Matrix-Isolated $Al_2OF_6^{2-}$ Ion in Molten and Solid LiF/NaF/KF

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A Raman spectrum consistent with that expected from an $Al_2OF_6^{2-}$ ion was observed when Na_2O was dissolved in a eutectic LiF/NaF/KF (FLINAK) melt at 500 °C, which contained a low concentration of either AlF_3 or Na_3AlF_6. Furthermore, it was possible to trap the $Al_2OF_6^{2-}$ ion in the frozen solid and to measure its Raman and IR spectra at 25 °C. A number of bands have been detected; among those, the two most characteristic bands of the $Al_2OF_6^{2-}$ ion at 494 (polarized) and 265 cm^{-1} in the FLINAK melt at 500 °C, and those at 509 and 268 (Raman) and ∼780 to ∼900 (IR) cm^{-1} for the compound matrix isolated in solid FLINAK at 25 °C. In the absence of added oxide, the dissolved aluminum fluoride was in the form of the octahedral AlF_6^{3-} ion, which has characteristic Raman bands at 542 and 325 cm^{-1} in the FLINAK melt at 500 °C. Whereas alumina, Al_2O_3, was found to be essentially insoluble in FLINAK melts, it was possible to dissolve sufficient amounts of Na_2O to convert most of the AlF_6^{3-} to the oxyfluoroaluminate, $Al_2OF_6^{2-}$. These solutions appeared to be metastable with respect to formation of insoluble alumina at higher temperatures. The present results can be compared to previous measurements on alumina dissolved in pure molten cryolite at much higher temperatures, where alumina solubility is low and broad bands due to oxide species are difficult to detect due to overlap with bands from AlF_6^{3-} and AlF_4^-.

Introduction

The oxide content of cryolite, Na_3AlF_6, is extremely important in the Hall−Héroult process for the production of aluminum metal because the most efficient operation of the electrolysis cells requires a well-controlled amount of alumina over a narrow concentration range between about 2 and 7 wt %.[1,2] At present there is no accurate, reliable on-line analytical method to monitor the oxide content. The solubility of alumina in the cryolite melt is about 10 wt % (19 mol %);[1] actual concentrations will vary in the industrial cell because of different compositions of the feedstock and because of the controlled addition of salts to enhance efficiency. The corrosive environment in the cells excludes the use of analytical sensors because they are not sufficiently robust. Measurement of total cell voltage can be an acceptable method if knowledge of the dependence on the alumina concentration can be improved.[3] There is considerable interest in the structure of the oxide species since this information may lead to an improved understanding of the cell reactions.

Førland and Ratkje[4] recognized that the dissolved oxide was not present as the free oxide ion but combined with the aluminum fluoride in the form of a complex molecular ion, of the type $Al_2OF_6^{2-}$ in dilute solutions, and probably $Al_2O_2F_4^{2-}$ in more concentrated solutions. Cryoscopic studies of alumina and other oxides in molten cryolite by Sterten[5] and Sterten and Skar[6] were consistent with these models. In dilute solutions 1 mol of Al_2O_3 was found to dissolve to give 3 mol of oxide-containing species, while in more concentrated solutions the number decreased toward 1.5, exactly what would be expected for the formation of oxide species with one and then two oxygen atoms. The existence of the same species and also $Al_3O_3F_6^{3-}$ (rings) in $MF-AlF_3-Al_2O_3$ (M = Li, Na, K) melts was deduced by Danek et al.,[7] on the basis of the LECO TC-436 nitrogen/oxygen chemical analysis technique in conjunction with carbothermal reduction. These concepts have been discussed in detail in reviews of cryolite solubility related to the production of aluminum.[1,2] Complexes with oxide bridges were required to account for the experimental results.[1,2,4] Attempts have been made to identify these complexes by various techniques. The mass spectroscopy does not work because gas-phase species above molten cryolite and oxide-saturated cryolite is mostly $NaAlF_4$ as the oxide species are not very volatile.[8] The oxide species reverts to some form of alumina, denoted γ or η, when cryolite freezes,[9] but previously no complex has been isolated in the solid phase. X-ray powder diffraction does not help because the η-form of Al_2O_3 is not an ordered crystalline phase according to our experience. Raman spectroscopic studies of oxide dissolved in cryolite by Gilbert et al.[10,11] indicated that nonbridging oxide bonds were unlikely, and Raman bands at about 200 and 510 cm^{-1} were assigned to bridged oxide species.

