Infrared and Raman Spectroscopic Investigations of the Nb(V) Fluoro and Oxofluoro Complexes in the LiF−NaF−KF Eutectic Melt with Development of a Diamond IR Cell

K. B. Andersen, E. Christensen, R. W. Berg, N. J. Bjerrum, and J. H. von Barner*

Department of Chemistry, Building 207, The Technical University of Denmark,
DK 2800 Lyngby, Denmark

Received September 1, 1999

A vacuum-tight cell for infrared spectroscopic investigations of extremely corrosive melts, e.g., molten fluorides, has been constructed and tested up to 750 °C. The cell has a gold-lined sample chamber and a diamond window transparent for the infrared light. It can be furnished with a gold piston that enables the recording of short-path-length FTIR spectra of liquid samples. Solutions of Nb(V) in LiF−NaF−KF eutectic (FLINAK) with and without oxide additions have been investigated by FTIR and Raman spectroscopy. The presence of NbF_7^{2-}, $NbOF_5^{2-}$, and $NbO_2F_4^{3-}$ complexes was established in the molten state at 600 °C. After solidification NbF_7^{2-} was still the only Nb(V) all-fluoro complex present. Three oxofluoro complexes, $NbOF_6^{3-}$, $NbOF_5^{2-}$, and $NbO_2F_4^{3-}$, have been identified in the solid state. Typical frequency regions for the different complexes are established. Finally, it was shown that K_2NbF_7 can be used as an indicator to determine the oxide content of the sample melts.

Introduction

The complex formation of niobium plays an important role in connection with the development of plating processes from molten salt baths. Most of the successful attempts to produce coherent surface layers of niobium metal have applied pure alkali fluoride mixtures, e.g., LiF−NaF−KF (FLINAK), or mixed chlorofluoro melts as molten salt solvents for high-valent niobium species, i.e., Nb(V) and Nb(IV).

A large number of papers have dealt with investigations of the redox chemistry of niobium in halide melts. Concerning the electrochemical behavior of niobium in FLINAK melts, we refer to a recent work by Mathiesen et al.[1]

We have previously investigated in FLINAK the fluoro- and oxofluoro complex formation of niobium in the +5 oxidation state by Raman spectroscopy.[2] From this investigation, it appears that the presence of oxide gives rise to formation of mono- and dioxofluoro complexes depending on the oxide to niobium molar ratio. The presence of oxide also seems to play an important role for the quality of the niobium metal plated from the halide-based melts, both in the case of all fluoride melts[3] and for mixed chloride−fluoride melts.[4]

It is important to clarify the fundamental complex chemistry in such melts and to find analytical methods to determine the oxide content. In this connection infrared spectroscopy (IR) offers an important supplement to Raman spectroscopy in order to identify the nature of the species formed in the melts. So far, only few attempts have been performed to apply IR spectroscopy on molten fluorides[5,6] probably because of the major experimental difficulties that have to be overcome in investigations of these extremely aggressive melts.

The main purpose of the present work is to develop an IR method that will enable us to investigate fluoride-containing molten salts in general and more specifically to use this method on the salt baths (e.g., FLINAK-based) applied for niobium plating. It is further of interest to find out whether K_2NbF_7 can be used as a probe compound to determine the oxide content in FLINAK melts as in the case of the corresponding tantalum compound.[7]

Experimental Section

The weighing and handling of the chemicals were performed in nitrogen- or argon-filled gloveboxes. The box atmosphere was continuously passed through an external molecular sieve system that removed water vapor. Thus, the water content was kept very low (dew point of approximately −45 °C). When not in use, the chemicals were stored in ampules sealed under vacuum.

The mixtures were weighed in glassy carbon crucibles (V25, Carbone-Lorraine) and transferred to a closed furnace for melting and equilibration (700 °C for 20 h) under an argon atmosphere (99.99% from Hede Nielsen A/S, Denmark). The molten mixtures were solidified in the furnace and transferred to the glovebox for further manipulations. The purification of the analytical grade alkali fluorides has been described previously.[2] K_2NbF_7 and Na_2O were synthesized in our laboratory according to a method recently reported.[3] $CsNbF_6$ was prepared in the following manner. At first, niobium metal (99.9% from Goodfellow) was mixed with a 40% hydrofluoric acid solution. Concentrated nitric acid was subsequently added dropwise in order to oxidize niobium to the +5 state. This reagent was then mixed in stoichiometric proportions with a solution of CsF (>99% from Fluka) in 40% hydrofluoric acid. A white precipitate was formed. The solvent was then removed by evaporation, and the remaining solid phase was recrystallized in 40% hydrofluoric acid. The product consisted of small white crystals of composition $CsNbF_6$ (identified by X-ray diffraction analysis[8]).

---

* To whom correspondence should be addressed.

(1) Mathiesen, F.; Christensen, E.; von Barner, J. H.; Bjerrum, N. J. *J. Electrochem. Soc.* **1996**, *143*, 1793.

