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# Electronic Absorption Spectra of Niobium Species in Halide Melts

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The results of spectroscopic studies of Nb anodic dissolution, dissolution of $NbCl_5$ and reaction of various niobium oxides with HCl in different chloride melts at 450-750$^0$C are presented. Nb(III) species, $NbCl_6^{3-}$, is the major product of niobium anodic dissolution at current densities up to 40 mA/cm$^2$. Addition of $NbCl_5$ to alkali chloride melts predominantly leads to the formation of Nb(V) species, $NbCl_6^-$. Upon increasing Nb(V) concentration $NbCl_6^-$ tend to decompose to Nb(IV) and $Cl_2$. Reaction of NbO and $NbO_2$ with HCl proceeds *via* an intermediate oxygen-containing Nb(IV) complexes. Oxygen-free Nb(IV) ions, $NbCl_6^{2-}$, were obtained by exchange reactions between metallic niobium and melts containing Bi(III), Ag(I) or Ni(II) chloro-ions. Electroreduction of Nb(III) on a tungsten working electrode below -1.45 V *vs.* $Cl_2/Cl^-$ led to the formation of metallic niobium, no evidence of intermediate reduction products was obtained.

## Introduction

Molten salts have a wide range of unique properties that make them particularly useful in many areas of modern technology. From the fundamental point of view understanding speciation of transition metals in halide melts leads to deeper understanding the nature of complex ion formation in ionic media. The most interesting and direct information about the structure of chloride melts can be procured from *in situ* electronic absorption spectroscopy measurements. In case of niobium the information obtained can be applied for optimizing industrial scale niobium production and refining.

Available data concerning the oxidation state of niobium and coordination properties of its species in molten halides are incomplete and often contradictory. There is no doubt about the existence of niobium(IV) and (V) species in molten niobium-containing alkali chloride based mixtures. The only question concerns the stability of $NbCl_6^-$ complex ions under an inert atmosphere. The other disputed moment involves the value of the lowest niobium oxidation state stable in chloride melts. According to the different points of view niobium-containing melts held in contact with the metal can contain $Nb^{2+}$, $Nb^{3+}$ or $Nb^{4+}$ ions (1).

Electronic absorption spectra (EAS) of dissolved oxygen-free niobium species were measured only in the eutectic mixture of sodium and cesium chlorides (2, 3). Spectra recorded after $NbCl_5$ dissolution contain only the low energy edge of an intense charge

transfer band at 400-450 nm (2, 3). According to the Raman and NMR spectroscopy measurements (4 – 6) $NbCl_6^-$ complex ions are formed during dissolution of niobium pentachloride under an inert atmosphere. The information about speciation, structure and coordination of lower oxidation state niobium complexes in chloride melts is more contradictive. Maslov and Vasin (2) reported that niobium(IV) ions are the intermediate products formed during niobium metal chlorination and the absorption maximum of this species lies at *ca.* 450-500 nm. Bachtler *et al.* (3) studied niobium tetrachloride dissolution and reported the broad absorption maxima of Nb(IV) complexes at 500-830 nm with a shoulder at *ca.* 730 nm. Voyiatzis *et al*. (5) indicated that according to the Raman spectroscopy measurements $NbCl_6^{2-}$ complex ions were formed upon reduction of niobium(V) chloride species by niobium or silver metal. Formation of paramagnetic niobium(IV) ions due to reaction between Nb and (Li-K)$Cl_{eut}$-$NbCl_5$ melt was also detected using $^{93}$Nb NMR spectroscopy (6). Some authors showed that niobium(III) ions, $NbCl_6^{3-}$, with absorption bands at 470, 625 and 1000 nm, were the only product of niobium metal anodic dissolution in fused alkali chlorides at low current densities (2, 7). Similar EAS were reported by Bachtler *et al.* after dissolution of $NbCl_2$, $NbCl_3$, $Na_4Nb_6Cl_{18}$ and a mixture of $NbCl_5$ and metallic niobium in (Na-Cs)$Cl_{eut}$ (7). Despite the similar character of the abovementioned spectra they were assigned to the complex ions of $Nb^{2+}$, $Nb^{3+}$ and polynuclear $Nb_6Cl_{12}^{n+}$ (3).

The speciation of oxygen-containing niobium chlorides in high-temperature melts is also unclear. It was shown that addition of oxygen species to molten CsCl-$NbCl_5$ mixture leads to the formation $NbOCl_5^{2-}$ complex ions and, at high niobium concentrations, $NbOCl_4^-$ complexes may also be formed (8). The EAS of niobium(V)-containing melts contain only the low energy edge of the charge transfer band (3). The spectra obtained by Bachtler *et al.* (3) after dissolving mixtures of $NbCl_4$ and $Na_2O$, $NbCl_3$ and $Na_2O$, or $NbOCl_3$ and $Nb_{met}$ in (Na-Cs)$Cl_{eut}$ were similar to each other and represented superposition of several absorption bands. Unfortunately the obtained absorption maxima were not assigned to specific niobium ions (3).

Thus, the existing experimental information concerning niobium speciation and coordination properties in alkali chloride based melts is incomplete and contradictive especially in the case of lower niobium oxidation state species and a further investigation of this problem is required.

In the present work we conducted spectroscopic studies of anodic dissolution of metallic niobium, dissolution of niobium pentachloride and chlorination of various niobium oxides (NbO, $NbO_2$, $Nb_2O_5$) by HCl in LiCl-KCl and NaCl-CsCl eutectics, and NaCl-KCl equimolar melts at 450-750 $^0$C. In a separate series of experiments the speciation of niobium was studied using spectroelectrochemistry and exchange reactions between niobium metal and bismuth, silver or nickel ions in NaCl-KCl based melts. Oxidimetric titration was employed to determine an average oxidation state of niobium in melt samples rapidly quenched under inert conditions (9).

## Experimental

The EAS were recorded between 190 and 1100 nm using a custom-built set up based on a fiber optic spectrophotometer AvaSpec-2048FT-2-SPU (Avantes). The samples

were heated in an optical furnace (Instron SFL model 1720), capable of achieving 1100 $^0$C. An Autolab PGSTAT 302N potentiostat/galvanostat was used to control the current passing through the cell or the red-ox potential of the system.

The details of the spectroscopy experimental procedures and preparation of solvent-salts were described elsewhere (10, 11). All preliminary manipulations with oxygen and moisture sensitive compounds were carried out in an argon filled dry box with strictly controlled moisture and oxygen content (MBraun).

Niobium-containing electrolytes were prepared by dissolving anhydrous $NbCl_5$ (99 %, Aldrich). In one series of experiments anodic dissolution of niobium metal (99.8 %, ChMz,) was studied using both galvanostatic and potentiostatic methods. To determine possible effect of oxygen species on niobium speciation the reactions of niobium oxides ($Nb_2O_5$, >99 % Reahim, $NbO_2$, and NbO, both 99.9 % Aldrich) with hydrogen chloride were investigated in molten alkali chloride mixtures.

