

Raman and Infrared Spectroscopic Studies of (NaF–KF)–K₂MoO₄–B₂O₃ Melts and the Mechanism of Electrodeposition of Molybdenum

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The structure of molybdenum and boron species in the ternary system (NaF–KF)–K₂MoO₄–B₂O₃ and the quasi-binaries (NaF–KF)–K₂MoO₄, (NaF–KF)–B₂O₃, K₂MoO₄–B₂O₃ were investigated by Raman (melts and solids) and IR (solids) spectroscopy. The Raman spectra of the melts show the Mo-containing species MoO₄^{2–} only in K₂MoO₄ oxofluoride melts. When B₂O₃ is added, the B₂O₃ network is broken down and anions of the BO₃F^{4–} and BO₂F₂^{3–} types may form. These anions may play a crucial role in the MoO₄^{2–} reduction mechanism by complexing O^{2–} ions liberated when molybdenum metal is depositing. The spectra of the fluoride-containing melts and solids do not show hetero-poly anions or oxide bridging molybdenum complexes. Such complexes have been suggested in the literature in order to explain the electroreduction of molybdate.

Electrodeposition of molybdenum from molten salts has been extensively investigated over recent decades in different types of molten electrolytes: alkali chlorides, fluorides, oxides, mixed oxochlorides and oxofluorides.^{1–6} Several studies have been devoted to technological aspects of molybdenum electrodeposition, but the mechanism of electrodeposition has seldom been studied. It has been established that the most effective electrodeposition of molybdenum coatings takes place from mixed molten oxofluoride electrolytes containing alkali fluorides, MoO₃ (or A₂MoO₄, where A is an alkali metal ion) and small additives of B₂O₃ (or SiO₂).³ Molybdenum electrodeposition could not be obtained using pure molybdate K₂MoO₄ or KF–K₂MoO₄ mixtures. Very small additions of B₂O₃, however, lead to smooth and adherent molybdenum deposits.^{3–5} Electrodeposition of molybdenum from the binary melt K₂MoO₄–B₂O₃ is also possible. The role of the oxide additives is not clear, but B₂O₃ (or SiO₂) additions may result in the formation of chemically active species that are able to complex oxygen ions and reduce the O^{2–} concentration when these ions are liberated during the reduction of MoO₄^{2–}. This makes it easier for the strong O^{2–} getter, Mo⁶⁺, to

be reduced at the electrode. The composition and structure of the above mentioned species have not yet been identified.

The addition of boron oxide to fluoride-containing melts will certainly form new oxygen-containing complexes in the melt. At low B₂O₃ additions it is reasonable to believe that these complexes will also have F[–] ions in the inner coordination sphere. To investigate how the ionic species in the fluoride-molybdate containing melts are changed with additions of B₂O₃, Raman spectroscopic and IR spectroscopic investigations of such melts and X-ray analysis of quenched samples were performed. These studies were made in the concentration range close to the composition used in the electrochemical processes³ and at varying B₂O₃:K₂MoO₄ molar ratios. Since electrodeposition of molybdenum is more effective in the case of excess boron oxide relative to molybdate, such compositions were studied in detail. Experimental studies were performed using the (NaF–KF) eutectic melt (molar ratio 40:60). The quasi-binaries (NaF–KF)–K₂MoO₄, (NaF–KF)–B₂O₃ and K₂MoO₄–B₂O₃ and the ternary (NaF–KF)–K₂MoO₄–B₂O₃ melts at different concentrations were investigated. Some data using the LiF–NaF–KF eutectic melt, FLINAK, were also obtained.

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Experimental

Chemicals. NaF and KF, p.a. quality from Merck, Germany, were dried for at least 24 h at 150 °C under

vacuum and then purified by melt recrystallization. Crystalline anhydrous boron oxide, p.a. quality from Merck, Germany, was dried in a nickel crucible in the following way: 2 h at 230 °C, 2 h at 450 °C and then kept in the molten state at 700 °C for 2 h under vacuum. The resulting B₂O₃ was crushed in a dry box in nitrogen atmosphere having <0.5 ppm water. K₂MoO₄, p.a. quality from Merck, Germany, was heated at 400 °C to constant weight.

Procedure. The different samples of the binary and ternary systems, in 500 mg batches, were prepared in a dry box and filled into graphite (pure oxide melts) or glassy carbon crucibles. The sample in the glassy carbon crucible contained in a quartz envelope was transferred to a vacuum line, evacuated to 0.1 mbar, back-filled with dry N₂ to approximately 400 mbar and melted. The quartz envelope with its content was then transferred back to the dry box where about 150 mg of the solidified melt was placed in a windowless Raman cell made of graphite. The cell was then placed in another optical quartz envelope that was evacuated and back-filled with dry N₂ to approximately 400 mbar. The cell was now ready for Raman spectroscopic measurements. The composition and the melting temperatures of the samples investigated are listed in Table 1.

Raman spectra were recorded using the 488 nm line of an argon laser, 100 mW (Spectra-Physics, model 164).

Table 1. Experimental matrix (the molar ratio NaF:KF = 40:60).