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Recent Raman studies by Gilbert et al.[12,13] were even more informative. Studies were performed on the sodium, lithium, and potassium cryolites for several cryolite ratios. The cryolite ratio, CR, is defined as the mole ratio of NaF to AlF_3. Difference methods were used to subtract the broad Raman spectrum of the cryolite solvent from the Raman spectrum of the mixtures to reveal peaks assigned to solute species of the type $Al_2OF_6^{2-}$ and $Al_2O_2F_4^{2-}$. Detailed assignment of the observed bands was hampered by the relatively low intensity of the oxide species because of the limited solubility of alumina in cryolite even at 1020 °C, and the severe overlap with the broad bands of the species present in the cryolite melts. For instance, at 1020 °C the main band in molten cryolite is centered at 555 cm^{-1} and has a full width at half-height (FWHH) of about 100 cm^{-1}. The presence of oxide species only results in a shoulder at about 510 cm^{-1} and a new band at about 200 cm^{-1} that is partly obscured by the Rayleigh wing.[12,13]

The present study was initiated with the goal to identify the complex ions that would be formed in molten eutectic mixtures of NaF/LiF/KF (FLINAK) at temperatures up to 800 °C. These studies can be considered matrix isolation experiments because the dissolved ions are kept at low concentration. Another part of this research was to investigate species formed when AlF_3 or Na_3AlF_6 was dissolved in FLINAK. In that research it was possible to isolate the AlF_6^{3-} ion in the solid FLINAK and to demonstrate that the spectrum of the octahedral AlF_6^{3-} ion persisted in the melt up to at least 750 °C. There was no evidence for the presence of any other species. Those results will be published separately.[14]

In the present study it was possible to isolate the $Al_2OF_6^{2-}$ ion in both the solid and molten phases. A number of Raman and infrared bands were identified. Assignments have been based on new theoretical ab initio molecular orbital calculations of vibrational frequencies and infrared[15,16] and Raman[16] intensities and by comparison with the reported[17] spectrum of the isoelectronic perfluorodimethyl ether $(CF_3)_2O$. As expected the spectrum of $Al_2OF_6^{2-}$ resembled that of the ether. The present experimental results show analogies to those recently reported for $B_2OF_6^{2-}$ species.[18]

Experimental Section

Samples were prepared from purified LiF, KF, NaF, and Na_2O as described previously,[14,19] by use of glovebox and premelting methods under a dry argon atmosphere (<5 ppm H_2O) or vacuum. Al_2O_3 (99.8% α-alumina, Aldrich) and Na_3AlF_6 (Fluka and Aldrich) were checked for purity.[14] The eutectic FLINAK melt was prepared in a glassy carbon crucible, in a closed furnace under argon, from the appropriate amounts of the three dry salts, further dried under vacuum at 200 °C, mixed, melted and treated at 700 °C for 20 h, and slowly cooled to room temperature. For the preparation of oxide mixtures clear pieces of FLINAK were selected, avoiding the middle region of the solid where impurities were mostly concentrated. Freshly prepared solid samples were returned to the glovebox for further manipulations and the transfer of representative pieces to Raman cells. Small pieces were loaded into a cup-shaped indentation (2 mm i.d., 1 mm depth) of a silver disk and kept under argon in the sample chamber for studies under the microscope with the Linkam temperature-controlled hotstage (Linkam HFS91/TP93) up to 600 °C as described recently.[18] Larger pieces of the samples were loaded into graphite windowless cells contained in a closed quartz tube under argon atmosphere for studies up to 750 °C in a larger furnace previously described.[20]

Raman spectra were measured with a DILOR XY 800 mm focal length CCD spectrometer with both the macro- and microscope entrances. Spectra were obtained with Ar^+ ion laser light of about 1 W power at 514.5 nm wavelength. The Rayleigh line was filtered with a Kaiser holographic SuperNotch-Plus filter (approximately 200 cm^{-1} cutoff) or with a double premonochromator. Raman light was dispersed with a single 1800 lines/mm grating onto a liquid-nitrogen-cooled CCD detector. The slits were set to 100 μm corresponding to a spectral resolution of about 5 cm^{-1}. A sheet polaroid analyzer—which permitted vertically (VV) or horizontally (VH) polarized light to pass—was used to obtain polarization data. Calibration of the wavenumber scale was achieved with neon lines superimposed on the spectrum, and wavenumbers reported are expected to be accurate to about 0.2 cm^{-1} for sharp peaks. Spectral files were collected as Labspec.tsf format files with the DILOR Labspec program and converted to Galactic.spc format files for use with the Grams32 suite of programs. All the band positions were found with the Grams32 curve resolution program employing mixed Gaussian−Lorentzian band shapes. Linear and nonlinear baselines gave essentially identical results in the 400−800 cm^{-1} region, but cubic baselines were required in the 200−400 cm^{-1} region. No smoothing was done.

Visual inspection of the molten samples that contained dissolved Na_2O revealed the melts to be cloudy, and it was assumed that this most likely was due to small solid particles of precipitated alumina. The cloudiness was more severe at higher temperatures and less of a problem at 500 °C. It became obvious that the $Al_2OF_6^{2-}$ ion slowly decomposed to produce insoluble alumina. Nevertheless, it was possible to get good Raman spectra in the windowless cell although the depolarization measurements were poor. Another consequence of the scattering from the particles was an increase in the scattering from the glass wall of the outer container. Raman spectra were obtained at 500 °C from the borosilicate glass coverslip on the Linkam and from the quartz glass containment tube for the windowless cell to establish if the weak bands indeed came from the $Al_2OF_6^{2-}$ ion. The coverslip exhibited a weak broad band centered at 480 cm^{-1} and a very weak band at about 630 cm^{-1}, while the quartz tube had a broad band centered at 450 cm^{-1} and weak bands at 490 and 600 cm^{-1}. With proper alignment, it was possible to avoid bands due to the glasses, and therefore we could exclude glass as the source of the weak bands in the oxide melts. There was also no indication of SiF_6^{2-} or BF_4^- species that often occur as impurities when fluorides are allowed to attack glass.