(2) von Barner, J. H.; Christensen, E.; Bjerrum, N. J.; Gilbert, B. *Inorg. Chem.* **1991**, *30*, 561.

(3) Christensen, E.; Wang, X.; von Barner, J. H.; Østvold, T.; Bjerrum, N. J. *J. Electrochem. Soc.* **1994**, *141*, 1212.

(4) Lantelme, F.; Berghoute, Y.; von Barner, J. H.; Picard, G. S. *J. Electrochem. Soc.* **1995**, *142*, 4097.

(5) Fordyce, J. S.; Baum, R. L. *J. Chem. Phys.* **1966**, *44*, 1166.

(6) Agulyanskii, A. I.; Bessonova, V. A. *Russ. J. Inorg. Chem.* **1984**, *29*, 44.

(7) Bjerrum, N. J.; Berg, R. W.; Christensen, E.; Kerridge, D. H.; von Barner, J. H. *Anal. Chem.* **1995**, *34*, 2129.

10.1021/ic991057t CCC: $19.00

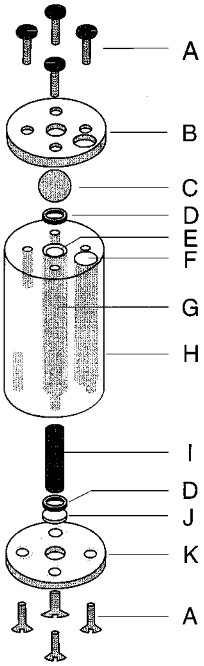

Figure 1. Expanded view of the cell designed for FTIR measurements on corrosive melts: (A) screws; (B) top lid; (C) nickel ball; (D) gold gasket; (E) gold lining; (F) thermocouple pocket; (G) sample chamber; (H) cell body; (I) gold piston; (J) diamond window; (K) bottom lid.

The mixing of samples and the preparation of KBr disks for solid-phase IR experiments were performed in the same manner as in our work on oxide determination in FLINAK$-K_2TaF_7$ melts.[7] The Raman spectra were recorded with the same instrument as in the latter work[7] and were obtained from the solid samples in Pyrex ampules sealed under vacuum.

A new cell for infrared experiments on liquid samples was constructed. This cell is generally suited for investigations of corrosive melts, such as fluorides. In the design of the cell special care was taken to ensure that the melts were only in contact with corrosion-resistant materials.

To find suitable materials, we investigated the corrosion behavior of a number of candidates in contact with FLINAK melts under an argon atmosphere. Nickel, which has often been used as a container material for molten fluorides, is moderately attacked by FLINAK melts at 700 °C. We found that the weight loss of a nickel plate with a surface area of 6.5 cm^2 was 0.7 mg/cm^2 over a 24 h period. When K_2NbF_7 (3 mol %) was added to the FLINAK melt, the corrosion was accelerated, now increasing to 3.2 mg/cm^2 (700 °C, 24 h). On the other hand gold seemed to be resistant to FLINAK melts at 700 °C; both in melts without and with K_2NbF_7 present we observed no measurable weight loss during a 24 h period.

Concerning window materials, ZnSe, Si, and diamond were tested. Of these only diamond could resist the FLINAK$-K_2NbF_7$ (3 mol %) melt (a small diamond piece weighed the same before and after treatment with the melt for 24 h at 700 °C in an argon atmosphere). Consequently, we decided to apply gold and diamond for all parts of the infrared cell that were in contact with the melt.

A drawing of the final cell design is shown in Figure 1. The body of the cell (H) is a thick-walled nickel tube (length = 50 mm, outer diameter = 26 mm, inner diameter = 5 mm). The inner part is lined with a gold tube (E). Recesses in the nickel tube (top and bottom) make it possible to place gold rings (D), which serve as a packing toward a nickel ball (C, $d = 8$ mm) and the diamond window (J). The latter consists of a type IIa diamond (D. Drukker & Zn, Amsterdam, The Netherlands). It is important to prevent evaporation of the samples into the evacuated chamber of the FTIR instrument. Thus, the sample chamber (G) can be closed vacuum-tight by two nickel disks (B and K) that are clamped to the cell house by screws (A). The temperature was measured by a chromel$-$alumel thermocouple placed in a pocket (F).

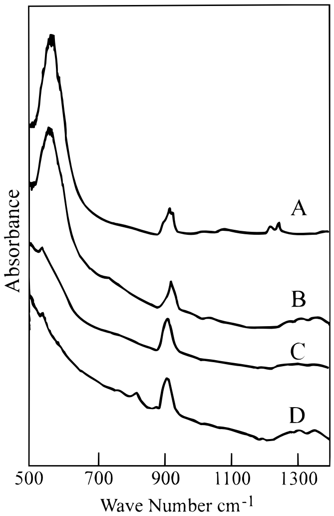

Figure 2. Room-temperature infrared spectra of selected solidified FLINAK$-K_2NbF_7$ (2.7 mol %) melts with various amounts of Na_2O added. The amounts of oxide added were (in mol %) (A) 0.0, (B) 0.5, (C) 1.0, and (D) 2.7.