System	Composition (mol%)	Recording temp./°C
NaF-KF	40:60	810
B ₂ O ₃	100	
NaF-KF-K ₂ MoO ₄	99:1	810
NaF-KF-K ₂ MoO ₄	95:5	810
NaF-KF-B ₂ O ₃	95:5	815
NaF-KF-B ₂ O ₃	85:15	820
NaF-KF-B ₂ O ₃	75:25	820
NaF-KF-B ₂ O ₃	71:29	820
NaF-KF-K ₂ MoO ₄ -B ₂ O ₃	70:1:29	800
NaF-KF-K ₂ MoO ₄ -B ₂ O ₃	70:3:27	810
NaF-KF-K ₂ MoO ₄ -B ₂ O ₃	70:5:25	810
NaF-KF-K ₂ MoO ₄ -B ₂ O ₃	70:7:23	810
NaF-KF-K ₂ MoO ₄ -B ₂ O ₃	70:15:15	810
NaF-KF-K ₂ MoO ₄ -B ₂ O ₃	94:1:5	815
NaF-KF-K ₂ MoO ₄ -B ₂ O ₃	90:5:5	810
K ₂ MoO ₄ -B ₂ O ₃	1:99	730
K ₂ MoO ₄ -B ₂ O ₃	5:95	750
K ₂ MoO ₄ -B ₂ O ₃	30:70	900
FLINAK-K ₂ MoO ₄ -B ₂ O ₃ ^a	70:1:29	700
FLINAK-K ₂ MoO ₄ -B ₂ O ₃ ^a	70:3:29	700
FLINAK-K ₂ MoO ₄ -B ₂ O ₃ ^a	70:5:27	700
FLINAK-K ₂ MoO ₄ -B ₂ O ₃ ^a	70:7:23	700
FLINAK-K ₂ MoO ₄ -B ₂ O ₃ ^a	70:15:15	700
FLINAK-K ₂ MoO ₄	99:1	615
FLINAK-K ₂ MoO ₄	95:5	615

^aB₂O₃ does not dissolve in FLINAK to any significant degree, and the melt concentrations given are certainly not correct.

The Raman cell^{7a} was aligned in an optical furnace,^{7b} and the scattered light was collected and analysed with a 0.85-m double monochromator (model 1403, Spex Industries) equipped with an RCA model C-31034 photomultiplier tube (PMT). The system was also interfaced to a PC, and the spectra recorded were digitalized and stored on disc. The spectra were obtained at 700–820 °C. The micro-Raman spectra have been recorded as previously.^{7c}

IR spectra were registered using Specord M 80 instrument (Carl Zeiss-Jena Industry). The pellets, consisting of 2 mg of the sample and 150 mg of KBr, were pressed in a dry box and placed in special cell with KBr windows. The spectra were obtained at room temperature in the range 200–4000 cm⁻¹.

Results

Data have been recorded to elucidate the structure of coordination polyhedra of molybdenum with O²⁻ and F⁻ anions. Some Raman and IR spectroscopic data can be found in the literature.^{8–17} In a discussion of the structure of molybdenum compounds, which may form in the alkali fluoride melts containing oxides like B₂O₃, it is also necessary to take into account the possibility of formation of mixed oxofluoro-complex anions of Mo⁶⁺ and B³⁺. Possible anions with molybdenum in lower oxidation states should also be considered. Figure 1 shows the Raman spectra of 1 and 5 mol% K₂MoO₄ dissolved in NaF-KF and FLINAK(insert), respectively. Infrared spectra of quenched samples of the (NaF-KF)-K₂MoO₄ system are shown in Fig. 2. Three Raman and two IR bands can be observed. Their positions and the intensity confirm the formation of the MoO₄²⁻ anion of T_d symmetry, which is characterised by four vibrations: all active in Raman and two, ν₃ and ν₄, in IR.^{13,14} The Raman spectra are characterised by a very intense band at 881 cm⁻¹ in NaF-KF and 887 cm⁻¹ in FLINAK. These bands are assigned to the symmetric stretching vibration ν₁ (A₁). The shoulders around 840 cm⁻¹ are assigned to the asymmetric stretching vibration ν₃ (F₂). The position of the lower frequency band at 327–323 cm⁻¹ also varies somewhat with melt composition. This band is assigned to the two degenerate bending modes, ν₂ (E) and ν₄ (F₂), which are very close to one another and are barely observed as separate Raman bands.¹³ ν₂ (E) should moreover be more intense than ν₄ (F₂) for MoO₄²⁻, and the first band therefore overlaps the second. However, for the spectrum of 1 mol% K₂MoO₄ in FLINAK, Fig. 1 (band 1 of insert), the two bands, ν₂ (E) and ν₄ (F₂), were observed as partially overlapping shoulders even if this is not very clear from the insert. The more intense counterpart at 324 cm⁻¹ may be assigned to ν₂ (E) and the less intense high frequency counterpart at 333 cm⁻¹ to ν₄ (F₂).

The IR spectrum of pure K₂MoO₄ has two intense bands at 833 and 335 cm⁻¹, which are assigned to the

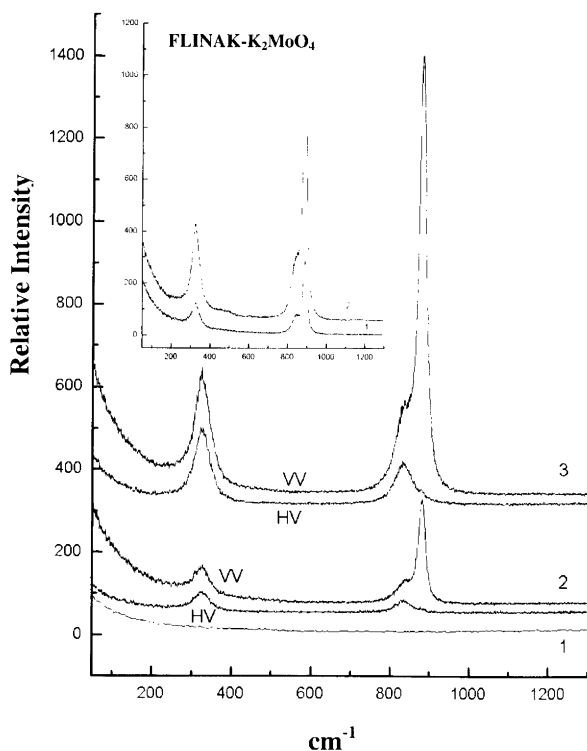


Fig. 1. Raman spectra of K_2MoO_4 containing melts at $810^\circ C$. (1) Pure NaF-KF, (2) 1 mol% K_2MoO_4 , (3) 5 mol% K_2MoO_4 . The insert to the figure shows the 1 and 5 mol% K_2MoO_4 melts recorded at $700^\circ C$. VV indicates that incident and scattered radiation is polarised perpendicular to the scattering plane. HV indicates that the incident radiation is polarised in the scattering plane and the scattered radiation analysed perpendicular to the scattering plane.