For the infrared experiments, disks were made by mixing 5−20 mg of sample with 300 mg of KBr in an agate mortar in the glovebox, transferring it to a die tool, and pressing it into clear 12 mm diameter disks by applying a pressure of 10 atm for 2 min. After this the disks were transferred directly to the

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sample chamber of the instrument, which was immediately evacuated. The instrument was a BOMEM DA3026 FTIR instrument, upgraded with a PCDA8 BOMEM computer. The source was a globar, the beam splitter was a KBr plate, and an MCT "wide range" detector was applied. The spectra were recorded as transmission spectra with the empty chamber serving as a reference. A Hamming function was applied prior to Fourier transformation calculations, to obtain a resolution of about 2 cm^{-1}. Other details have been explained elsewhere.[21] The spectra were converted to absorbance units, and the FLINAK spectrum was subtracted prior to analysis of the bands with the Grams/386 program.

Results and Discussion

FLINAK. There were no observable bands in the Raman spectrum of solid or molten FLINAK. The IR spectrum also was quite free of bands. Since the solid is a eutectic mixture of LiF, NaF, and KF, the absence of vibrational bands was expected because each crystal has a cubic structure with no allowed Raman bands and only one allowed infrared band at a low wavenumber outside the range of our instrument. Although there was no well-defined feature in the Raman spectrum of the FLINAK melt, the Rayleigh wing extended beyond 300 cm^{-1}. It is well-known that alkali-metal halides have a feature in the low-wavenumber region due to the polarizability changes associated with short-lived ion pairs and other aggregates.[22−25] No attempts were made to study these features as they just contribute a slowly decreasing background. Most of the spectra were recorded with a notch filter with a cutoff of about 200 cm^{-1}, which tended to distort the baseline in the 200−250 cm^{-1} region. Above 250 cm^{-1}, the baselines were relatively flat and quantitative studies of relative intensities were possible.

FLINAK with 5 mol % AlF_3 (or Na_3AlF_6) Added. Cryolite, Na_3AlF_6, has a well-documented crystal structure, known to contain discrete octahedral AlF_6^{3-} ions at all temperatures up to the melting point.[14,22,26,27] A recent X-ray crystallographic study has shown that the AlF_6^{3-} ion is almost a perfect octahedron in the high-temperature phase.[27] The Raman spectrum of solid cryolite has been assigned on this basis.[14,26] A regular octahedron belongs to the point group O_h and has six fundamental vibrational bands: $\nu_1(A_{1g}$, Raman active), $\nu_2(E_g$, Raman active), $\nu_5(F_{2g}$, Raman active), and ν_3- and $\nu_4(F_{1u}$, infrared active), with ν_6 being an inactive F_{2u} mode. For solid cryolite at room temperature the peaks are observed at 554 cm^{-1}, $\nu_1(A_{1g})$; 395 cm^{-1}, $\nu_2(E_g)$; and 345 cm^{-1}, $\nu_5(F_{2g})$. Three Raman bands characteristic of the hexafluoroaluminate ion were identified in the solids formed from FLINAK melts containing small amounts (5−10 mol %) of either AlF_3 or Na_3AlF_6. The three allowed Raman bands of the matrix-isolated octahedral complex ion were observed at 560.5 cm^{-1}, $\nu_1(A_{1g})$; 380 cm^{-1}, $\nu_2(E_g)$; and 326 cm^{-1}, $\nu_5(F_{2g})$, at 25 °C. The $\nu_2(E_g)$ mode was quite weak, but this is normally seen for octahedral complexes. Peak positions, half-widths, and relative intensities for the bands were measured for samples at different temperatures from room temperature through the melting transition and into the molten state.[14] Raman spectra for a sample of 10 mol % Na_3AlF_6 in FLINAK are shown in Figure 1, at room temperature, just below the melting point and in the molten state. In molten FLINAK at 455 °C, the $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{2g})$ modes of the AlF_6^{3-} ion were observed at 542, 365 (vw), and 324 cm^{-1}, respectively. Details of this study have been reported elsewhere.[14] The IR absorbance spectrum for a sample of 5 mol % AlF_3 in FLINAK at room temperature is shown in Figure 2 (lower curve). A band at ~594 cm^{-1} with a broad shoulder at ~622 cm^{-1} can be seen. These bands are interpreted as components of $\nu_3(F_{2u})$ in different alkali-metal ion environments, occurring at slightly higher wavenumber than in K_3AlF_6, where it was observed[28] at ~568 cm^{-1}.

