

The Dissociation of Fluoroaluminates in FLiNaK and CsF–KF Molten Mixtures: A Raman Spectroscopic and Solubility Study

F. Auguste,[†] O. Tkatcheva,[‡] H. Mediaas,[‡] T. Østvold,[‡] and B. Gilbert^{*†}

Laboratory of Analytical Chemistry and Electrochemistry, B6C, The University of Liège, Liège B-4000, Belgium, and Department of Chemistry, Sem Sealandsvet 12, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

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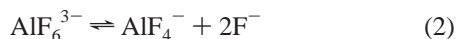
By using a new furnace design, M_3AlF_6 ($M = Na, K, Cs$) and mixtures of small amounts of AlF_3 in FLiNaK (46.5 mol % LiF, 11.5 mol % NaF, 42 mol % KF) and CsF–KF eutectic have been investigated over a wide temperature range (25–1050 °C) by Raman spectroscopy. The peak positions and their relative intensities have been measured as a function of temperature. In FLiNaK, up to 750 °C, the bands shift gradually to lower wavenumbers, and their halfwidths increase in agreement with published data. However, it is shown from solubility measurements and Raman data that, in these conditions, the mixture is not totally molten and the spectra correspond mainly to AlF_6^{3-} in the solid state. When the mixture is completely molten, a new band appears clearly on the high-frequency side of the main band of the spectrum, and its intensity grows up when the temperature is increased. The present results are a clear confirmation of the dissociation of AlF_6^{3-} into AlF_5^{2-} and AlF_4^- that our study of the Raman bands of the fully melted systems $MF-AlF_3$ ($M = Na, K, Li$) previously suggested. On these systems, it is then important to know if the spectra belong mainly to solid or liquid fluoroaluminates before drawing any conclusion concerning the liquid phase structure.

Introduction

The solvent in the Hall–Héroult process of aluminum production is cryolite (Na_3AlF_6). Considering the industrial interest of this electrolyte, the structure of molten cryolite has been extensively studied.¹ It is generally agreed that Na_3AlF_6 is totally ionized in Na^+ and AlF_6^{3-} as follows:



Many experiments have shown that the AlF_6^{3-} anion further dissociates, but the dissociation scheme is still under discussion. For many years, it has been assumed that AlF_6^{3-} dissociates at least partially into AlF_4^- and F^- ions² according to the equilibrium



The Raman spectra of the NaF– AlF_3 mixtures were also interpreted in terms of both the AlF_6^{3-} and AlF_4^- anions.^{3–5}

In 1986, Dewing,⁶ in an attempt to account for various thermodynamic anomalies, presented a different dissociation scheme which considered the following two equilibria:



On the basis of the suggestion made by Dewing,⁶ detailed Raman spectroscopic investigations of molten alkali fluorides containing AlF_3 have been conducted over the past 15 years.^{7–12} A significant effort has been devoted to the

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* Corresponding author. E-mail: B.Gilbert@ulg.ac.be.

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[‡] Norwegian University of Science and Technology.

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improvement of the instrumentation used for Raman studies of corrosive molten salts, and despite the difficulties originating from corrosion, vapor pressure, and high temperatures, high quality Raman spectra could be obtained on a routine basis.⁹

All the mixtures were then reinvestigated in a large composition range. At first, because of the experimental difficulties, the recordings were made at the lowest melting temperature. In a second step, because the dramatic influence of the temperature was recognized, the measurements were made at constant temperature, chosen as the highest melting point of the series of mixtures under investigation.⁷⁻⁹