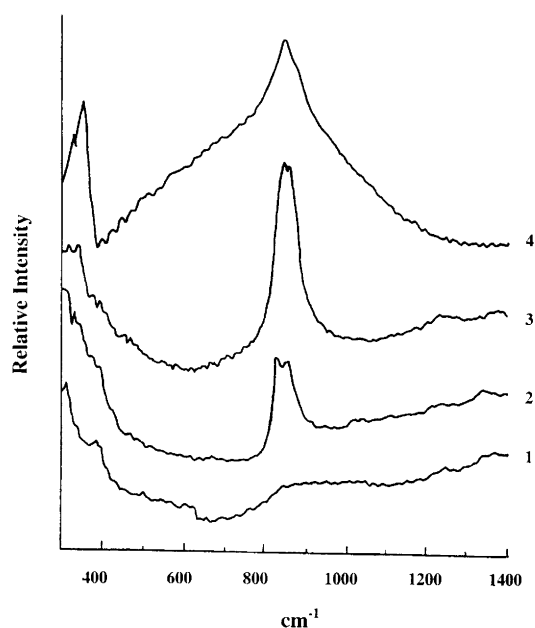
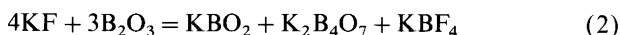


Fig. 2. IR spectra of quenched (NaF-KF)- K_2MoO_4 melts at $20^\circ C$. (1) Pure NaF-KF, (2) 1 mol% K_2MoO_4 , (3) 5 mol% K_2MoO_4 , (4) pure K_2MoO_4 .

vibrations ν_3 (F_2) and ν_4 (F_2), respectively. The IR spectra of quenched (NaF-KF)- K_2MoO_4 melts have an intense band around 840 cm^{-1} , assigned to the asymmetric stretching vibration ν_3 (F_2). The 335 cm^{-1} band is not very pronounced in the mixtures. The assignment of the bands observed in Raman and IR are given in Table 2. A comparison of the present spectra for these melts and solids with the spectra of different oxygen- and fluoride-containing polyhedra found in the literature⁸⁻¹⁷ shows that the very stable and discrete anion MoO_4^{2-} exists even for very low K_2MoO_4 concentrations. Evidence of mixed oxofluoride polyhedra of molybdenum is not present. This observation is important because the O^{2-} and F^- anions may substitute each other to some degree in complexes formed in oxofluoride melts, and especially in melts with a large excess of F^- . The formation of mixed oxofluoride compounds could therefore have been possible. The results obtained, however, show that the O^{2-} anion is clearly preferred as a nearest neighbour to Mo^{6+} relative to F^- . This observation may explain why the electrodeposition of molybdenum does not take place from pure K_2MoO_4 or KF- K_2MoO_4 melts. To enhance the formation of Mo metal a competing O^{2-} complexing agent must be present in the melt to reduce the O^{2-} concentration during electrodeposition to prevent the complexation



Studies of (NaF-KF)- B_2O_3 melts found in the literature do not give much information about the structure of boron oxide species, especially in the region of low B_2O_3 concentrations. Some data are, however, available.^{18,19} For pure boron oxide the formation of six-membered boroxole rings connected in networks is confirmed by Raman spectroscopic studies of glasses and liquids.²⁰ Both the O^{2-} and the F^- anions have strong tendencies to complex the B^{3+} cation, especially in the low boron oxide concentration range. The formation of mixed oxofluoride and even fluoride species could be expected. On the base of cryoscopic studies,²¹ it was suggested that the reaction



might take place in KF- B_2O_3 melts. In LiF- B_2O_3 and NaF- B_2O_3 melts, the formation of the volatile BF_3 was observed by Makyta.²¹ Maya,²² however, did not observe BF_3 above NaF- B_2O_3 melts. A characteristic feature of boron is its ability to form polyhedra with coordination numbers 3 and 4. The structure of boron polyhedra in the oxide systems, A_2O - B_2O_3 , has been investigated by Raman and X-ray diffraction studies in the concentration range up to 70 mol% of A_2O .^{23,24} Infrared and Raman spectroscopic studies of the solid and liquid systems $NaBF_4$,²⁵ B_2O_3 -NaF- $NaBF_4$ ²² and KBF_4 - B_2O_3 ,²⁶ in which the formation of different oxofluoride species is claimed, will be used in our discussion to elucidate what happens with B_2O_3 in fluoride- K_2MoO_4 containing melts. Literature data are given in Table 3.

Table 2. Raman and IR frequencies (in cm⁻¹) of the MoO₄²⁻ anion in different alkali fluoride mixtures (melt and solid state) and in pure K₂MoO₄.

Compound/system	ν_1 (A ₁) symmetric stretching vibration	ν_2 (E) bending vibration	ν_3 (F ₂) asymmetric stretching vibration	ν_4 (F ₂) bending vibration	Method/ Ref.
Na ₂ MoO ₄ in 10 m NaOH	897	317	837	325	13
Ba ₂ [MoO ₄]	792	328	808	373	14
Present results:					
1% K ₂ MoO ₄ in NaF-KF:					
Melt	881 vs	327 s	840 sh	(327)	Raman
Solid			830, 850 s	330 w	IR
5% K ₂ MoO ₄ in NaF-KF:					
Melt	881 vs	323 s	835 sh	(323)	Raman
Solid			837, 850 s	340 w	IR
K ₂ MoO ₄ (solid)			833 sh	335 s	IR
1% K ₂ MoO ₄ in FLINAK (melt)	887 vs	324 s	845 sh	333 sh	Raman
5% K ₂ MoO ₄ in FLINAK (melt)	887 vs	323 s	845 sh	331 sh	Raman

vs, very strong; s, strong; w, weak; sh, shoulder.