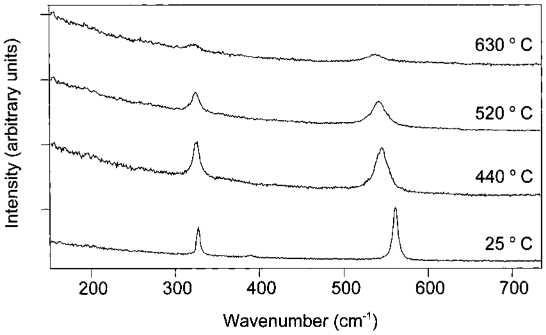

Figure 1. Raman spectra obtained for a 10 mol % mixture of Na_3AlF_6 in FLINAK versus temperature. The two lower spectra were obtained from the solid at 25 and 440 °C, whereas the two upper ones came from melts at 520 and 630 °C.

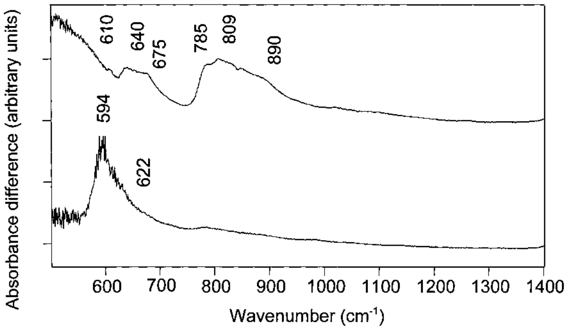

Figure 2. Infrared spectra at 25 °C, for a 10 mg sample of 5 mol % AlF_3 in FLINAK, dispersed in a 300 mg KBr disk (lower curve), and for a 5 mg sample of 5 mol % Na_2O and 5 mol % AlF_3 in FLINAK, dispersed in a 300 mg KBr disk (upper curve).

FLINAK with 5 mol % AlF_3 (or Na_3AlF_6) Added and with Added Al_2O_3. Attempts to dissolve alumina in FLINAK were not successful: With 10 mol % added AlF_3 (or Na_3AlF_6), there was no indication of any dissolved oxide in the melt even after 20 h of equilibration at 550 °C. Although the melts were very cloudy, it was still possible to detect the Raman spectrum of AlF_6^{3-} and thereafter in the solid at room temperature, but no other bands were observed. Raman bands due to α-alumina were not detected in the frozen solid, so the added α-alumina probably converted into the γ- or η-form.[1,2,9] The cloudy melts gave no indication of a Raman band for an oxide complex near 400−

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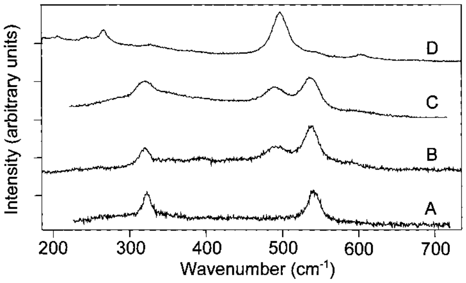

Figure 3. Raman spectra of FLINAK melts with increasing amounts of $Al_2OF_6^{2-}$, made from Na_2O reacted with Na_3AlF_6 (or AlF_3), all at 500 °C: (A) 5 mol % Na_3AlF_6 in a FLINAK melt, (B) 0.6 mol % Na_2O and 5 mol % Na_3AlF_6 in a FLINAK melt, (C) 1 mol % Na_2O and 5 mol % Na_3AlF_6 in FLINAK, (D) 5 mol % Na_2O and 5 mol % AlF_3 in a FLINAK melt.

500 cm^{-1}, as one would expect when considering the following experiments with oxide added as Na_2O (see below). The low solubility of alumina in FLINAK was expected because the solubility of alumina in pure sodium and potassium cryolite is only about 10 wt % at 1000 °C, and the solubility is known to decrease with temperature and lithium ion content.[9]

