscopy, and was shown to contain chains of fluoride bridged $(VO_2F_4)_n$ groups. The $(NH_4)_3[Mo(VI)O_2F_5](s)$ compound was probably a double salt with composition $\{(NH_4)_2[Mo(VI)O_2F_4]NH_4F\}$, and did not contain seven-coordinated molybdenum. The work by Griffith and Wickins,[28] and the examples above show that a coordination of six is clearly preferred for the dioxo complexes. Due to this, and the spectral similarities of $NbO_2F_4^{3-}$ and $TaO_2F_x^{(x-1)-}$, it is also likely that the latter has an octahedral coordination. As in the case of niobium, a possible fluoride bridge is impossible to detect since it is probably Raman inactive. The lack of IR data for the $TaO_2F_x^{(x-1)-}$ complex in the molten state, makes it difficult to rule out such bridges. As already mentioned, an oxide bridged species would have a polarised Raman band in the range 600–800 cm^{-1}. Such a band is not found for the tantalum dioxofluoro complex. It is therefore likely that the complex is either a monomeric $TaO_2F_4^{3-}$ species, or a fluorine bridged species similar to that of vanadium in $K_2VO_2F_3(s)$ or molybdenum in $(NH_4)_2[Mo(V)O_2F_3](s)$.

Tantalum(v) oxofluoride complexes with a ratio of n_O/n_{Ta} above 3

The band at 850 cm^{-1} shifts to lower frequencies as oxide is added to the system (Fig. 6), but then remains constant for melts with $n_O/n_{Ta} > 4$ (Fig. 7). The behaviour of the spectra shown in Fig. 6 can probably be explained by $TaO_2F_4^{3-}$ coexisting with a tantalum oxofluorine complex $TaO_nF_x^{(2n-x-5)-}$ with $n > 3$. Due to the low solubility of tantalum complexes in melts with n_O/n_{Ta} around 3, the general intensity of the Raman spectra in Fig. 6 is low. The spectra shown in Fig. 7 are, however, more intense. This fits well with the solubility data. The tantalum concentration is now back to the value given by the amount added. The spectra in Fig. 7 are characterised by four bands at 320 (dp), 740 (dp), 840 (p) and 1050 (p) cm^{-1}. The intensity of the latter increases relative to the other three when the oxide content increases in the melt, and seems very similar to the band at 1045 cm^{-1} observed in the niobium case.[17]

As for the other three bands, their relative intensity seems to be constant and they are probably due to the same species. The spectral behaviour is similar to that for the peaks at 310 (dp), 750 (dp) and 820 (p) ascribed to the possible $NbO_4F_2^{5-}$ complex,[17] and are therefore probably due to a $TaO_4F_x^{(3+x)-}$ species. The polarised band at 840 cm^{-1} and the depolarised band at 740 cm^{-1} are probably of a similar origin as the two bands at 870 and 790 cm^{-1} observed for the dioxofluoro complex. The bands appear as a pair, and are due to symmetric and asymmetric Ta–O vibrations, in this case probably in the TaO_4^{3-} entity. Tetrahedral complexes are extremely rare for niobium and tantalum, and the value of x in $TaO_4F_x^{(3+x)-}$ is likely to be higher than 0. The band at 320 cm^{-1} is then probably due to a Ta–O–F bending vibration.

The absence of bands between 320 cm^{-1} and 740 cm^{-1} makes the presence of oxide bridges unlikely in the $TaO_4F_x^{(3+x)-}$ complex. With no IR data available, it is difficult to determine whether or not there are fluoride bridges present in the species. The same problem was discussed for the $NbO_4F_2^{5-}$ complex,[17] and it was assumed that the niobium species was a monomer like all the other $NbO_xF_y^{(2x+y-5)-}$ complexes found in molten FLiNaK. The same assumption is made for the $TaO_4F_x^{(3+x)-}$ ion. The number of fluorine atoms in the complex is also difficult to determine, but it is likely that the tantalum atom is octahedrally coordinated giving $x = 2$. The high frequency band at 1050 cm^{-1} must be due to a new tantalum complex. Since the intensity of the band continues to increase with oxide additions in melts with $n_O/n_{Ta} > 4$, it is probably due to an even more oxide rich species than $TaO_4F_2^{5-}$. In Raman spectroscopic studies of the high temperature β-Ta_2O_5 phase by Balachandran and Eror,[31] it was shown that tantalum may form both five- and six-coordinated polyhedra with oxygen: "Chains of edge-shared pentagons are fused together with the formation of octahedral sites between adjacent chains. These distorted polyhedra are condensed with considerable variation in the bond lengths." In the corresponding Nb(v) oxofluoride melts,[17] the band at 1044 cm^{-1} were assigned to the possible existence of $(NbO_6)_n$ network structures. The band at 1050 cm^{-1} is probably of a similar origin; a symmetric vibration of a very strong Ta=O bond in a distorted five- and/or six-coordinated tantalum polyhedron.

Conclusion

Raman spectroscopy and oxygen and tantalum solubility measurements of Na_2O–FLiNaK–K_2TaF_7 melts show that at least five different tantalum oxofluoro species are formed. The solubility data indicate the formation of different $Ta_xO_yF_z^{(2y+z-5x)-}$ complexes where x, y and z take values depending on the n_O/n_{Ta} ratio in the melt. From the Raman measurements, the existence of TaF_7^{2-} (C_s), $TaOF_5^{2-}$ (C_{4v}) at ratios up to 2 is well established. Also the existence of $TaOF_6^{3-}$ and/or dimeric $Ta_2O_2F_{2x+1}^{(2x-1)-}$ species cannot be excluded. The dioxofluoro complex is probably $TaO_2F_4^{3-}$ (C_{2v}), and a polarised band at 980 cm^{-1} in these melts suggests the presence of yet another tantalum oxofluoro complex. At $n_O/n_{Ta} = 3$ the solubility data indicates precipitation of a solid compound $AlkTaO_3$. At $n_O/n_{Ta} > 3$ the solubility data are consistent with a dissolution of the $AlkTaO_3$ solid, and a formation of a $TaO_4F_x^{(x+3)-}$ species. The tantalum tetraoxofluoride complex is possibly $TaO_4F_2^{5-}$ (C_{2v}). The solubility data indicates a precipitation of an oxide rich solid at $n_O/n_{Ta} > 4$. The Raman spectra indicate the existence of $TaO_4F_2^{5-}$ species as well as $(TaO_5)_n$ or $(TaO_6)_n$ network like structures in these melts. The major difference between the niobium and the tantalum systems is the solubility of the $AlkMO_3$ solid (M = Nb, Ta). The solubility of $AlkNbO_3$ in molten FLiNaK at 700 °C is found to be more than seven times larger than that of $AlkTaO_3$. The lack of a stable $TaO_3F_x^{(1+x)-}$ complex is probably the reason for the lower solubility of $AlkTaO_3$.

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