Initial results obtained on molten $\text{AlF}_3 - \text{MF}$ (with $\text{M} = \text{Li, Na, K}$) showed that, in specific conditions (low temperature and high MF content), the main peak, originally attributed to AlF_6^{3-} , is clearly distorted and possibly indicates the presence of another complex species. Actually, in all cases, the most intense spectrum components are made of three distinct bands whose relative intensities vary when the composition and/or the temperature is changed. For example, in the $\text{NaF}-\text{AlF}_3$ system, the main species existing in a 1:1 molar mixture is AlF_4^- , with the fundamental vibrational bands observed at 622 cm^{-1} (ν_1 , strong and polarized), 760 cm^{-1} (ν_3 , weak and depolarized), and 320 and 215 cm^{-1} (ν_4 and ν_2 , medium and depolarized). These are the only bands, all due to the AlF_4^- tetrahedron, which were observed at temperatures between the melting point of NaAlF_4 up to $1000 \text{ }^\circ\text{C}$. When the mole fraction of NaF is gradually increased, two new bands appear: one strong and polarized at 560 cm^{-1} , and another weak and depolarized around 345 cm^{-1} . If the amount of NaF is increased further, again two new additional bands appear, one as a shoulder at 510 cm^{-1} (strong, polarized) and the other around 320 cm^{-1} (weak and depolarized). It was also found that the relative intensities between these three groups of bands are clearly influenced by temperature.^{8,10} A decrease in temperature produced an increase of the 560 and 510 cm^{-1} band intensities while the intensity of the 622 cm^{-1} band decreased. The other $\text{MF}-\text{AlF}_3$ systems (with $\text{M} = \text{Li, K, Cs}$) exhibit the same general features, but the peak positions can be slightly different.

The structural and thermodynamic behaviors, as a function of temperature and melt composition (even with dilution in NaCl and KCl), have consequently been interpreted, qualitatively and quantitatively, on the basis of the dissociation model presented by Dewing,⁵ the main Raman bands at 510 , 560 , and 622 cm^{-1} being assigned, respectively, to AlF_6^{3-} , AlF_5^{2-} , and AlF_4^- .⁷⁻¹¹

The evidence for the existence of AlF_5^{2-} given by Raman spectroscopy has been criticized by several authors.^{12,13} One of the reasons for the criticism is that the group theory predicts two main symmetrical vibrations for the presumed bipyramidal AlF_5^{2-} anion and only one is actually observed.¹³

This problem has already been discussed and explained through a pseudorotation at high temperature leading to a coalescence of the two very similar vibrations into a single one.^{8,14,15} This phenomenon has already been noticed for other structures, such as the K_3ZrF_7 crystal¹⁶ which contains isolated ZrF_7^{3-} pentagonal bipyramid (D_{5h}) species. The vibrational analysis predicts two symmetrical vibrations. The room temperature spectrum shows only one A_1'' mode at 544 cm^{-1} . But at liquid nitrogen temperature, this band splits into two at 551 and 536 cm^{-1} . Such splitting is attributed to the separation of axial (551 cm^{-1}) and equatorial (536 cm^{-1}) symmetric stretching frequencies of the pentagonal bipyramid species. The second reason is that the low frequency peak assigned to AlF_6^{3-} occurs mainly as a weak shoulder,⁷⁻¹¹ and its existence has therefore been questioned. Recently, by using a 360° viewing device, Brooker et al.¹² have presented interesting Raman results obtained on mixtures of AlF_3 in FLiNaK (46.5 mol % LiF , 11.5 mol % NaF , 42 mol % KF). The spectra were recorded from the solid state ($25 \text{ }^\circ\text{C}$) up to $750 \text{ }^\circ\text{C}$. The expected advantage of using FLiNaK as solvent is its low melting point ($450 \text{ }^\circ\text{C}$). This allowed experiments at much lower temperatures than with the $\text{MF}-\text{AlF}_3$ binaries. Brooker et al. found only one main peak in the 550 cm^{-1} range, clearly assigned to octahedral AlF_6^{3-} in the solid state.¹⁷⁻¹⁸ The frequency of this band decreased gradually when the temperature was increased. This behavior was interpreted on the basis of the assumption of only one discrete species, AlF_6^{3-} , while AlF_5^{2-} as well as AlF_4^- were excluded. These authors, however, did not measure the solubility of AlF_3 in FLiNaK . They actually noticed the presence of solid particles which was proposed as due to undissolved aluminum oxides as the particles seemed to disappear upon using sublimed AlF_3 . Their conclusion therefore was based on the assumption that AlF_3 (or $\text{Na}_3\text{-AlF}_6$) was fully soluble in molten FLiNaK regardless of the temperature. Preliminary experiments where our molten mixtures could be observed visually showed that this assumption is probably not correct, since the melt, made with sublimed AlF_3 , stayed milky white up to about $720 \text{ }^\circ\text{C}$. Above this temperature, the melt became transparent. This indicates that a solid phase exists at lower temperatures.