*In situ* spectroscopy measurements were performed in NaCl-KCl based melts during electrochemical reduction and oxidation of niobium species. Glassy carbon rod, tungsten wire or niobium plate were used as working electrodes. A molybdenum wire dipped into NaCl-CsCl-$PbCl_2$ melt served as a counter electrode and silver wire in NaCl-CsCl-AgCl (1 mol. %) melt acted as the reference electrode.

In a separate series of experiments the speciation of niobium was studied using exchange reactions of metallic niobium with bismuth, silver or nickel ions in NaCl-KCl melts. Starting NaCl-KCl-$BiCl_3$ melt was prepared by chlorinating metallic bismuth (>98 %, Reahim) by chlorine gas in the molten salt mixture. Nickel and silver chloride containing melts were prepared by dissolving anhydrous nickel chloride (98 %, Aldrich) and silver chloride (99 %, Aldrich), respectively, in NaCl-KCl with HCl gas bubbled through the electrolyte for two hours to eliminate traces of absorbed moisture.

The concentration of niobium and its average oxidation state in melts samples were determined by chemical analysis of quenched melt samples (9, 12).

## Results and discussion

Dissolution of Niobium Pentachloride in Chloride Melts

Dissolution of niobium pentachloride in molten alkali chlorides was studied in NaCl-KCl, NaCl-CsCl and LiCl-KCl based melts and the progress of the dissolution was followed by in situ spectroscopy measurements. In most instances the spectra contained only the low energy edge of the charge transfer band. The oxidation state of niobium in quenched melt samples of the obtained electrolytes was close to five (Table I). This result is in a good agreement with the literature data and indicates that $NbCl_6^-$ species constituted the main product of this reaction (2-6).

At relatively high niobium concentrations in the melt $NbCl_6^-$, however, partly decomposed yielding $NbCl_6^{2-}$ and chlorine gas:

$$NbCl_6^- + Cl^- \rightarrow NbCl_6^{2-} + \frac{1}{2} Cl_2 \quad [1]$$

**TABLE I.** $NbCl_5$ dissolution in molten alkali chlorides.

| Exp. No | Melt composition | $NbCl_5$ mass, g | Tempe-rature, $^0C$ | Mass of salt, g | Final melt characteristics | | |
|---|---|---|---|---|---|---|---|
| | | | | | $\omega_{Nb}$,wt. % | $n_{Nb}$ | Colour of quenched melt |
| 1 | NaCl-KCl | 0.032 | 750 | 5.506 | 0.14 | 4.95 | white |
| 2 | NaCl-KCl | 0.084 | 750 | 5.450 | 0.43 | 4.85 | white |
| 3 | NaCl-KCl | 0.794 | 750 | 8.309 | 1.20 | 4.75 | gray-yellow |
| 4 | NaCl-KCl | 1.042 | 750 | 8.054 | 3.81 | 4.5 | purple |
| 5 | NaCl-CsCl | 1.012 | 550 | 7.477 | 3.20 | 4.85 | yellow |
| 6 | NaCl-CsCl | 0.985 | 750 | 7.842 | 3.17 | 4.70 | yellow |
| 7 | NaCl-CsCl | 0.101 | 750 | 5.025 | 0.57 | 4.95 | white |
| 8 | LiCl-KCl | 0.170 | 450 | 5.183 | 0.39 | 4.9 | pale-yellow |
| 9 | LiCl-KCl | 0.200 | 600 | 5.184 | 0.46 | 4.8 | pale-yellow |
| 10 | LiCl-KCl | 0.075 | 750 | 5.180 | 0.15 | 4.75 | pale-yellow |
| 11 | LiCl-KCl | 1.008 | 750 | 8.281 | 0.93 | 4.6 | purple |

Average oxidation state of niobium in the melts obtained after dissolving $NbCl_5$ in NaCl-KCl mixture at 730-750 $^0C$ decreased from 4.95 to 4.5 upon increasing niobium concentration from 0.14 to 3.8 wt. %. In (Na-Cs)$Cl_{eut}$ the effect of increasing total niobium concentration in the melt on average oxidation state of niobium was less pronounced, and in the melt containing 3.2 wt. % of Nb the average oxidation state of niobium was 4.7 at 750 $^0C$ and 4.85 at 550 $^0C$ (Table I). Similar results were obtained in the lithium-potassium chlorides eutectic mixture, the average oxidation state of niobium at 0.4 wt. % Nb and 450 $^0C$ was 4.9, whereas at 0.9 wt. % Nb and 750 $^0C$ this value decreased to 4.6. Such dependence of niobium oxidation state on concentration has been observed earlier and can be explained by thermodynamic instability of niobium pentachloride at high temperatures (13-16). These findings agree very well with the results of recent studies of Nb(V) behavior in the ionic liquids (17). Babushkina *et al.* reported that in a mixture of 80% 1-butyl-1-methylpyrrolidinium chloride and 20% $NbCl_5$ over 70% niobium were present as Nb(V) at room temperature but only 25% at *ca.* 110 $^0C$ (17). Decreasing concentration of free $Cl^-$ anions resulted in stabilizing Nb(V) chloro-species (17). Using standard procedures of HSC Chemistry software we calculated equilibrium concentrations of different niobium chlorides and chlorine gas at various temperatures when $NbCl_5$ was introduced in an inert system, Figure 1, (18). Rising temperature leads to higher concentration of niobium tetrachloride in agreement with our previous observations. Figure 1 reflects the results calculated for the neat compounds. Chloride melts have high chloride ion concentration and under such conditions the equilibrium of the reaction [1] will be shifted to the right resulting in higher concentration of Nb(IV) species in molten chlorides compare to the gas phase. Increasing stability of Nb(V)-containing melts with average radius of salt-solvent cation can be explained by substitution of potassium ions by cesium (having lower ionic momentum) in the second coordination sphere. This substitution results in stabilizing complexes having the metal in higher oxidation state (19).

The presence of Nb(IV) species after dissolving $NbCl_5$ in the melt was detected spectroscopically in NaCl-KCl equimolar and LiCl-KCl eutectic mixtures at 750 $^0C$ after resolving the final spectra into overlapping Gaussian bands. For example, in NaCl-KCl based melt containing 0.43 wt. % Nb, the average oxidation state of niobium, determined oxidimetrically, was 4.85 and the position of the resolved maximum, at 16400 $cm^{-1}$ (610 nm), is close to that found for $NbCl_6^{2-}$ ions (see later). The diffuse reflectance spectra of

quenched concentrated niobium-containing chloride electrolytes (Figure 2) also confirm the presence of niobium ions in the oxidation state below five.