Table 3. Band positions (in cm⁻¹) and their assignments in boron coordination polyhedra of tetrahedral (T_d) and planar (D_{3h}) structure in oxide and fluoride systems.

System ^a	Ion	Sym.	ν_1	ν_2	ν_3	ν_4	Method	Ref.
NaBF ₄ (m)	BF ₄ ⁻	T _d	772 vs	358 s	(1065)	530 s	Raman	25
NaBF ₄ -NaF(m)								
(92-8)(mol%)	BF ₄ ⁻	T _d	775 vs	360 s	(1065)	532 s	Raman	25
KBF ₄ (s)	BF ₄ ⁻	T _d	770 vs		1070	530, 533	IR	29
KF-KBF ₄ (s)								
(90-10)(mol%)	BF ₄ ⁻	T _d			1070		IR	29
Na ₂ O-B ₂ O ₃ (s)								
(<60 mol%Na ₂ O)	BO ₄ ⁵⁻	T _d	770		970	470	Raman	23
Aqueous solution	B(OH) ₄ ⁻	T _d	754	379	945	533	Raman	27
Aqueous solutions	BF ₄ ⁻	T _d	770				Raman	22
with different	BF ₃ OH ⁻		763				Raman	22
types of	BF ₂ (OH) ₂		753				Raman	22
polyanions	B(OH) ₄ ⁻		745				Raman	22
	B ₃ F ₆ O ₄ ³⁻		610				Raman	22
BF ₃ (g)	BF ₃	D _{3h}	888	718	1505	482	Raman	27
Not given	BO ₃ ³⁻	D _{3h}	920	750	1250	650	Raman	27
Not given	H ₃ BO ₃	D _{3h}	1060	668, 648	1490-1428	545	Raman	27
3Na ₂ O-B ₂ O ₃ (s)	BO ₃ ³⁻	D _{3h}	895	1570(2ν ₂)	1275	588	Raman	23
3Li ₂ O-B ₂ O ₃ (m)	BO ₃ ³⁻	D _{3h}	910 vs		1225 w	600 w	Raman	28
LaBO ₃ (s)	BO ₃ ³⁻	D _{3h}	939 w	717	1280 s	608, 588	IR	28

vs, very strong; s, strong; w, weak; sh, shoulder. ^as, Solid; m, molten; g, gas.

Results from the present investigation of the (NaF-KF)-B₂O₃ system are shown in Fig. 3 as Raman spectra of melts and in Fig. 4 as IR spectra of quenched samples. The Raman frequencies observed are presented in Table 4. The Raman spectrum of pure B₂O₃ is characterised by a very strong peak at 807 cm⁻¹ [Fig. 3 (line 6)]. This band is assigned to the symmetric ring-breathing vibration of the boroxole ring, involving mainly the oxygen atoms in the ring. Pulsed neutron-diffraction measurements³⁰ in vitreous and molten B₂O₃ revealed the presence of well defined molecular units of the BO₃ type whose structure does not change significantly with

increasing temperature. The way these units are connected changes especially above the glass transition temperature, T_g, indicating an opening of boroxole rings. In a Raman scattering study²⁰ the B₂O₃ structure at T_g (540 K) is estimated to consist of partly (50% of B atoms) in boroxole rings, and partly of chains of BO₃ triangles. As the temperature increases above T_g the boroxole rings are gradually broken up into chains. Melting B₂O₃ leads to a breaking up of about 1/3 of the boroxole rings, which change into chains of BO₃ triangles. The structure of vitreous boron oxide has been a much debated issue for many years.^{31a} According to NMR^{31b,c} and neutron

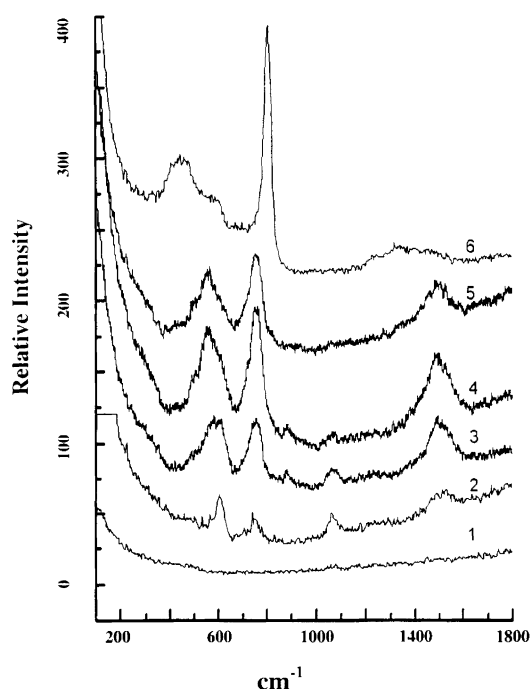


Fig. 3. Raman spectra of (NaF-KF)-B₂O₃ melts at 820 C. (1) Pure NaF-KF, (2) 5 mol% B₂O₃, (3) 15 mol% B₂O₃, (4) 25 mol% B₂O₃, (5) 29 mol% B₂O₃, (6) pure B₂O₃.