FLINAK with 5 mol % AlF_3 (or Na_3AlF_6) Added and with Added Na_2O. (a) $Al_2OF_6^{2-}$ in the Molten State. The presence of oxide, added in the form of Na_2O, resulted in a number of new Raman bands that grew in intensity with the Na_2O concentration *and* at the expense of the bands of AlF_6^{3-} (at about 540 and 326 cm^{-1}). Thus, as examples, in Figure 3, spectra for molten samples of FLINAK with 5 mol % AlF_3 (or Na_3AlF_6) with added Na_2O are shown at 500 °C along with a spectrum of 5 mol % Na_3AlF_6 in FLINAK at the same temperature. We assign the new band at 494 cm^{-1} to the symmetric stretching (breathing) vibration of the oxide species, $Al_2OF_6^{2-}$. $Al_2O_2F_4^{2-}$ is not likely to be present because the same bands were found for Al:O ratios ranging from 5:1 to 1:1 and because the melts were quite dilute. Polarization measurements were sufficiently conclusive to establish that this band was polarized. A wavenumber difference of 47 cm^{-1} is found between the $Al_2OF_6^{2-}$ peak at 494 cm^{-1} and the $\nu_1(A_{1g})$ peak of the AlF_6^{3-} ion at 541 cm^{-1}. This difference is essentially of the same magnitude as the difference between the most intense peak at 555 cm^{-1} in molten cryolite and the oxide peak at about 510 cm^{-1}, as reported by Gilbert et al.[12,13] Although the positions of these peaks are temperature and concentration dependent,[12,13] it seems reasonable to suggest that both sets of peaks have analogous origins.[14] The peak maxima in FLINAK melts for the ν_1 mode of the AlF_6^{3-} ion (541 cm^{-1}) and the stretching mode of $Al_2OF_6^{2-}$ ion (494 cm^{-1}) are much lower than for these ions in cryolite melts. At the high temperature needed to melt the cryolite (1020 °C), the frequencies of the $\nu_1(A_{1g})$ band of the AlF_6^{3-} ion and the strongest stretching band of the $Al_2OF_6^{2-}$ ion are about 15 cm^{-1} higher than what was found for the corresponding bands in the FLINAK melt at 500 °C. This observation suggests that the electrostatic field of the alkali-metal ions have a strong influence on the Al−F bond strength. In FLINAK, Li^+ and K^+ ions apparently lower the Al−F bond strength, causing the frequency to decrease. Further support for this interpretation comes from the observation that the peak position of the 494 cm^{-1} band due to $Al_2OF_6^{2-}$ has a large temperature coefficient similar to that of the ν_1 mode of AlF_6^{3-} found previously.[14] The effect of temperature is further discussed in a separate section below.

Melts of several compositions—with different ratios of Na_2O to AlF_3—were prepared in an attempt to see if the concentration of $Al_2OF_6^{2-}$ relative to AlF_6^{3-} could be varied. In general the intensity of the 494 cm^{-1} band of $Al_2OF_6^{2-}$ exceeded that of the 541 cm^{-1} band of AlF_6^{3-} when the mole ratio of added Na_2O to AlF_3 exceeded 0.5. As shown in Figure 3, it was possible to convert almost all of the AlF_6^{3-} to the oxide complex. However, the tendency of the $Al_2OF_6^{2-}$ to transform into insoluble η-alumina made a quantitative study difficult. The best spectrum of the $Al_2OF_6^{2-}$ ion in FLINAK at 500 °C was obtained for a sample with 5 mol % Na_2O and 5 mol % AlF_3 (Figure 4). In this spectrum, the band of $Al_2OF_6^{2-}$ at 494 cm^{-1} was very intense, while the Raman bands of AlF_6^{3-} at 325 and 541 cm^{-1} were barely detectable. Additional bands of $Al_2OF_6^{2-}$ could also be identified, as listed in Table 1.

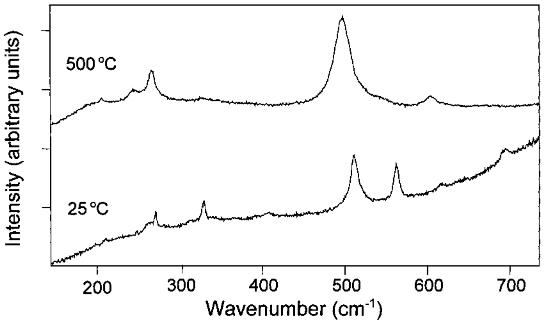

Figure 4. Raman spectrum of $Al_2OF_6^{2-}$ made from 5 mol % Na_2O and 5 mol % AlF_3, in a FLINAK solid at 25 °C (lower curve) and in a FLINAK melt at 500 °C (upper curve).

(b) $Al_2OF_6^{2-}$ in the Solid State. The Raman spectrum obtained from the same (premelted) solid sample—consisting of 5 mol % Na_2O and 5 mol % AlF_3 in FLINAK—is shown in Figure 4 (bottom curve). The IR spectrum is shown in Figure 2 (upper curve). Obviously it is possible to trap—in the solid FLINAK eutectic matrix—an oxide-containing species that we believe must be the $Al_2OF_6^{2-}$ ion. The most intense room-temperature Raman band at 509 cm^{-1} is assigned to the oxide-bridged totally symmetric stretching mode of the $Al_2OF_6^{2-}$ ion, the same band that was observed at 494 cm^{-1} in the FLINAK melt at 500 °C. Additional bands of the oxide complex at room temperature correspond to similar bands detected when the oxide complex is in the molten state (Table 1). It should be noted that the wavenumber maximum of the oxide Raman peak at 494 cm^{-1} was found to be very temperature sensitive (infrared data were only obtained at room temperature).