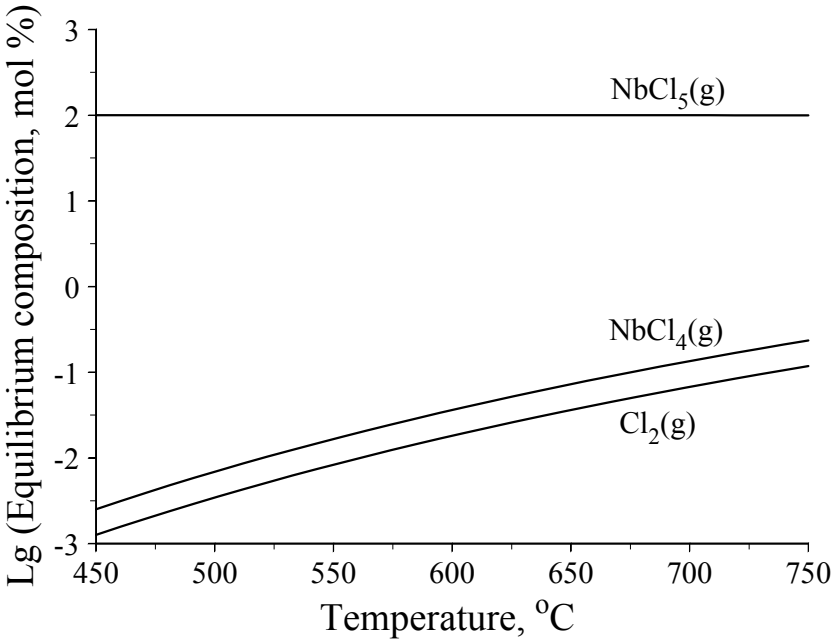



Figure 1. Results of thermodynamic modeling of niobium pentachloride stability at different temperatures.

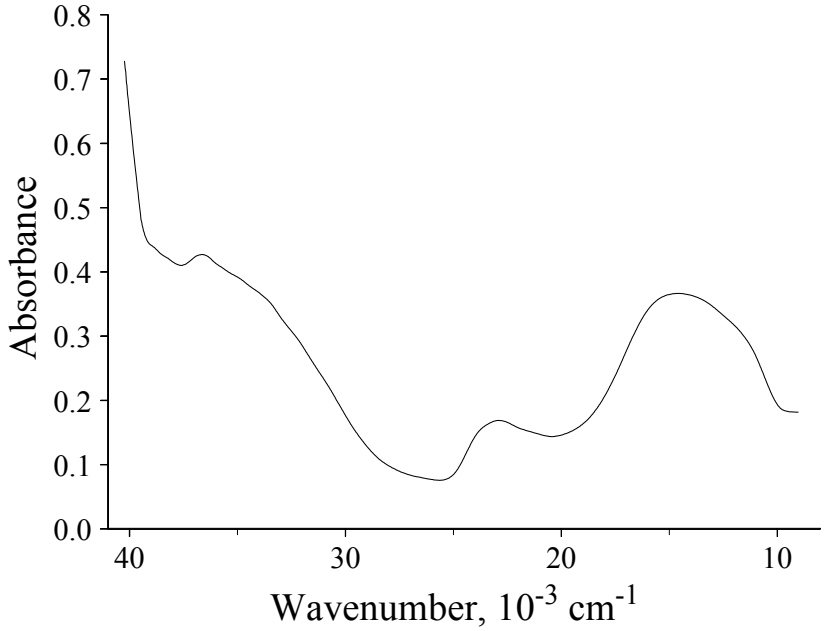
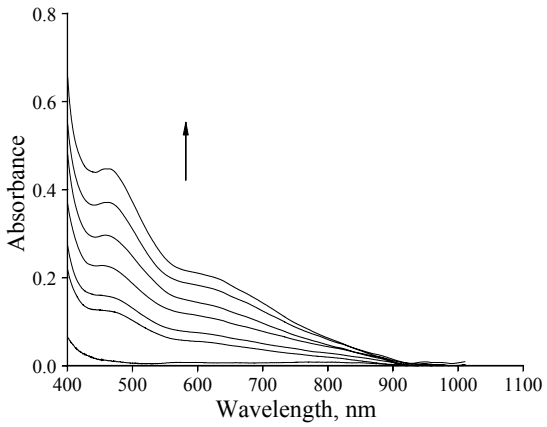



Figure 2. Diffuse reflectance spectra of quenched melt sample obtained after dissolving $NbCl_5$ in NaCl-KCl melt at 750 $^0$C ($\omega_{Nb}$=3.8 wt. %, $n_{Nb}$=4.5).

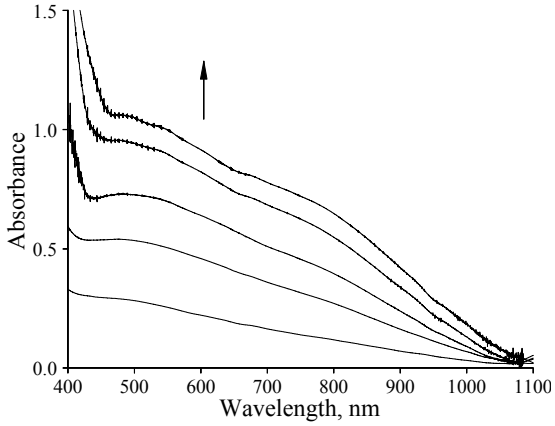
Anodic Dissolution of Niobium Metal in Chloride Melts

Typical examples of the absorption spectra recorded during anodic dissolution of niobium metal in a variety of chloride melts are presented in Figure 3. Increasing current

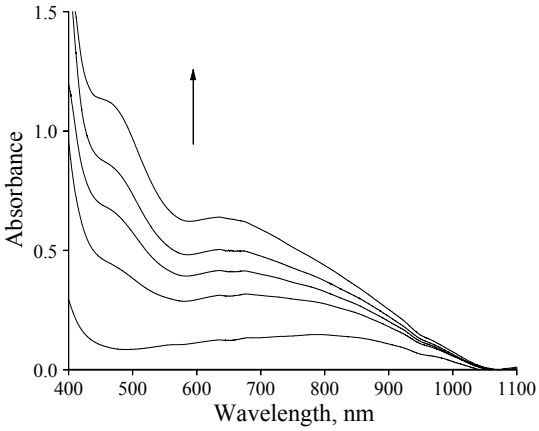
density (up to 40 mA/cm$^2$), changing melt composition and temperature did not influence the spectral picture. Within the accuracy limits of the oxidimetric method it was found that the major product of the anodic dissolution of metallic niobium in chloride melts under given conditions were Nb(III) species (Table II). The spectral curves recorded in (Na-Cs)$Cl_{eut}$ agree well with reported earlier for the melts obtained after anodic dissolution of niobium metal, its reaction with $NbCl_5$, and dissolution of $NbCl_2$, $NbCl_3$ and $Na_4Nb_6Cl_{18}$ (2,3). Taking into account literature data and the results of oxidimetric analysis we conclude that anodic dissolution of niobium metal in chloride melts at low current densities leads to the formation of niobium(III) species. Based on the number and position of the absorption maxima we assume the octahedral structure of niobium(III) chloro-complexes formed. Absorption bands at *ca*. 480 and 700 nm can be attributed to the spin-allowed d-d transitions in $NbCl_6^{3-}$ species: $^3T_{1g} \rightarrow {}^3T_{1g}(P)$ and $^3T_{1g} \rightarrow {}^3T_{2g}$, respectively.