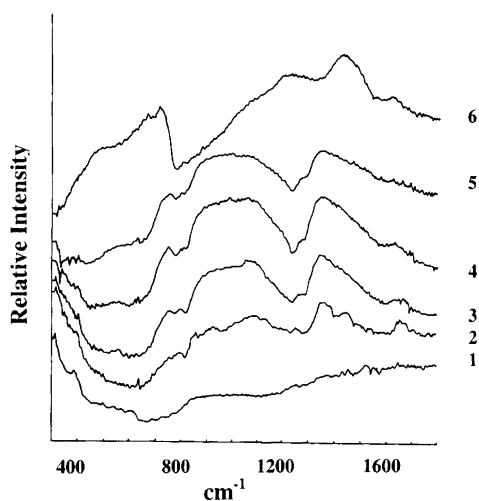


Fig. 4. IR spectra of quenched (NaF-KF)-B₂O₃ melts at 20 °C. (1) Pure NaF-KF, (2) 5 mol% B₂O₃, (3) 15 mol% B₂O₃, (4) 25 mol% B₂O₃, (5) 29 mol% B₂O₃, (6) pure B₂O₃.

diffraction data,^{31a} ca. 85 and 60%, respectively, of all boron atoms are connected in boroxole rings. Recent ¹⁷O-NMR results^{32a} along with previous ¹¹B-NMR studies^{32b} have been used to devise a structural model for B₂O₃ that consists of micro-domains in the glassy network which are rich or poor in boroxole rings.

Addition of alkali fluorides to B₂O₃ leads to depolymerization. The transformation of B₂O₃ structures from those which occur in pure B₂O₃ to those which are stable when B₂O₃ dissolves in fluoride melts can be described as explained below.

Melts concentrated in B₂O₃. A small addition of NaF and KF into liquid B₂O₃ may introduce F⁻ anions into the network, and can cause formation of polyhedra of tetrahedral structure with F⁻ ions connected to the boroxole rings without destroying the network. The B₃O₆F⁴⁻ complex, having BO₃F⁴⁻ groups of possible C_{3v} symmetry, may be responsible for the Raman band at 755 cm⁻¹. Continued addition of alkali fluorides may cause further depolymerization of the boroxole network, and isolated boroxole rings containing fluoride ions with the composition, BO₂F₂³⁻, etc. may form. Tetrahedral polyhedra of the type BO₃F⁴⁻ have been suggested.²²

Melts with less than 30 mol% B₂O₃. Data for B₂O₃ with low concentrations in fluoride melts have not been found in the literature. For pure oxide melts, A₂O-B₂O₃, the formation of the small isolated highly charged orthoborate species BO₃³⁻ was observed at molar ratio 75/25. At high A₂O concentrations the coordination number of boron is 3.^{23,28} It is reasonable to believe that isolated B-O-F complexes will form in fluoride melts with low B₂O₃ contents. Isolated metaborate, B₃O₆³⁻, rings, pyroborate, B₂O₅⁴⁻ and ortoborate BO₃³⁻, with and without F⁻ included are possible candidates. The formation of BO₃F⁴⁻ in B₂O₃-NaF glasses,²² BF₄⁻ in NaF-NaBF₄ melts,²⁵ and BO₃³⁻ in H₃BO₃²⁷ with frequencies close to those observed in the present (NaF-KF)-B₂O₃ binary melts are reported. The Raman spectra of (NaF-KF)-B₂O₃ melts with 25 and 29 mol% B₂O₃ are completely different from those observed in the pure oxidic melts and solids at the same B₂O₃ content. The Raman spectrum at 29 mol% B₂O₃ [Fig. 3 (line 5)] is characterized by a wide band at 500-600 cm⁻¹ consisting of three bands: 500, 555-560 and 600 cm⁻¹, and their relative intensity varies with the B₂O₃ concentration.

Table 4. Raman frequencies (in cm⁻¹) for (NaF-KF)-B₂O₃ melts and their assignments.

NaF-KF (mol%)	B ₂ O ₃ (mol%)	Raman spectra (melts)					
		[BO ₃ F] ⁴⁻ (C _{3v})	[BO ₃] ³⁻ (D _{3h})	[BO ₂ F ₂] ³⁻ (C _{2v})	[BO ₃ F] ⁴⁻ (C _{3v})	[BO ₃] ³⁻ (D _{3h})	[BO ₃ F] ⁴⁻ (C _{3v})
0	100		585			807	
71	29	500	560	ca. 600			755, 1495
75	25	500	555	ca. 600	757	880	1065, 1490
85	15	495	570	ca. 600	757	880	1065, 1490
95	5			ca. 600	750		1065, 1510

A strong band at ca. 755 cm⁻¹ and a broad band at 1495 cm⁻¹ are also observed. The intensity of all these bands reaches a maximum at 25 mol% B₂O₃ [Fig. 3 (line 4)]. Bands at 880 and 1065 cm⁻¹ also appear for B₂O₃ concentrations <29 mol%. At lower B₂O₃ contents the bands at 600 and 1065 cm⁻¹ are very pronounced [Fig. 3 (lines 2 and 3)]. The Raman band at 770 cm⁻¹ [Fig. 3 (lines 2–5)] and the very broad IR band around 1000 cm⁻¹ (Fig. 4) are indicative for BO₃F⁴⁻ formation in the melts and solids.