(c) Effect of Temperature and Time. As mentioned, the Raman band due to the symmetric stretching (breathing) mode of the $Al_2OF_6^{2-}$ ion was detected at 494 cm^{-1} in molten FLINAK at 500 °C, and at 509 cm^{-1} in the solid at 25 °C. Since this seemed a significant frequency shift, the sample of 5 mol % Na_2O and 5 mol % AlF_3 in FLINAK was studied over a temperature range from 25 to 550 °C. This study confirmed the identification of the bands: Peak maxima and half-widths of the two most intense spectral bands from the samples at different temperatures appeared to change smoothly through the melting point into the melt and up to 550 °C. The effect of temperature on the peak maximum and half-width of the bands was considerable (Figure 5). The behavior is consistent with the assignments (Table 1). The two most characteristic bands of the $Al_2OF_6^{2-}$ ion shifted from 509 (FWHH = 13) and 268 (FWHH = 4) cm^{-1} in the FLINAK solid at 25 °C to 493 (FWHH = 27) and 265 (FWHH = 14) cm^{-1} in the FLINAK melt at 550 °C. Similar behavior has been reported for the bands from AlF_6^{3-} in FLINAK.[14] The smooth transition through the melting point suggests a disordered structure for the ion in solid FLINAK, having a structure somewhat similar to what it has in the melt.

Table 1. Raman and IR Spectral Data (cm^{-1}) for $M_2OF_6^{x-}$ Compounds (M = C, Al, B)[a]

$(CF_3)_2O$	$(AlF_3)_2O^{2-}$					$(AlF_3)_2O^{2-}$	$(BF_3)_2O^{2-}$
liquid[b], Mode, C_{2v} symmetry, 25 °C, ref 17	FLINAK(s), 25 °C, this work	FLINAK(s), 400 °C, this work	FLINAK (l), 500 °C this work	calculated, D_{3d} symmetry		(Na,K)F−AlF_3−Al_2O_3 (l), 1020 °C ref 12	FLINAK(s,l), 25 and 500 °C, ref 18
				ref 15[d]	ref 16[e]		
$\nu_3(A_1)$ R 1329 w; IR vs	IR 890 vs			IR 1011, 554[f]	IR A_{2u} 1097, 604[f]		IR 1225, −
$\nu_{14}(B_1)$ R 1250 vvw; IR vs	IR 809−785 vs			IR ∼677, ∼392[f]	IR E_u 753, 502[f]		IR 971, −
$\nu_1(A_1)$ R 1279 w	691 m IR 675 w	670 vw	670 vw	R 703 R 672	R E_g 742, 0.37[g] $\rho = 0.75$ dp		
$\nu_{12}(B_1)$ R 1170 vvw; IR vs	IR 640 w			IR 584, 176[f]	IR A_{2u} 654, 178[f]		IR 577, −
$\nu_{17}(B_1)$ R 970 vvw; IR s	613 w IR 610 vw	605 w	601 m[c]	R 664	R A_{1g} 772, 0.12[g] $\rho = 0.10$ p		R 703, 709 s p
$\nu_6(A_1)$ R 852 vs	509 vs	498 vs	494 vs p	R 446	R A_{1g} 492, 3.2[g] $\rho = 0.00$ p	530 w	R −, 650 w p
$\nu_2(A_1)$ R 747 m, p	407 w		380 vw	IR 348, ∼52[f]	IR E_u 380, 90[f]	450 w	
$\nu_{13}(B_1)$ R 690 vw, dp				IR 323, 120[f]	IR A_{2u} 341, 157[f]		
$\nu_{20}(B_2)$ R 650 vw, dp	268 m	266 m	265 s[c]	R 200	R A_{1g} 214, 0.50[g] $\rho = 0.37$ p		R 430, 430 w[c]
$\nu_{15}(B_1)$ R 574 w, dp	260 m	245 w	242 m[c]	R 293 R 288	R E_g 301, 0.42[g] $\rho = 0.75$ dp		
$\nu_4(A_1)$ R 527w, p	235 vw			IR ∼226, ∼1.6[f]	IR E_u 235, 3.9[f]		
$\nu_5(A_1)$ R 368 s, p	208 vw		206 w[c]	R 183 R 173	R E_g 181, 0.24[g] $\rho = 0.75$ dp	200 w	
$\nu_{16}(B_1)$ R 355 w, sh, dp				IR 96 0.5[f] IR 92, 0.03[f]	IR E_u 51, 0.18[f]		
$\nu_7(A_1)$ R 178 w, p				inact 79[h]	inact A_{1u} 13[h]		

[a] IR = infrared, R or no label = Raman, dp = depolarized, p = polarized, s = strong, v = very, w = weak. For the $Al_2OF_6^{2-}$ ion in FLINAK (this work), the peak maximum wavenumber and FWHH (in parentheses) are given versus temperature. [b] Not all IR bands given[17] are included. [c] Polarization dependence could not be determined, due to scattering from particles. [d] Done[15] with the DGauss 2.3.1 quantum mechanical software and triple-ζ plus polarization (TZP) basis sets under the generalized gradient approximation (GGA) using the Becke88 and Lee−Yang−Parr for the exchange and correlation functionals and without any fixed symmetry. The optimized Al−O and Al−F distances and F−Al−F angles were 1.73 and 1.75 Å and 104.3° and 104.9°, respectively. The Al−O−Al angle was 180°, and the symmetry was given as the staggered D_{3d} symmetry. Unfortunately, only calculated *infrared* intensities were given. [e] Done[16] with the Gaussian-92 program based on the restricted Hartree−Fock method and with the RHF 6-31+G* basis set. No preassumed symmetry was imposed. ρ denotes the depolarization ratio calculated. Optimized Al−O and Al−F distances and O−Al−F angles were 1.702 and 1.716 Å and 113.8°, respectively. The Al−O−Al angle was 180°, and the symmetry was strictly given as the staggered D_{3d} symmetry. [f] Calculated intensity for the infrared-active mode (denoted IR), given in km/mol units.[15,16] [g] Calculated intensity for the Raman-active mode (denoted R), given in Å^4/AMU units.[16] [h] The A_{1u} mode is neither Raman nor infrared active.