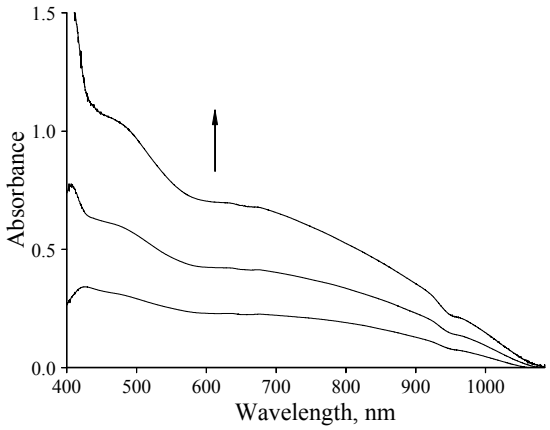

(Li-K)$Cl_{eut}$, 600 $^0$C, 0.01 A/cm$^2$




(Na-Cs)$Cl_{eut}$, 600 $^0$C, 0.01 A/cm$^2$




(Na-K)$Cl_{eqm}$, 750 $^0$C, 0.02 A/cm$^2$




(Na-Cs)$Cl_{eut}$, 750 $^0$C, 0.01 A/cm$^2$

Figure 3. EAS obtained during niobium anodic dissolution in different molten chlorides using galvanostatic regime.

In a special series of experiments anodic dissolution of niobium in NaCl-KCl equimolar mixture was carried out at 750 $^0$C under potentiostatic conditions. Initial potential of niobium anode (corrosion potential) was equal to -1.5÷-1.6 V (*vs.* chlorine reference electrode). During potentiostatic anodic dissolution we varied the applied potential from -1.35 to -1.15 V. The EAS recorded (Figure 4) were similar to the spectra

obtained when niobium was dissolved at a constant current rather than fixed potential (Figure 3). Therefore we conclude that at potentials below -1.15 V the anodic dissolution of niobium proceeds in one three-electron step. Unfortunately we were not able to perform the anodic dissolution experiments in spectroscopy cells at higher electrode potentials due to geometrical limitations, the diaphragm we employed to separate the cathode from the bulk of the melt did not conduct high currents required.

**TABLE II.** Niobium anodic dissolution in galvanostatic mode. Current density 10-40 mA/cm$^2$.

| Exp. | Experiment conditions | | | Final melt characteristics | | |
|---|---|---|---|---|---|---|
| No | Melt composition | T, $^0$C | Mass of salt, g | $\omega_{Nb}$,wt. % | $n_{Nb}$ | Colour of quenched melt |
| 1 | NaCl-CsCl | 600 | 8.217 | 0.112 | 3.1 | blue |
| 2 | NaCl-CsCl | 750 | 6.532 | 0.066 | 3.2 | blue |
| 3 | LiCl-KCl | 450 | 4.902 | 0.244 | 3.1 | violet |
| 4 | LiCl-KCl | 600 | 6.147 | 0.142 | 2.9 | grey |
| 5 | LiCl-KCl | 750 | 4.935 | 0.207 | 3.0 | grey |
| 6 | NaCl-KCl | 750 | 5.628 | 0.162 | 3.2 | grey |

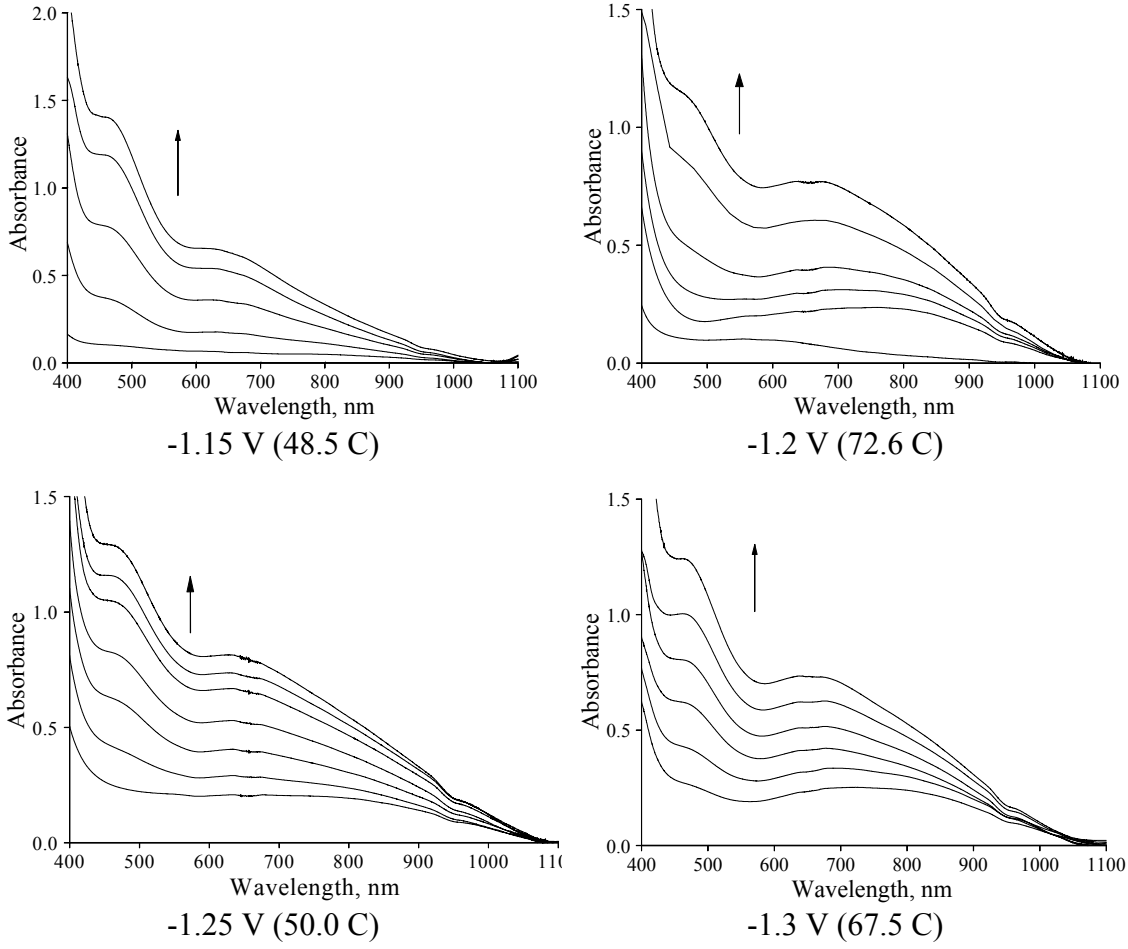



Figure 4. EAS measured during potentiostatic anodic dissolution of niobium metal in chloride melts (potential value and amount of electricity passed given for each set of data).