The IR spectra of the melts were obtained as reflectance spectra. We applied the method where spectra of molten samples with short path lengths (thin film spectra) are related to spectra of an opaque melt (thick film spectra).[9,10] To obtain thin film spectra, the cell was furnished with a moveable gold piston (I). The lower end of the piston was polished and served as a reflecting backplate for the IR beam. The cell was loaded with a few milligrams of the premixed sample (finely ground powder) in such a way that the diamond window was just covered. The thick-film spectra were collected without piston. In this case the cell was loaded with an amount of sample giving a melt layer of approximately 2 mm.

The cell was assembled within the glovebox. Subsequently, it was transferred to a homemade metal core (aluminum bronze) furnace that was fitted to the sample chamber of the FTIR instrument. The furnace could be heated to 750 °C by four rod-shaped heating elements connected to a proportional integral derivative regulated power supply responding to a chromel$-$alumel thermocouple placed in the core.

Spectra of solid samples (in KBr disks) were recorded as transmission spectra (a FTIR spectrum of the empty chamber served as the reference).

The FTIR instrument was a Bomem DA3.026 instrument upgraded with a PCDA8 computer system and software also supplied by Bomem. Prior to recording of the interferograms of molten samples, a phase correction procedure was performed on the entire optical system including the heated cell. The source was a globar type infrared source. A KBr beam splitter and an MCT "wide range" detector were applied. In the FT calculations a "boxcar" apodization function was used for the melt spectra, leading to a resolution of 4 cm^{-1}. The solid-phase spectra were recorded with a resolution of 1 cm^{-1}, and a Hamming function was used for their apodization.

Results

FTIR Spectra. Figure 2 shows the influence of oxide additions on the infrared spectra of solidified FLINAK$-K_2NbF_7$ melts. The upper spectrum (Figure 2A), where no oxide has been added, shows a strong band at 565 cm^{-1}. This band gradually diminished when oxide was added and totally disappeared when the formal (i.e., based on added oxide) O/Nb molar ratio reached 0.5. For O/Nb ratios in the region 0.4$-$1.1, a new band appeared at 535 cm^{-1}. At higher frequencies (at around

---

(8) Berg, R. W.; von Barner, J. H.; Christensen, E.; Nielsen, K. *Molten Salt Forum,* submitted.

(9) Hvistendahl, J.; Rytter, E.; Øye, H. A. *Appl. Spectrosc.* **1983**, *37*, 182.

(10) Hvistendahl, J.; Klaeboe, P.; Rytter, E.; Øye, H. A. *Inorg. Chem.* **1984**, *23*, 706.

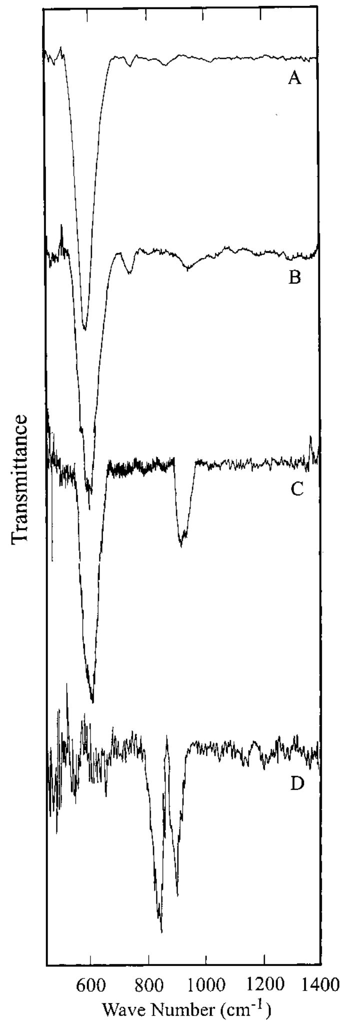

Figure 3. Infrared spectra at 600 °C of FLINAK−K_2NbF_7 (2.7 mol %) melts with Na_2O added. The amounts of oxide added were (in mol %) (A) 0.5, (B) 1.0, (C) 2.4, and (D) 5.4.

900 cm^{-1}) three bands were seen at 910, 923, and 932 cm^{-1}, respectively, for samples with only minor amounts of oxide present (spectra A and B of Figure 2). For higher oxide contents (spectra C and D of Figure 2) the 923 and 932 cm^{-1} bands vanish but the band at 910 cm^{-1} remains. When the O/Nb ratio approaches 1, two new bands start to grow at 809 and 880 cm^{-1}, respectively (Figure 2D).

Reflectance spectra of the melts at 650 °C can be seen in Figure 3. Each spectrum has been obtained from thin- and thick-film FTIR spectra. It has been shown[9,10] that a spectrum with the same band positions as in normal IR transmission spectra is obtained by calculating the internal transmittance t^* from

$$t^* = 1 - I_{tn}/I_{tk} \qquad (1)$$

where I_{tn} and I_{tk} are spectral intensities for a thin- and a thick-film sample, respectively. The molten state spectra have further been corrected for background effects due to the FLINAK solvent and apparatus. A minor band around 750 cm^{-1} seen sometimes in the uncorrected spectra probably was due to the beam splitter.