The cloudy appearance of melts was a characteristic feature throughout this study. Since efforts to prepare cleaner melts were unsuccessful, it seemed possible that the solid particles were produced while the experiments were in progress. To investigate this, the sample of 5 mol % Na_2O and 5 mol % AlF_3 in FLINAK was left molten at 500 °C for 24 h and then at 550 °C for another 24 h period. The Raman spectra obtained versus time were stable during the first 24 h and then clearly showed a large decrease in the intensity of the 494 cm^{-1} band of $Al_2OF_6^{2-}$ relative to the 541 cm^{-1} band of AlF_6^{3-} (see Figure 6). This observation suggests the reaction

$$3Al_2OF_6^{2-} + 6F^- \rightarrow \eta\text{-}Al_2O_3 + 4AlF_6^{3-}$$

which would eventually consume all the $Al_2OF_6^{2-}$. There was no evidence of other reactions in the form of new peaks. The glass containment vessel of the windowless Raman cell was not etched even after several days at the temperature of molten FLINAK. The conclusion is that $Al_2OF_6^{2-}$ is metastable in FLINAK melts at 550 °C. The Raman spectrum of α-alumina has a strong and sharp characteristic peak at 417 cm^{-1}. Since we were unable to detect this peak, we assume that the alumina precipitates as a disordered form, referred to as η-alumina as suggested by Foster.[9]

(d) Assignment of Bands of $Al_2OF_6^{2-}$. For the AlF_3 group in an $Al_2OF_6^{2-}$ ion, we expect Al−F stretching and AlF_3 bending vibrations to occur around ∼600 and ∼350 cm^{-1}. The Al−O−Al stretching is normally found at ∼500 cm^{-1}. For the inherent low symmetry this means that intense couplings of normal modes are probable.

It is to be expected that the $Al_2OF_6^{2-}$ ion will have the structure of two tetrahedrons connected through a bridged oxygen atom. Although a bent Al−O−Al bond was expected, theoretical calculations[15] by ab initio quantum mechanical methods with DGauss 2.3.1 software and TZP basis sets at the GGA level of computation (Becke88 and Lee−Yang−Parr for the exchange and correlation functionals) have indicated a *linear* Al−O−Al configuration. The optimum geometry was found to have D_{3d} symmetry, although the absence of degenerate E modes for the calculated frequencies suggested a lower symmetry. Unfortunately, only calculated *infrared* intensities were reported.[15] The molecular orbital calculations have been repeated[16] at the restricted Hartree−Fock level using the Gaussian-92 program and the 6-31+G* basis set with tight convergence criteria and without any preassumed symmetry of the $Al_2OF_6^{2-}$ ion, confirming convergence to the D_{3d} symmetry and the linear Al−O−Al bond. These calculations involved determinations of harmonic force constants of the normal modes, and both infrared and Raman frequencies as well as the intensities were calculated,[16] aiding the assignment of the Raman and IR spectra (see Table 1).

Under D_{3d} symmetry the 21 vibrations of $Al_2OF_6^{2-}$ transform as (R = Raman, IR = infrared, ia = inactive)

$$\Gamma_{\text{vibration}} = 3A_{1g}(\text{R, p}) + 3E_g(\text{R, dp}) + 1A_{1u}(\text{ia}) + 3A_{2u}(\text{IR}) + 4E_u(\text{IR})$$

The six Raman-active bands predicted from the calculations[16] were found to be in reasonable agreement with those observed in the Raman spectrum. In particular polarized A_{1g} bands were calculated at 492 and 214 cm^{-1} for the bridged-oxygen symmetric stretching and bending modes, and these appear to correspond to the strongest observed Raman bands at 494 and