## Chlorination of Niobium Oxides in Chloride Melts

*In situ* spectroscopy measurements were applied to study reactions of different niobium oxides with hydrogen chloride in alkali chloride melts. When niobium

pentoxide was chlorinated, the average oxidation state of niobium in the obtained melt was equal to five and the EAS contained only the low energy edge of a charge transfer band indicating that only niobium ions having $d^0$-electronic configuration, *i.e.* $Nb^{5+}$, were formed. According to the thermodynamic calculations the reaction between $Nb_2O_5$ and HCl at high temperatures leads to formation $NbOCl_3$. Taking in account our experimental results, thermodynamic calculations and literature data concerning the structure of oxygen-containing niobium chloride species in fused salts we assume that $NbOCl_5^{2-}$ complex ions were formed in chloride melts during the reaction of niobium(V) oxide and hydrogen chloride.

Studying the reaction of NbO and $NbO_2$ with HCl in molten alkali metal chlorides resulted in somewhat more complicated picture. Thermodynamic calculations also predict that niobium oxychloride $NbOCl_3$ should be the only niobium-containing reaction product formed when gaseous HCl is taken in excess. When amount of HCl is less than required by stoichiometry for the formation $NbOCl_3$, niobium(IV) oxychloride can be formed as a byproduct. Interestingly, that formation of niobium oxygen-free chlorides by reacting NbO or $NbO_2$ with HCl is thermodynamically forbidden. When the chlorination of niobium(II) or (IV) oxide by HCl in fused alkali chlorides was followed spectroscopically we initially observed the appearance and growth of an absorption band at *ca.* 800 nm (Figure 5a). Further chlorination led to decreasing this band and shifting the edge of the charge transfer band to the higher wavelengths (Figure 5b). The spectra contained an isosbestic point at 540 nm, Figure 5b, indicating that the total concentration of niobium in the melt remained unchanged during this stage of the process. Similar spectral picture was observed for both $NbO_2$ and NbO under different experimental conditions.

From the analysis of all available data we suppose that chlorination of $NbO_2$ and NbO by HCl gas involves two following stages:

$$NbO_2 + 2\ HCl = NbOCl_2 + H_2O \quad [2]$$
$$2\ NbOCl_2 + 2HCl = 2\ NbOCl_3 + H_2 \quad [3]$$
$$NbO + 2\ HCl = NbOCl_2 + H_2 \quad [4]$$
$$2\ NbOCl_2 + 2HCl = 2\ NbOCl_3 + H_2 \quad [5]$$

Further experiments were performed to ascertain the nature and characterize the intermediate product of chlorination. The spectra recorded were similar for different temperatures and various types of alkali chloride mixtures (Figure 6). The results of oxidimetric titrations indicate predominant formation of niobium(IV) species (Table III). Deviations of oxidation state to the higher values result from the partial oxidation of Nb(IV) into Nb(V) by HCl. Oxidation state values below four, obtained in the case of NbO chlorination, most likely were caused by niobium(II) oxide particles captured during melt sampling procedure and trapped in the quenched melt samples subjected to the analysis.

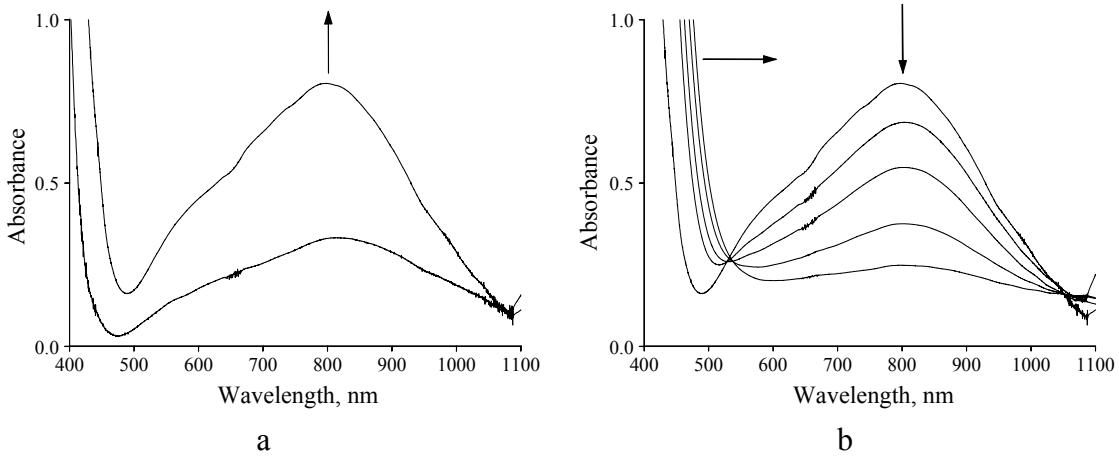



Figure 5. Spectroscopic study of $NbO_2$ chlorination by HCl in $(Na\text{-}Cs)Cl_{eut}$ at 600 $^0$C (a – phase of initial increase of absorption maxima at 800 nm, b – consecutive stage of peak decrease).