Only one band situated at 583 cm^{-1} appears in the spectra of the melts with no (Figure 3A) and 0.5 mol % oxide added (O/Nb = 0.18, Figure 3B). In the spectrum of the melt with an O/Nb molar ratio of 0.9 (Figure 3C), a sharp and intense band is seen at 920 cm^{-1}. The band at 583 cm^{-1} seems to move to a slightly higher frequency (592 cm^{-1}). Addition of oxide up to an O/Nb molar ratio of two (Figure 3D) drastically changes the IR spectrum near 900 cm^{-1}. The 920 cm^{-1} vibration vanishes, and two new bands at 820 and 880 cm^{-1} appear.

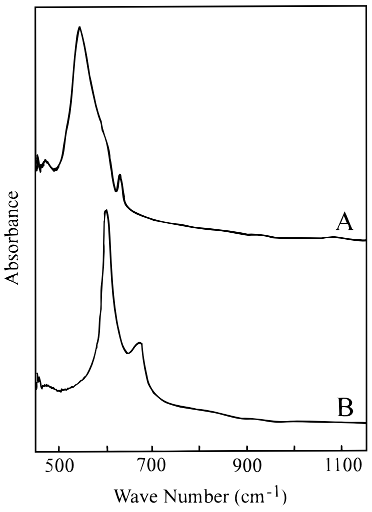

Figure 4. Room-temperature infrared spectra of (A) K_2NbF_7 and (B) $CsNbF_6$.

Table 1. Infrared Vibrational Frequencies of Nb(V) Fluorocomplexes in Different Media

species	medium[a]	vibrations (cm^{-1})	reference
NbF_7^{2-}	K_2NbF_7, solid	633, 557, 485	6
NbF_7^{2-}	K_2NbF_7, solid	631, 549, 470, 330, 306	5
NbF_7^{2-}	KF−LiF melt, 750 °C	555	5
NbF_6^{-}	K_2NbF_7 melt, 800 °C	640, 602	6
NbF_7^{2-}	K_2NbF_7, solid	632, 551	this work
NbF_6^{-}	$CsNbF_6$, solid	670, 601	this work
$NbF_n^{(n-5)-}$	FLINAK, solidified	565	this work
$NbF_n^{(n-5)-}$	FLINAK melt, 600 °C	583	this work

[a] Solids measured at room temperature if nothing else stated.

Certainly, these spectral changes indicate that a number of different fluoro- and oxofluoro complexes are formed depending on the oxide content of the melts. To clarify the situation, we have measured the IR spectra of solid $CsNbF_6$ and K_2NbF_7. These well-defined compounds are known to contain NbF_6^- anions of octahedral[8,11] symmetry and NbF_7^{2-} of approximately C_{2v} symmetry.[12,13] The IR results are shown in Figure 4. It can be seen that K_2NbF_7 (Figure 4A) has a characteristic strong band at 551 cm^{-1} and a weak band at 632 cm^{-1}. In the IR spectrum of $CsNbF_6$ (Figure 4B), a major band is situated near 600 cm^{-1} and a minor band appears at 670 cm^{-1}.

Nb(V) Fluoro Complexes. The obtained infrared results are collected in Table 1, together with literature data. It is evident that strong IR vibrations for the NbF_7^{2-} ion in solid K_2NbF_7 have previously been observed[5,6] in a region near 550 cm^{-1} at room temperature as well as a weak band near 633 cm^{-1}. We thus consider our 633 and 551 cm^{-1} bands to be due to vibrations of the C_{2v} distorted NbF_7^{2-} complex. They can be assigned to the symmetric and antisymmetric Nb−F stretching vibrations. In the Raman spectrum[2,11] of crystalline K_2NbF_7, the symmetric stretching vibration gives rise to the strong signal near 630 cm^{-1}.

Concerning our IR spectrum of solid $CsNbF_6$, we ascribe the strong band at 600 cm^{-1} to the ν_3 vibration of the octahedral NbF_6^- ion. This agrees well with the assignment of a frequency

---

(11) Keller, O. L. *Inorg. Chem.* **1963**, *2*, 783.
(12) Hoard, J. L. *J. Am. Chem. Soc.* **1939**, *61*, 1252.
(13) Brown, G. M.; Walker, L. A. *Acta Crystallogr.* **1966**, *20*, 220.