The variation in band position and the relative intensities with B₂O₃ contents allow us to make an interpretation of the data. The BO₃F⁴⁻ polyhedra (C_{3v} symmetry) are observed for all B₂O₃ concentrations <30 mol%. These polyhedra may be involved in different structural fragments, e.g. metaborate type rings with 0 to 3 F⁻ anions. Therefore the positions of the bands of the BO₃F⁴⁻-containing polyhedra may change somewhat depending on the fragments in which BO₃F⁴⁻ is incorporated. The BO₃F⁴⁻ polyhedra are characterized by the bands at 500, 757 and 1490 cm⁻¹. The band at 757 cm⁻¹ is assigned to the symmetric stretching vibration (ν₁). The presence of the tetrahedral BO₂F₂³⁻ polyhedra (C_{2v} symmetry), also involved in different structural fragments, is confirmed by the bands around 600 cm⁻¹. Consequently we observe a mixture of at least three different polyhedra, BO₃³⁻, BO₂F₂³⁻, BO₃F⁴⁻, in the melt. It is, however, difficult to distinguish the set of vibrations assigned to each type, and therefore only qualitative statements can be made. At 5 mol% B₂O₃ we accordingly observe major amounts of BO₂F₂³⁻ and small amounts of BO₃F⁴⁻. With an increase in the B₂O₃ concentration to 15 and 25 mol%, the fraction of BO₃F⁴⁻ is increasing and becomes predominant at 30 mol% B₂O₃. Small amounts of the isolated orthoborate units, BO₃³⁻, are reasonable at the higher B₂O₃ compositions. This is characterized by the 880 cm⁻¹ (ν₁) band of very low intensity in Fig. 3 (line 5).

The band at 1060 cm⁻¹ is of special interest. Usually this band is assigned to one of the vibrations of tetrahedral boron. In the present case the 1060 cm⁻¹ intensity is increasing as the concentration of B₂O₃ decreases, as can be seen from Fig. 3 (lines 2–4). According to cryoscopic studies,²¹ KBO₂ is formed in KF melts at low B₂O₃ concentrations. The intensity of the 1060 cm⁻¹ band may therefore increase with decreasing B₂O₃ concentrations, since it may be due to a B–O vibration not mentioned above.

The IR spectra of the (NaF–KF)–B₂O₃ quenched samples, shown in Fig. 4 (lines 2–5), are characterized by a very broad band around 1000 cm⁻¹. This confirms CN=4. The bands observed in IR may be divided in two groups. Group 1 contains the 700, 1250 and 1450 cm⁻¹ bands, Fig. 4 (line 6). These bands may be attributed to oxygen-containing boron polyhedra. The second group, containing the 550, 750–800, 900–1100 and 1350 cm⁻¹ bands, appears only in the fluoride-containing melts, Fig. 4 (lines 2–5). These may be

assigned to the oxofluoride- and oxygen-containing species, which are products of the decomposition of the B–O–B network. BF₄⁻ does not seem to be present at all in the NaF–KF–B₂O₃ melts investigated here.

B₂O₃ did not dissolve in FLINAK as easily as in NaF–KF melts, and X-ray phase analysis of quenched (NaF–KF)–B₂O₃ melts²⁹ showed that: (a) the X-ray lines of KF gradually disappeared in the 25–30 mol% B₂O₃ range for the ternary and in the 30–50 mol% B₂O₃ range for the KF–B₂O₃ binary; (b) the NaF lines in the ternary did not vanish. These results indicate that oxofluoride boron polyhedra do not form so easily when boron has to compete with Li⁺ or Na⁺ for the O²⁻ ions. The lower field strengths of K⁺ will allow the formation of the O–B–F complexes more easily, and the low solubility of B₂O₃ observed in FLINAK is understandable.

Solid K₂MoO₄–B₂O₃ samples containing 1, 5 and 30 mol% of K₂MoO₄ were studied by micro-Raman spectroscopy. Quenched samples of K₂MoO₄–B₂O₃ melts were made for Raman analysis. These samples turned out to be glasses of different colours: at 1 mol% K₂MoO₄ light blue, at 5 mol% dark blue and at 30 mol% dark red–brown. Traditional Raman spectra (with a right angle between incident and scattered light) of these melts did not show the bands of the MoO₄²⁻ ion. This was most probably due to the dark colour of the melts, which reduced the intensity of the collected light. The IR spectra of the same samples were also featureless. Using the micro-Raman set-up, however, spectra were obtained. To some extent the band positions and intensities of these spectra varied according to where the glassy samples had been collected. Those taken from areas close to the graphite surface of the container in which the two oxides had been fused and mixed showed new bands relative to samples from the bulk. This indicates improper mixing. The Mo-containing species MoO₄²⁻ was, however, observed, together with bands most probably due to Mo-aggregated species. It was decided that further work was needed before these data could be presented in detail.

Raman spectra of the (NaF–KF)–K₂MoO₄–B₂O₃ melts at 70–94 mol% (NaF–KF) are shown in Figs. 5 and 6. Bands due to the different boron-containing polyhedra can be observed in addition to the MoO₄²⁻ bands. In Figs. 7–9 Raman spectra of some (NaF–KF)–K₂MoO₄–B₂O₃ melts with 1 and 5 mol% K₂MoO₄ are compared. In all the spectra the intense bands of the very stable MoO₄²⁻-containing species are observed. Bands due to other Mo species do not occur. It is also clear that the introduction of K₂MoO₄ does not influence the structure of the (NaF–KF)–B₂O₃ melt significantly even at rather high K₂MoO₄ additions.

Infrared spectra of quenched (NaF–KF)–K₂MoO₄–B₂O₃ melt samples are shown in Fig. 10. These spectra also