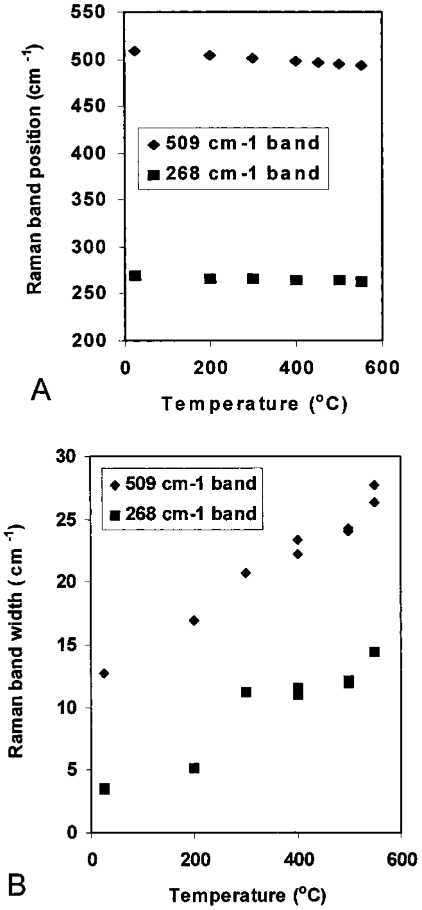

Figure 5. Peak positions (A) and FWHH bandwidths (B) in wavenumbers versus temperature for the two most intense Raman bands of $Al_2OF_6^{2-}$. Results are for the 5 mol % Na_2O and 5 mol % AlF_3 in FLINAK.

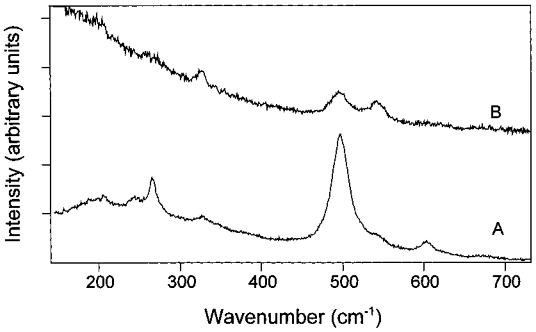

Figure 6. Raman spectra of a sample with 5 mol % Na_2O and 5 mol % AlF_3 in FLINAK: (A) a melt at 550 °C when remelted after preparation (spectrum stable for 24 h), (B) a melt after 24 h at 550 °C.

242 cm^{-1} in molten FLINAK at 500 °C. As seen in Table 1 the fit between calculated values and those observed is so good that it seems reasonable to assume that the ion found is indeed $Al_2OF_6^{2-}$. The same applies to room temperature, and as discussed, there is a gradual correspondence between the bands seen in the melt and in the solid phase. The peaks in the infrared fit into this picture. The lack of an entirely perfect fit is to be expected, partly due to imperfections in the restricted Hartree–Fock model and partly due to the simplification made to exclude the cations from the model.

The Raman spectrum of $Al_2OF_6^{2-}$ in molten FLINAK exhibits a striking similarity to the spectrum of perfluorodimethyl ether, CF_3OCF_3 or C_2OF_6, in the liquid phase, reported by Bürger and Pawelke.[17] These authors also made normal coordinate calculations using an overall C_{2v} symmetry with pseudo-C_3 symmetry of the CF_3 groups and with a C–O–C bond angle of 115°. Although the IR normal mode calculations gave strongly mixed modes, a very strong Raman band at 854 cm^{-1} could be assigned to a mode involving predominantly C–O stretching while a strong Raman band 368 cm^{-1} was assigned to a symmetric mode of essentially CF_3 rocking and another Raman line at 178 cm^{-1} was assigned to be mostly C–O–C deformation.

Previously, in our laboratory we have found IR and Raman evidence for the formation of $B_2OF_6^{2-}$ in FLINAK melts.[18] The situation was completely analogous to the aluminum case studied here, although those bands were of much lower intensity. That was presumably why only the strongest bands were seen in the Raman spectrum.

To facilitate comparisons of IR and Raman bands observed, all data for $Al_2OF_6^{2-}$ are presented in Table 1, along with the values calculated theoretically, and the corresponding observed values for C_2OF_6 and $B_2OF_6^{2-}$ from the literature.

Conclusions

Raman spectra obtained for mixtures of Na_2O dissolved in the eutectic FLINAK melt at 500 °C, which contained a low concentration of either AlF_3 or Na_3AlF_6, exhibited new bands. The new bands have been assigned to the oxyfluoroaluminate ion, $Al_2OF_6^{2-}$. Furthermore, it was possible to trap the $Al_2OF_6^{2-}$ ion in the frozen FLINAK solid and to measure its Raman and IR spectra at 25 °C. Although a number of bands have been detected, the two most characteristic bands of the $Al_2OF_6^{2-}$ ion were found at 494 (polarized) and 265 cm^{-1} in the FLINAK melt at 500 °C. These bands occurred at 509 and 268 cm^{-1} in the FLINAK solid at 25 °C. In the absence of added oxide, the dissolved aluminum fluoride was in the form of the octahedral AlF_6^{3-} ion, which has characteristic Raman bands at 542 and 325 cm^{-1} in the FLINAK melt at 500 °C. Whereas alumina, Al_2O_3, was found to be essentially insoluble in FLINAK, it was possible to dissolve sufficient amounts of Na_2O to convert most of the AlF_6^{3-} to the soluble oxyfluoroaluminate, $Al_2OF_6^{2-}$. The $Al_2OF_6^{2-}$ ion was found to be metastable in molten FLINAK, reacting slowly to produce insoluble γ- or η-alumina.

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