Table 2. Infrared Vibrational Frequencies of Nb(V) Oxofluorocomplexes in Different Media

species	medium	vibration (cm^{-1})		reference
		$\nu_{Nb=O}$	ν_{Nb-F}	
$NbOF_5^{2-}$	$K_2NbOF_5 \cdot H_2O$, solid	932		11
$NbOF_5^{2-}$	$RbNbOF_5$, solid	917	581, 536	15
$NbOF_5^{2-}$	$CsNbOF_5$, solid	905	576, 525	15
$NbOF_5^{2-}$	K_2NbF_7, hydrolyzed melt	940	560	6
$NbOF_n^{(n-3)-}$	FLINAK, solidified melt	912	540	2
$NbOF_x^{(3-x)-}$	LiF−KF, hydrolyzed melt	920		5
$NbOF_6^{3-}$	$(NH_4)_3NbOF_6$, solid	917	533, 464	15
$NbOF_n^{(n-3)-}$	FLINAK, solidified melt	909, 923, 932	535	this work
$NbOF_n^{(n-3)-}$	FLINAK, melt	920	592	this work
$NbO_2F_4^{3-}$	$K_3NbO_2F_4$, solid	890, 811		16
$NbO_2F_4^{3-}$	$K_2NaNbO_2F_4$, solid	894, 825	513	17
$NbO_2F_4^{3-}$	FLINAK, solidified melt	879, 809		2
$NbO_2F_4^{3-}$	FLINAK, melt	882, 820		this work

at 602 cm^{-1}, which has been quoted in a study[6] of crystals of this ion. The IR band around 670 cm^{-1} may originate from the ν_1 vibration of NbF_6^-; a band assigned to ν_1 was observed in the Raman spectrum of $CsNbF_6$ at 683 cm^{-1} by Keller.[11] Although ν_1 vibrations from regular octahedral species are IR-forbidden, they have sometimes been seen as weak signals in the IR spectra. However, the 670 cm^{-1} band can also be a component of ν_3.[8] It should be noted that we see no peak at 580 cm^{-1} where a band has been ascribed previously to NbF_6^- by Peacock and Sharpe.[14] Unfortunately, these authors gave no information from what sort of sample this frequency was found.

Regarding the solidified solution of K_2NbF_7 in FLINAK (Figure 1A), the IR band observed at 565 cm^{-1} has a frequency that is too low to indicate the presence of NbF_6^- (as mentioned above, this ion has its most characteristic IR vibration near 600 cm^{-1}). The strongest IR band for NbF_7^{2-} in pure K_2NbF_7 has been observed at around 549−557 cm^{-1}, i.e., slightly lower than 565 cm^{-1}. However, it is not unusual to observe minor differences in band positions for a certain complex when the surroundings change; in our case the presence of Li^+ ions in the FLINAK solvent may well have this effect. Therefore, we believe that the 565 cm^{-1} band originates from the NbF_7^{2-} complex.

The band at 583 cm^{-1}, present in the spectra of the melts at 600 °C with O/Nb molar ratios less than ca. 0.4, is most likely also due to niobium fluoro complexes of the $NbF_n^{(n-5)-}$ type. As can be seen from Table 1, a frequency of 583 cm^{-1} is located between the positions of the strongest IR bands assigned to NbF_7^{2-} (555 cm^{-1}) and NbF_6^- (602 cm^{-1}) in other molten fluoride media.[5,6] Thus, it is not possible from IR spectra alone to decide which of these two complexes is present. However, on the basis of Raman spectra from previous work,[2] we suggest that NbF_7^{2-} is formed in FLINAK melts.

An explanation for the displacement of the strongest IR band toward higher frequencies, when going from the solid salt (K_2NbF_7) over solidified solutions to molten solutions, could be that the NbF_7^{2-} anion becomes less distorted. This view is supported by the feature that the IR-forbidden symmetric stretch vibration ν_1 (632 cm^{-1}) appears in the spectrum of the pure salt but is not seen in the IR spectrum of the diluted molten solution.