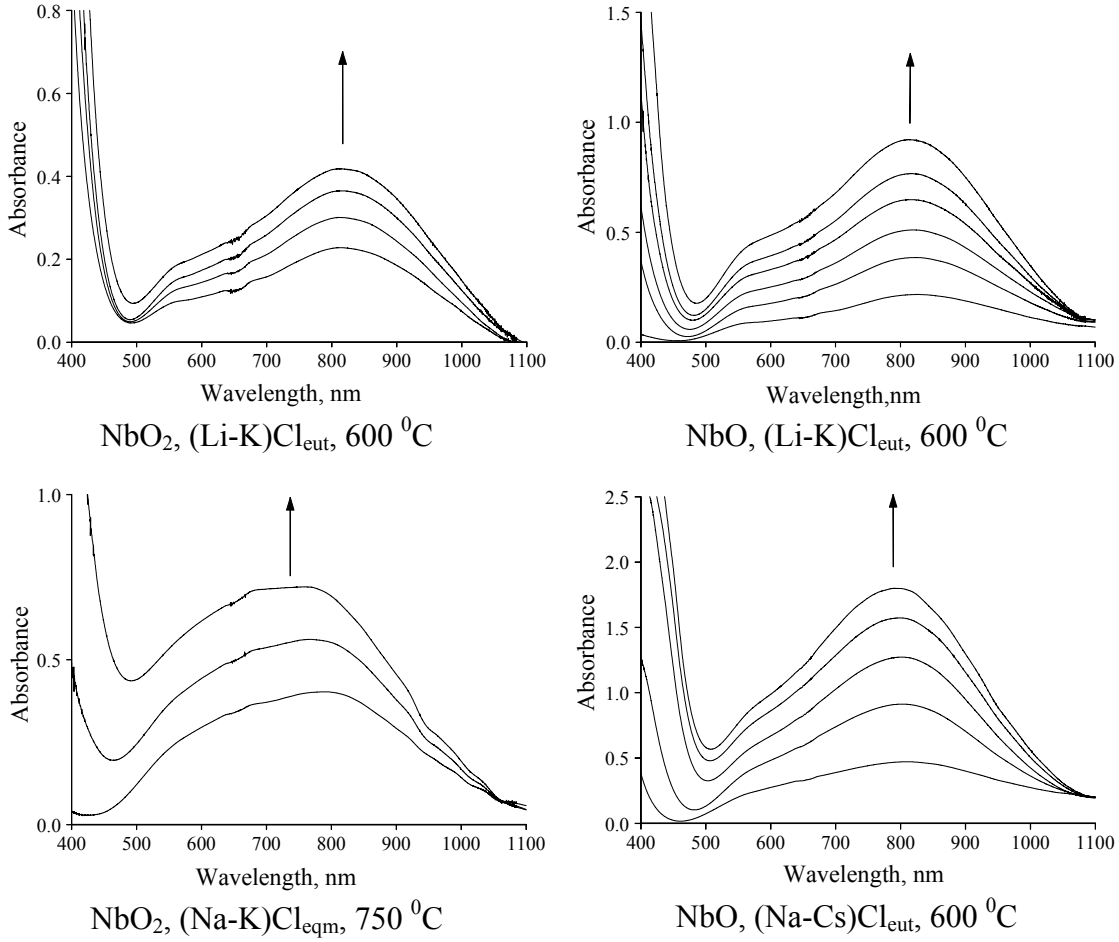



Figure 6. EAS measured during interaction of NbO or $NbO_2$ with hydrogen chloride in alkali chloride melts.

Based on the experimental results and taking into account the coordination properties of vanadyl-ions (niobium closest analog) in alkali chlorides (20) we assume that

$NbOCl_4^{2-}$ chloride complexes are formed as intermediates in reactions of NbO and $NbO_2$ with hydrogen chloride.

**TABLE III.** Niobium anodic dissolution in galvanostatic mode. Current density 10-40 mA/cm$^2$.

| Exp. No | Experiment conditions | | | Final melt characteristics | | |
|---|---|---|---|---|---|---|
| | Oxide | Melt composition | T, $^0$C | $\omega_{Nb}$,wt. % | $n_{Nb}$ | Colour of quenched melt |
| 1 | $NbO_2$ | LiCl-KCl | 450 | 0.284 | 4.4 | blue |
| 2 | $NbO_2$ | LiCl-KCl | 600 | 0.327 | 4.5 | blue |
| 3 | $NbO_2$ | LiCl-KCl | 750 | 0.239 | 4.6 | blue |
| 4 | $NbO_2$ | NaCl-KCl | 750 | 0.130 | 4.0 | blue |
| 5 | $NbO_2$ | NaCl-CsCl | 600 | 0.050 | 4.3 | light-blue |
| 6 | $NbO_2$ | NaCl-CsCl | 750 | 0.056 | 4.0 | light-blue |
| 7 | NbO | LiCl-KCl | 450 | 0.146 | 3.5 | blue |
| 8 | NbO | LiCl-KCl | 600 | 0.384 | 4.3 | blue |
| 9 | NbO | LiCl-KCl | 750 | 0.371 | 4.2 | blue |
| 10 | NbO | NaCl-KCl | 750 | 0.096 | 3.6 | blue |
| 11 | NbO | NaCl-CsCl | 600 | 0.018 | 4.8 | light-blue |
| 12 | NbO | NaCl-CsCl | 750 | 0.103 | 3.8 | light-blue |

## Exchange Reactions between Niobium Metal and Oxidizing Ions

The exchange reactions between metallic niobium and the melts containing ions-oxidizers can be used for preparing oxygen-free niobium containing melts. We chose bismuth(III), silver(I) and nickel(II) ions as oxidizing species because they exhibit rather strong oxidation properties. The values of the formal standard potentials $E^*_{Me^{n+}/Me}$ decrease in the following sequence: bismuth > silver > nickel (21).

The spectra recorded during the reaction between bismuth(III)-containing melt and Nb metal are presented in Figure 7. Only one maximum, *i.e.*, at 610 nm, was observed in the spectra. The oxidation state of niobium in the melt obtained was close to four. Similar results were obtained when silver(I) ions were used as oxidants, there was again the only absorption peak at 610 nm (Figure 7) and oxidimetrically determined oxidation state of niobium in a quenched melt was 3.9±0.2. Bismuth(III) and silver(I) ions have $d^0$-electronic configuration and do not absorb in the visible part of the spectrum. Chloride complexes of nickel have a characteristic absorption spectrum in studied wavelengths range. During the reaction between $Ni^{2+}$ and Nb in a NaCl-KCl based melt we observed gradual decrease of intensity of absorption bands belonged to Ni(II), no new maxima appeared in the spectra (Figure 7). Taking in account relatively weak oxidation properties of Ni(II) formation of niobium complexes with $d^0$-configuration ($NbCl_6^-$) seems unlikely. We suppose that niobium(IV) ions formed have considerably smaller extinction coefficients compare to Ni(II). To check such assumption we used more concentrated nickel-containing electrolyte where lowered niobium metal plate. This time due to high initial nickel(II) concentration we were not able to record its spectrum but the final spectrum looks similar to those obtained previously bismuth and silver containing melts (Figure 7). The oxidation state of niobium in quenched melt was again close to four thus confirming the formation of Nb(IV) species during the reaction of Nb with Ni(II) ions.