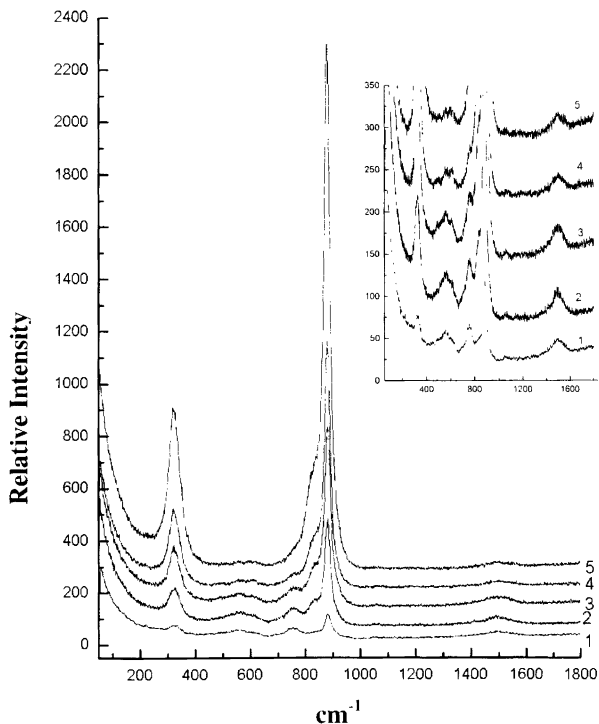


Fig. 5. Raman spectra of (NaF-KF)-K₂MoO₄-B₂O₃ melts at 810 °C. Concentrations are given as molar ratios of (NaF-KF):K₂MoO₄:B₂O₃. (1) 70:1:29, (2) 70:3:27, (3) 70:5:25, (4) 70:7:23, (5) 70:15:15. The insert in the figure gives the same data, but the y-axis is expanded.

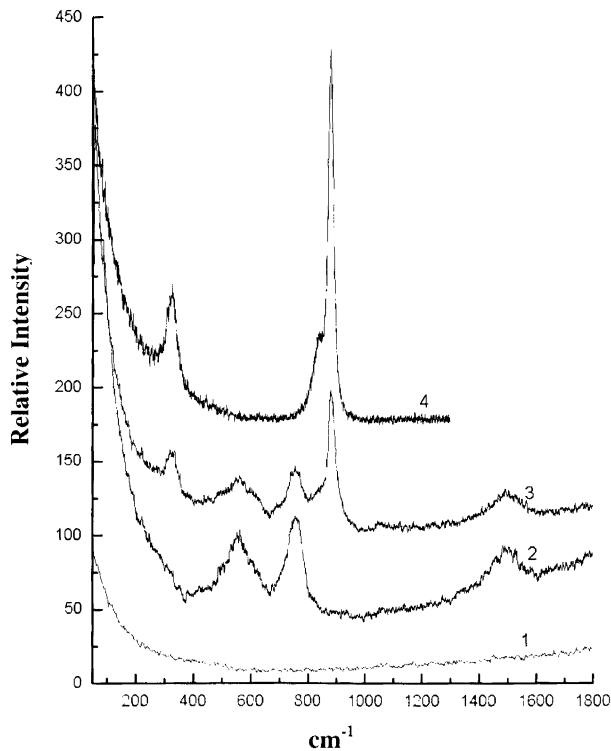


Fig. 7. Raman spectra of (NaF-KF)-K₂MoO₄-B₂O₃ melts at 810 °C. Concentrations are given as molar ratios of (NaF-KF):K₂MoO₄:B₂O₃. (1) 100:0:0, (2) 71:0:29, (3) 70:1:29, (4) 99:1:0.

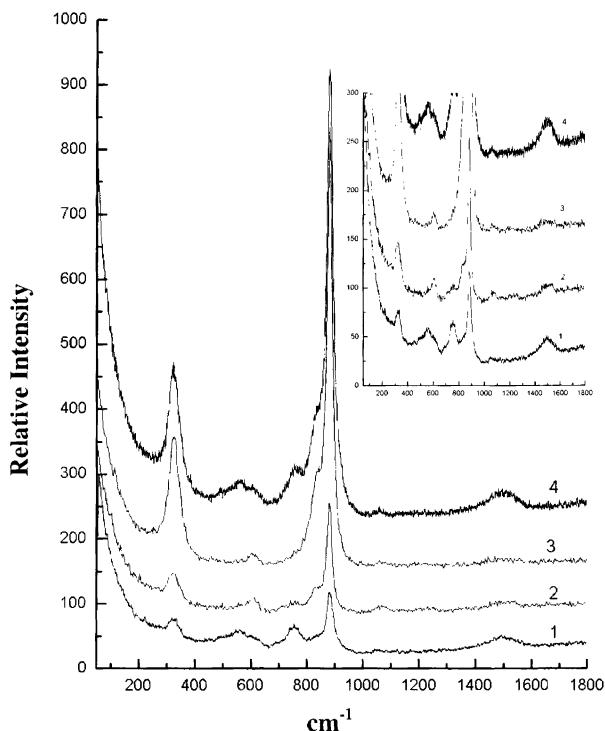


Fig. 6. Raman spectra of (NaF-KF)-K₂MoO₄-B₂O₃ melts at 810 °C. Concentrations are given as molar ratios of (NaF-KF):K₂MoO₄:B₂O₃. (1) 70:1:29, (2) 94:1:5, (3) 90:5:5, (4) 70:5:25. The insert in the figure gives the same data, but the y-axis is expanded.

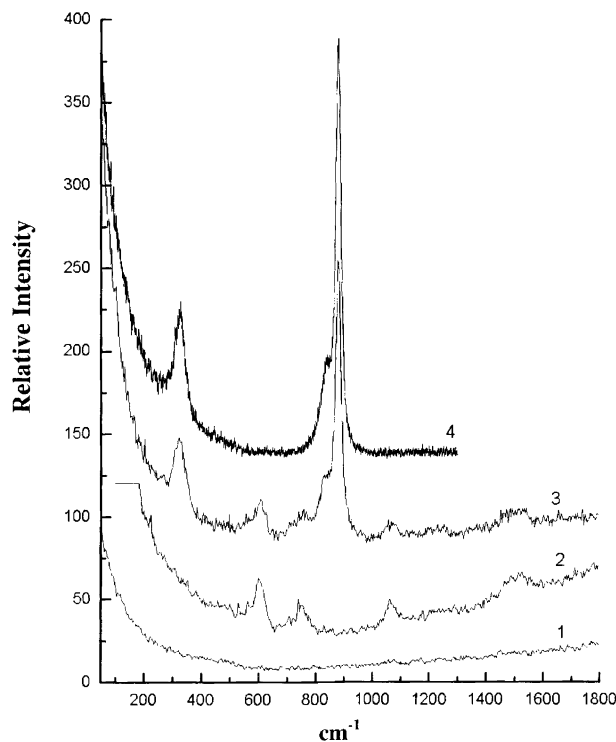


Fig. 8. Raman spectra of (NaF-KF)-K₂MoO₄-B₂O₃ melts at 810 °C. Concentrations are given as molar ratios of (NaF-KF):K₂MoO₄:B₂O₃. (1) 100:0:0, (2) 95:0:5, (3) 94:1:5, (4) 99:1:0.