Oxofluoro Complexes of Nb(V). From Table 2 it appears that $NbOF_n^{(n-3)-}$ type complexes have IR bands that can be divided into two types: (1) lower frequency bands in the region 500−600 cm^{-1} due to Nb−F vibrations and (2) higher frequency bands near 910 cm^{-1} arising from Nb═O double bonds. When an oxide, up to an O/Nb molar ratio of 1, is added to the FLINAK−K_2NbF_7 system, we observe IR bands that also fall within these regions. Therefore, we assign the bands at 535 cm^{-1} and around 910 cm^{-1} in the IR spectra of the solidified melts (Figure 2) to $NbOF_n^{(n-3)-}$ type complexes. The vibrational frequencies for different $NbOF_n^{(n-3)-}$ complexes do not differ much, so the observation of bands near 910 cm^{-1} do not give much possibility to distinguish between the different kinds of monooxofluoro complexes. Except for the $K_2NbOF_5 \cdot H_2O$ salt, which, according to Keller,[11] has a band at 932 cm^{-1}, the rest have vibrations at frequencies between 905 and 917 cm^{-1}. The presence of perhaps three bands in this region in the spectra of the samples with no or small amounts of oxide added (spectra A and B of Figure 2) may indicate that several salts containing monoxofluoro complexes coexist. On the other hand, a splitting of the Nb═O vibrations from one such complex could also play a role. Furthermore, it may be noted that we see a band at 932 cm^{-1}, i.e., at the same frequency as the strongest band[11] of $K_2NbOF_5 \cdot H_2O$. For the solid samples with more oxide present it seems that only one monooxofluoro complex, characterized by IR bands at 910 and 535 cm^{-1}, is present. If we turn to the lower frequency bands, Agulianskii and Bossanova[6] suggested that a band found at approximately 560 cm^{-1} in the IR spectrum of molten K_2NbF_7, which had been in contact with the atmosphere, could arise from the $NbOF_5^{2-}$ complex. Pausewang et al.[15] found strong IR bands for the same ion at 525 and 536 cm^{-1} in the spectra of solid $CsNbOF_5$ and $RbNbOF_5$, respectively. In the same work solid $(NH_4)_3NbOF_6$ was reported to show low-frequency IR bands due to Nb−F vibrations in the $NbOF_6^{3-}$ complex at 464 cm^{-1} (strong) and 533 cm^{-1} (medium). Unfortunately, 464 cm^{-1} is below the frequency region, which has been measured in the present work. Considering intensities of the bands, we observe that our 910 cm^{-1} band is much more intense than the 535 cm^{-1} band (spectra C and D of Figure 2). For $NbOF_5^{2-}$ in rubidium and cesium salts[15] the intensities of the bands near 910 and 530 cm^{-1} are of the same magnitude. Further, we do not observe bands similar to the medium-intensity vibrations near 580 cm^{-1} reported for $NbOF_5^{2-}$ in the Rb and Cs salts. The band positions and intensity ratios observed in the present work seems to fit the ones[15] of the $NbOF_6^{3-}$ ion in $(NH_4)_3NbOF_6$. This could point to the presence of this complex in our solid samples. However, it is not safe on the basis of IR spectra alone to finally determine the nature of the monooxofluoro complexes present in our solidified melts. We will return to this question in the paragraph about Raman spectra.

Concerning the melts, the bands at 920 and 592 cm^{-1} both grow when oxide is added up to an O/Nb molar ratio of 1. In light of what has been said above we assign these bands to the presence of $NbOF_n^{(n-3)-}$ complexes. No other band due to niobium monooxofluoro complexes seems to be present in the melt spectra.

Keller[11] registered Raman bands near 600 cm^{-1} (presumably an A_1 or E vibration) for the $NbOF_5^{2-}$ complex both in the solid state and in HF solution. If we assume that the 600 cm^{-1} vibration also is IR-active, which is the case for both A_1 and E type vibrations under C_{4v} symmetry (such as $NbOF_5^{2-}$), it seems likely that the 592 cm^{-1} band arises from $NbOF_5^{2-}$ rather than from $NbOF_6^{3-}$, since the latter ion should have no vibrations[2,15] at frequencies near 600 cm^{-1}. We have previously[2] observed bands at 921 and 583 cm^{-1} due to $NbOF_5^{2-}$ in the Raman spectrum of a melt with a composition similar to that in Figure

---

(14) Peacock, R. D.; Sharp, D. W. A. *J. Chem. Soc.* **1959**, 2762.

(15) Pausewang, G.; Schmitt, R.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1974**, *408*,

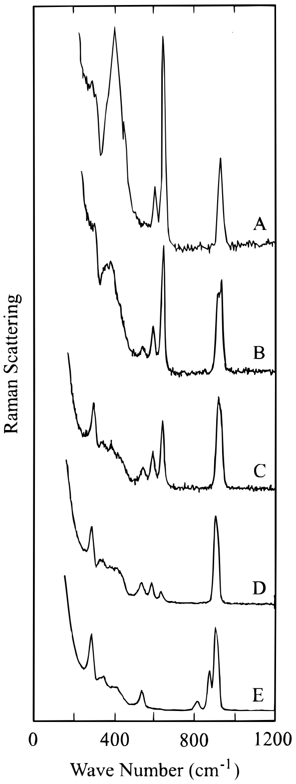

Figure 5. Room-temperature Raman spectra of solidified FLINAK−K_2NbF_7 (2.7 mol %) melts with various amounts of Na_2O added. The amounts of oxide added were (in mol %) (A) 0.0, (B) 0.5, (C) 1.0, (D) 1.5, and (E) 2.4.

3C. These frequencies are very close to the ones in the IR spectrum, bringing further support to our assignment.

The two bands at 820 and 880 cm^{-1} that we observe both in the solid state and in the melt, where the O/Nb ratio is near 2, compare well with frequencies of $NbO_2F_4^{3-}$ ions of C_{2v} symmetry observed previously both in Raman[2] and in IR spectra.[16,17] It is therefore obvious to assign these bands to stretch vibrations of the NbO_2 group in this complex.

Raman Spectra. From Figure 5 it can be seen how additions of oxide (Na_2O) to a FLINAK−K_2NbF_7 (3 mol %) mixture affect the Raman spectra of the solidified melts.