Analysis of spectroscopy and oxidimetry data indicates that oxygen free niobium(IV) chloro-ions are formed as a result of the studied exchange reactions:

$$4\ Bi(III) + 3\ Nb \rightarrow 4\ Bi + 3\ Nb(IV) \qquad [6]$$

$$4\ Ag(I) + Nb \rightarrow 4\ Ag + Nb(IV) \quad [7]$$
$$2\ Ni(II) + Nb \rightarrow 2\ Ni + Nb(IV) \quad [8]$$

The octahedral $NbCl_6^{2-}$ complex ions are formed in chloride melts and the peak observed around 600 nm corresponds to the only spin-allowed electronic transition $^2T_{2g} \rightarrow {}^2E_g$ in this six-coordinated species.

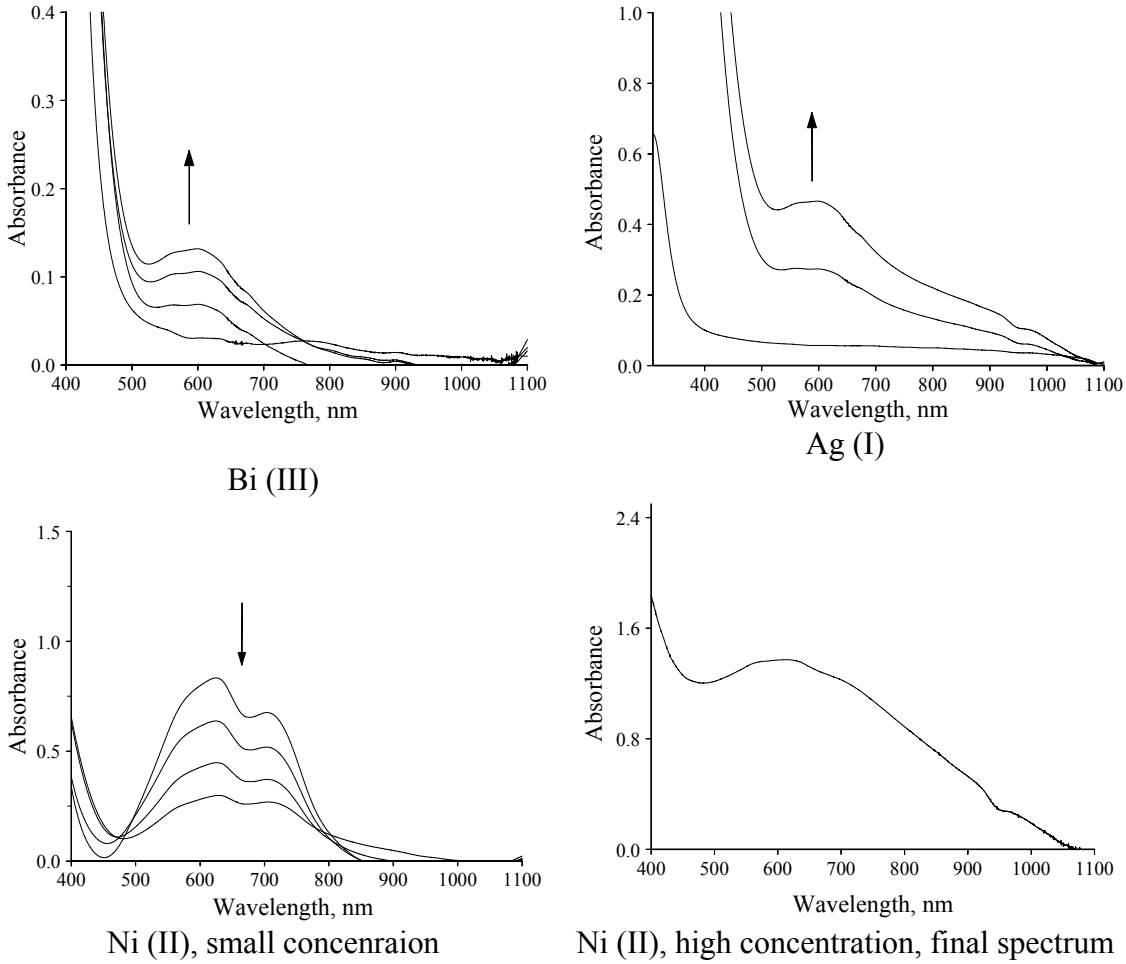



Figure 7. EAS recorded in the course of exchange reactions of niobium metal with ions-oxidizers in NaCl-KCl based melts at 750 $^0$C.

Spectroelectrochemistry Studies in Niobium-Containing Chloride Melts

In a special series of experiments the spectroelectrochemical method was applied to studying niobium speciation in chloride melts. The equimolar mixture of sodium and potassium chlorides was chosen as a solvent because of its higher technological significance for niobium electrorefining.

We carried out potentiostatic electroreduction and electrooxidation of $NbCl_3$-NaCl-KCl electrolytes prepared by niobium metal anodic dissolution (at -1.3 V *vs* chlorine reference electrode). The results obtained are presented in Figures 8 – 10.

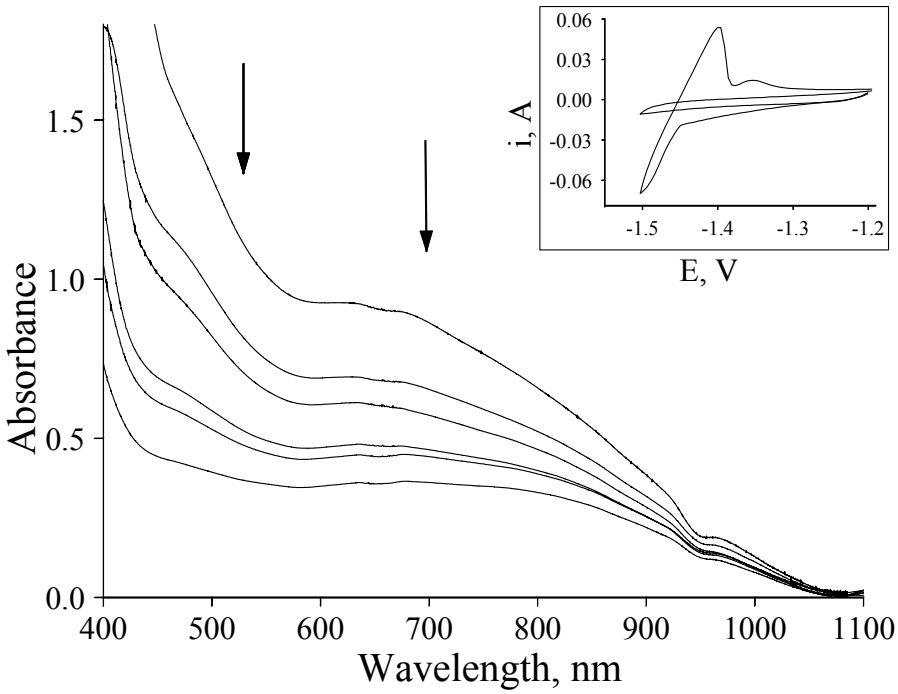



Figure 8. EAS changes during potentiostatic cathodic reduction of $NbCl_3$-NaCl-KCl melt at -1.5 V. Insert shows a cyclic voltammogram of the starting and final melts ($Cl_2/Cl^-$ reference electrode).