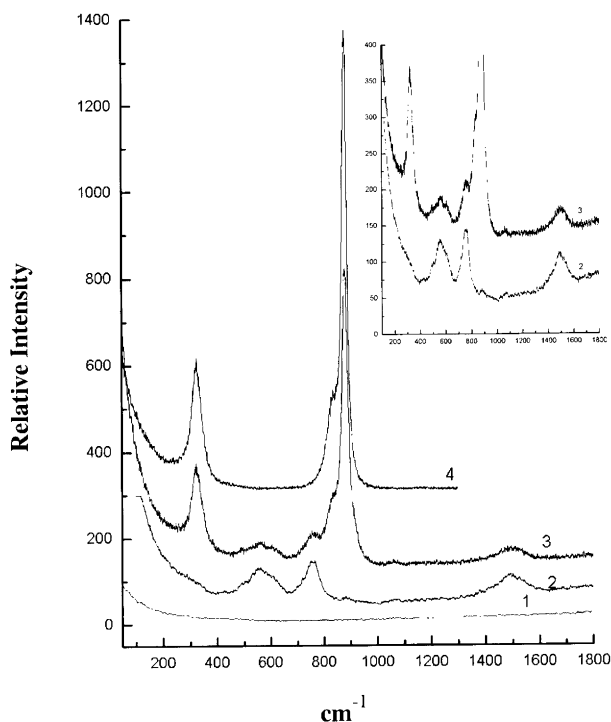


Fig. 9. Raman spectra of (NaF-KF)-K₂MoO₄-B₂O₃ melts at 810 °C. Concentrations are given as molar ratios of (NaF-KF):K₂MoO₄:B₂O₃. (1) 100:0:0, (2) 75:0:25, (3) 70:5:25, (4) 95:5:0. The insert to the figure gives the same data as for curves 2 and 3, but the y-axis is expanded.

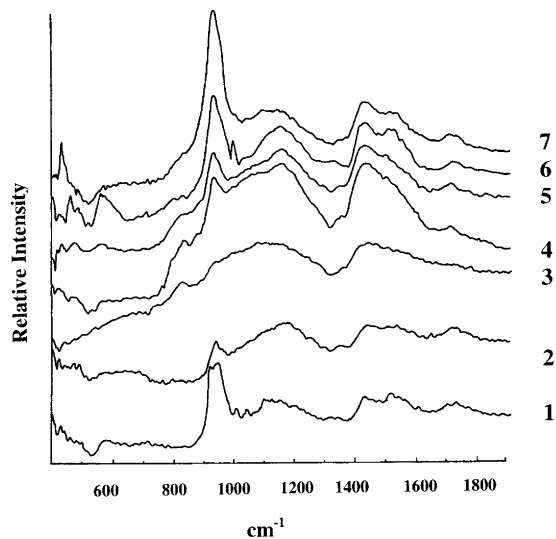


Fig. 10. IR spectra of quenched (NaF-KF)-K₂MoO₄-B₂O₃ melts at 20 °C. Concentrations are given as molar ratios of (NaF-KF):K₂MoO₄:B₂O₃. (1) 90:5:5, (2) 94:1:5, (3) 70:1:29, (4) 70:3:27, (5) 70:5:25, (6) 70:7:23, (7) 70:15:15.

give evidence for the Mo-containing MoO₄²⁻ species only.

The above results are important for an understanding of how boron oxide is promoting the reduction of the MoO₄²⁻ ion to metal during electrodeposition of molyb-

denum. Danek *et al.*¹ have proposed that heteropoly anions of the type BMo₆O₂₄⁹⁻ will promote effective electrodeposition of molybdenum from KF-K₂MoO₄-B₂O₃ melts. The above data, however, indicate strongly that molybdenum is present only as the Mo-containing MoO₄²⁻ species in oxofluoride containing melts. The mechanism involving boron as a complexing agent for O²⁻ ions during electroreduction of MoO₄²⁻ therefore seems to be realistic.

For the K₂MoO₄-B₂O₃ binary more data are needed to give an explanation for the effect of B₂O₃ on the electroreduction mechanism.

Conclusion

The structure of molybdenum and boron species in the ternary system (NaF-KF)-K₂MoO₄-B₂O₃ and the quasi-binaries (NaF-KF) K₂MoO₄, (NaF-KF)-B₂O₃, K₂MoO₄-B₂O₃ are presented in this paper. The discussion is based on Raman and IR spectroscopic studies of melts and quenched samples, respectively. The interpretation of the spectra for the fluoride-containing melts gives no evidence for the heteropoly anions or oxide-bridging molybdenum complexes, which have been suggested in the literature to explain the effect of these complexes on the electroreduction process. Raman spectra of fluoride containing melts show the Mo-containing MoO₄²⁻ species only. When B₂O₃ is added, the B₂O₃ network of the pure oxide is broken down and anions of the BO₃F⁴⁻ type may form. These anions may play a crucial role in the MoO₄²⁻ reduction mechanism by binding O²⁻ ions liberated when molybdenum metal is deposited. For the K₂MoO₄-B₂O₃ liquids it was not possible to obtain Raman spectra. The micro-Raman data of the solid glasses also showed the Mo-containing MoO₄²⁻ species.

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