The spectrum of the sample with no added oxide shows bands at 930, 910 (shoulder), 640, 595, 392, and 300 (shoulder) cm^{-1} (Figure 5A). When oxide is added, the bands at 640 and 392 cm^{-1} diminish, the bands at 925, 910, and 595 cm^{-1} grow, and simultaneously a new band at 545 cm^{-1} shows up (spectra B−D of Figure 5). For an O/Nb molar ratio of approximately 1 (Figure 5E) two new bands at 880 and 820 cm^{-1} appear. The band at 925 cm^{-1} gradually disappears when oxide is added, and it has completely vanished at an O/Nb ratio of 0.56 (Figure 5D). The weak bands (or shoulders) that appear on some of the spectra in the vicinity of 400 cm^{-1} have previously[7] been ascribed to spurious bands due to the Pyrex glass ampules that we use as containers.

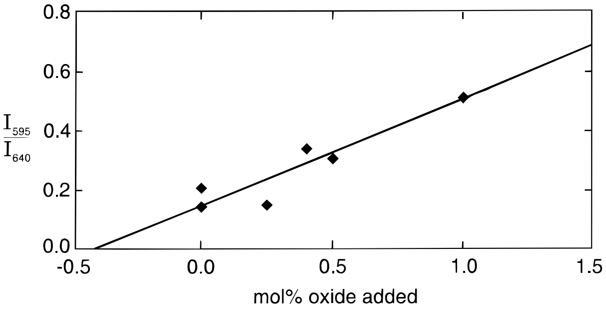

Figure 6. Intensity ratios of Raman bands at 595 and 640 cm^{-1} against added oxide for solidified FLINAK−K_2NbF_7 (2.7 mol %)−Na_2O melts.

As can be seen from Table 3, NbF_7^{2-} and NbF_6^{-} in solids have characteristic Raman bands at 631 and 683, respectively.[2,11] These are due to symmetric stretch vibrations (ν_1), and will give rise to intense bands in the Raman spectra. The band that we observe in the 600−700 cm^{-1} region (at ca. 640 cm^{-1}) decrease in intensity with increasing oxide content. This makes us believe that the 640 cm^{-1} band is a ν_1 vibration from niobium(V) fluoro complexes. The frequency seems to indicate that the complex is NbF_7^{2-}. The minor shift (9 cm^{-1} compared to NbF_7^{2-} in pure K_2NbF_7) is probably due to the change of surroundings when K_2NbF_7 is dissolved in FLINAK (e.g., presence of Li^+ and Na^+). It should be noted that the bands at 392 and 282 cm^{-1} in the Raman spectra of the solidified melts also compare rather well with frequencies of NbF_7^{2-} in K_2NbF_7 crystals.[2,11]

The presence of bands at 925 and 910 cm^{-1} in the solidified melts clearly indicate the occurrence of terminal niobium−oxygen double bond vibrations (see Table 3). As mentioned before, bands in this region do not depend much on the type of $NbOF_n^{(n-3)-}$ complex present. It seems like the 910 and 545 cm^{-1} vibrations grow simultaneously (spectra B−D of Figure 5) and that the decreases in intensities of the 925 and 595 cm^{-1} bands are also coupled (spectra C and D of Figure 5). Keller[11] assigned Raman bands near 600 cm^{-1} to the $NbOF_5^{2-}$ complex, and we have previously[2] related a vibration at 545 cm^{-1} in the Raman spectrum of solid K_3NbOF_6 to the $NbOF_6^{3-}$ ion (see Table 3). Thus, we ascribe the bands at 910 and 545 cm^{-1} to vibrations in $NbOF_6^{3-}$ and those at 930 and 595 cm^{-1} to vibrations in the $NbOF_5^{2-}$ complex.

The presence of bands in the 900 cm^{-1} region in the spectrum of the sample, without added oxide (Figure 5A), indicates that an oxide impurity in the salts during the mixing process has

Table 3. Raman Vibrational Frequencies of Nb(V) Fluoro- and Oxofluoro Complexes in Different Media

		vibrations (cm^{-1})		
species	medium	$\nu_{Nb=O}$	ν_{Nb-F}	reference
NbF_7^{2-}	K_2NbF_7, solid		791, 631, 388, 275	2
NbF_7^{2-}	K_2NbF_7, solid		782, 630, 388	11
NbF_6^{-}	$CsNbF_6$		683, 562, 280	11
$NbF_n^{(n-5)-}$	FLINAK, solidified melt		640, 392, ∼300	this work
$NbOF_5^{2-}$	$K_2NbOF_5 \cdot H_2O$, solid	935	600, 295	11
$NbOF_5^{2-}$	HF solutions	920−935	595, 290	11
$NbOF_n^{(n-3)-}$	FLINAK, melt	921	583, 307	2
$NbOF_6^{3-}$	K_3NbOF_6, solid	910	545, 295	2
$NbOF_n^{(n-3)-}$	FLINAK, solidified melt	925, 910	595, 545, 295	this work
$NbO_2F_4^{3-}$	FLINAK, melt	878, 815	360, 284	2
$NbO_2F_4^{3-}$	FLINAK, solidified melt	880, 820		this work