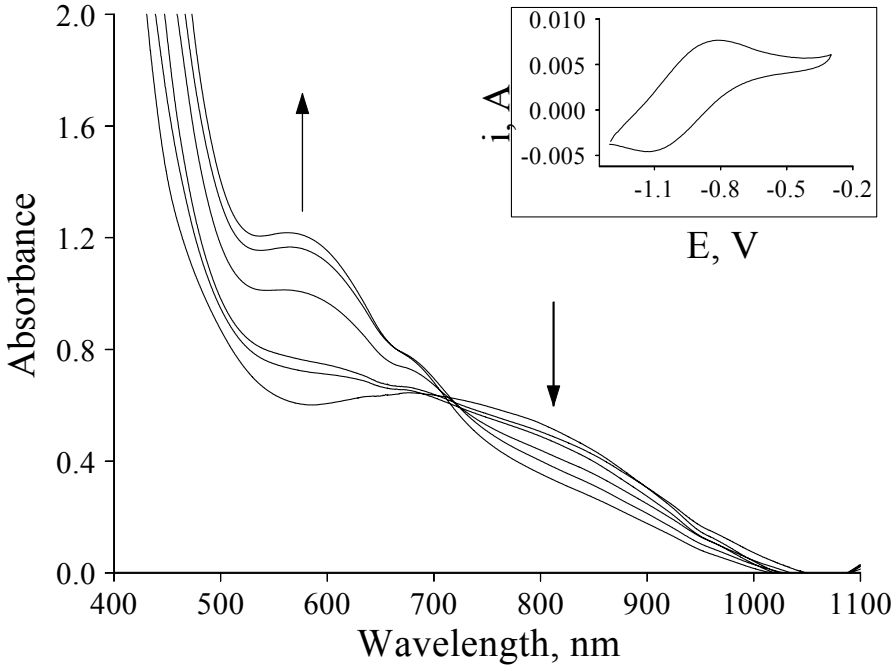



Figure 9. EAS recorded during potentiostatic anodic oxidation of $NbCl_3$-NaCl-KCl melt at -0.9 V Insert shows a cyclic voltammogram of the starting melt ($Cl_2/Cl^-$ reference electrode).

Electroreduction of niobium on a tungsten working electrode at potentials below -1.45 V led to the formation of metallic niobium, no evidence of any intermediate product formation was obtained (Figure 8). Potentiostatic electrolysis at -1.0÷-0.8 V on a glassy-carbon anode resulted in the formation of niobium(IV) ions (Figure 9). Further oxidation

(at potentials up to -0.5 V) led to the disappearance of absorption bands in the visible part of the spectrum due to Nb(V) species formation.

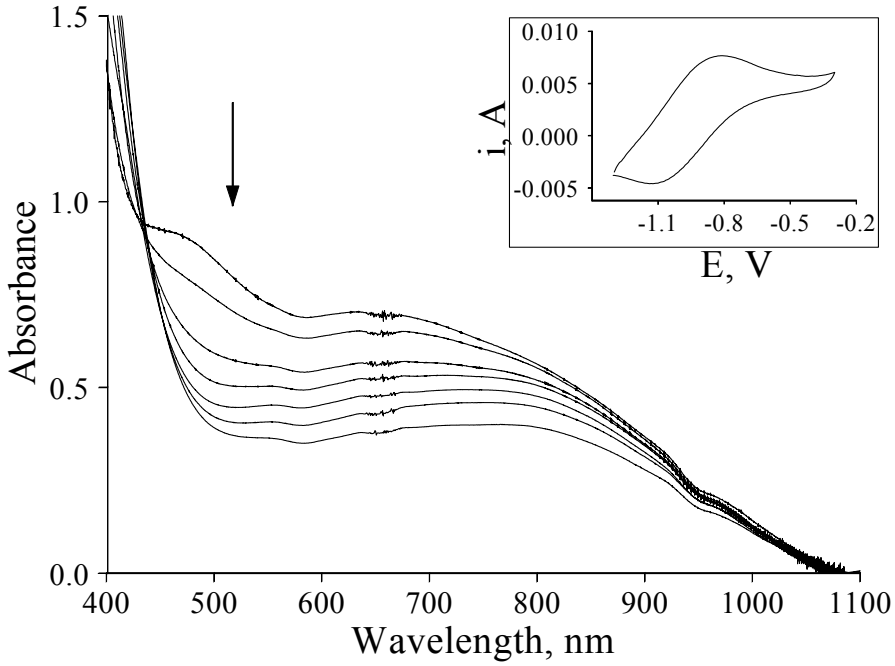



Figure 10. EAS recorded during potentiostatic anodic oxidattion of $NbCl_3$-NaCl-KCl melt at -0.4 V. Insert shows a cyclic voltammogram of the starting melt ($Cl_2/Cl^-$ reference electrode).

## Conclusions

Physico-chemical behaviour of niobium in chloride melts was studied using high temperature electronic absorption spectroscopy and spectroelectrochemistry. Addition of $NbCl_5$ to the chloride melts leads to the formation of predominantly niobium(V) species, $NbCl_6^-$. Increasing niobium(V) concentration results in partial decomposition of $NbCl_6^-$ ions to Nb(IV) species and $Cl_2$. $NbO^{3+}$ ions constitute the final product of niobium(V), (IV) and (II) oxides chlorination by HCl. When NbO and $NbO_2$ react with hydrogen chloride the intermediated oxygen-containing niobium(IV) complexes are formed. Niobium(III) complexes, $NbCl_6^{3-}$, are formed during anodic dissolution of niobium metal at low current densities and potentials below -1.15 V *vs.* chlorine reference electrode. Oxygen free niobium(IV) ions, $NbCl_6^{2-}$ are formed in the course of exchange reactions between metallic niobium and NaCl-KCl-based melts containing Bi(III), Ag(I) or Ni(II) chloro-ions. The electrochemical reduction of $NbCl_3$-NaCl-KCl leads to formation of metallic niobium. Niobium (IV) ions are formed during potentiostatic electrolysis at -1.0÷-0.8 V. Further oxidation (at the potentials up to -0.5 V) leads to the formation of Nb(V) species. The electronic absorption spectra of all formed soluble niobium species were recorded in $(Li\text{-}K)Cl_{eut}$, $(Na\text{-}K)Cl_{eqm}$ and $(Na\text{-}Cs)Cl_{eut}$ mixtures at 450-750 $^0$C.

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