Table 4. Typical Vibrational Frequencies of Nb(V) Fluoro and Oxofluoro Complexes[a]

complex	vibrations (cm^{-1})	typical region
NbF_6^-	670−683(ν_1,R), 601−602(ν_3,IR), 562(ν_2,R), 280(ν_5,R)	670−683(R), 601−602(IR)
NbF_7^{2-}	782−791(R), 630−640($\nu_{Nb-F,ss}$,R), 549−565(IR), 388−392($\nu_{Nb-F,as}$,R), 330(IR), 306(IR), 275(R)	630−640(R), 549−565(IR)
$NbOF_5^{2-}$	905−935($\nu_{Nb=O}$, R and IR), 576−592(IR), 583−600(R), 525−536(IR), 295−307(R)	583−600(R), 576−592(IR)
$NbOF_6^{3-}$	909−917(R and IR), 545(R), 533−535(IR), 464(IR), 295(R)	545(R), 464(IR)
$NbO_2F_4^{3-}$	878−894($\nu_{NbO2,ss}$, R and IR), 809−820($\nu_{NbO2,as}$, R and IR), 513(IR), 360(R), 284(R)	878−894(R,IR), 809−920(R,IR)

[a] Legend: R, Raman-active; IR, infrared-active.

reacted with the niobium fluoro complexes to form oxofluoro complexes. From a plot of internal, i.e., within the same spectrum, intensity ratios of selected bands due to fluoro complexes and oxofluoro complexes vs the amount of added oxide it may be possible to determine the magnitude of this oxide impurity oxide, as was the case for FLINAK−K_2TaF_7 mixtures.[7] If we apply the intensity of the band at 640 cm^{-1} as the denominator (Nb−F from fluoro complexes) and the intensity of the band at 595 cm^{-1} as the numerator (Nb−F from oxofluoro complexes), a plot as shown in Figure 6 can be produced. For low values of the applied intensity ratio (i.e., minor concentrations of oxofluoro complex) a linear relation may give a reasonable fit. From the plot in Figure 6 it can be seen that this is in fact the case for additions of oxide up to 1 mol %. The intercept with the abscissa is near −0.4, which implies that approximately 0.4 mol % oxide was already present in the FLINAK−K_2NbF_7 mixture from the start. If we instead apply the intensity of the 910 cm^{-1} band as the denominator, a similar value is obtained, although the magnitude in this case is somewhat more uncertain, since the 910 cm^{-1} band is overlapped to some extent by other bands in the same region.

Conclusions

It has been demonstrated that our diamond window cell is suited for infrared spectroscopic measurements on molten fluorides up to temperatures of 750 °C.

On the basis of the discussions in the previous sections, we conclude that NbF_7^{2-} ions exist in FLINAK−K_2NbF_7 melts with no or only small amounts of oxide present. With increasing oxide content (O/Nb molar ratio up to 1) the NbF_7^{2-} complex disappears and monooxo fluoro complexes are formed according to

$$NbF_7^{2-} + O^{2-} \rightarrow NbOF_n^{(n-3)-} + (7-n)F^- \qquad (2)$$

In the molten state $NbOF_5^{2-}$ seems to be the only monooxofluoro complex formed, whereas vibrations from both $NbOF_5^{2-}$ and $NbOF_6^{3-}$ appear in the vibrational spectra of the solidified melts.

The presence of $NbO_2F_4^{3-}$ complexes in FLINAK melts with an O/Nb molar ratio around 2 and is confirmed by IR spectroscopy, which shows the same vibrations as in the Raman spectrum.[2]

From the previous discussion, it seems that the vibrational frequencies for a certain complex differ somewhat according to the cationic surroundings. If we, however, compare the values obtained in this work with those given in the literature, it looks like a specific vibration falls within a certain frequency region. In Table 4 these regions are listed for the different fluoro- and oxofluoro complexes of Nb(V). In addition, this table presents the most characteristic vibrations for each specific complex. By use of the table, it should be easily possible to recognize the different niobium-containing species in FLINAK.

Finally we would like to point out that the use of a plot (Figure 6) of the intensity ratio of the Raman bands at 600 and 640 cm^{-1} (from solidified melts) vs added oxide makes it possible to determine the initial oxide content in a FLINAK solvent. Hence, K_2NbF_7, when added in known amounts, can be used as a probe for oxide impurities in FLINAK molten salt baths.

Acknowledgment. Thanks are expressed to the Danish Council for Technical Research, which has supported this work financially. Further thanks are due to Mette Rosén for assistance with the solid-state IR measurements and preparation of the chemicals.

IC991057T

---

(16) Pausewang, G.; Rüdorf, W. *Z. Anorg. Allg. Chem.* **1969**, *364*, 69.
(17) Dehnicke, K.; Pausewang, G.; Rüdorf, W. *Z. Anorg. Allg. Chem.* **1969**, *366*, 64.