Since the 90° viewing windowless cell concept⁶ cannot be used for nontransparent mixtures, a new furnace and cell design has been developed. This system allows measurement to be performed from the top of a melt, which is now simply contained in a graphite crucible. By using a cooled quartz window, protected from most of the vapor condensation, recordings could be made in the temperature range $25-1050 \text{ }^\circ\text{C}$, on the same melt system as used by Brooker et al. In addition, Na_3AlF_6 , Cs_3AlF_6 , K_3AlF_6 , and mixtures of small amounts of AlF_3 in the eutectic $\text{CsF}-\text{KF}$ (43 mol % KF , 57

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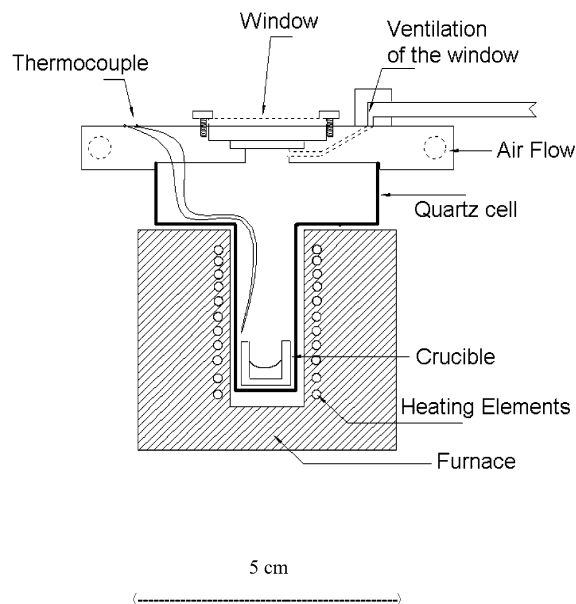


Figure 1. Cross-section of cell container allowing recording of Raman spectra of solid and liquid samples up to 1050 °C.

mol % CsF) have then been investigated by Raman spectroscopy from the solid to the fully molten state.

Solubility measurements of cryolite have also been performed in the FLiNaK eutectic in the temperature interval 500–750 °C in order to confirm the hypothesis of low solubility of AlF_3 and Na_3AlF_6 in FLiNaK at these temperatures.

The purpose of this work is to investigate the phenomena occurring during the solid–liquid transition, which need to be taken into account to fully understand the structural behavior of fluoroaluminates.

Experimental Section

Chemicals. Na_3AlF_6 was hand-picked cryolite from Greenland, dried under vacuum at 400 °C for 6–8 h. Alkaline fluorides, NaF (Merck Zur analyse), KF (Merck Zur analyse), and LiF (Alfa 99.5%), were purified by slow crystallization from the melt under N_2 atmosphere. CsF (Aldrich, 99.9%) was slowly dried under vacuum at 500 °C, and AlF_3 (BDH, fluortran) was purified by sublimation at 1000 °C under vacuum in a graphite container. The mixtures were prepared in a nitrogen-filled drybox in which the water content never exceeded 5 ppm. The weighed salts for Raman analysis were premelted under nitrogen atmosphere in a glassy carbon crucible before being added to the Raman cell.

Apparatus for Spectroscopy. The improved data presented in this paper were possible owing to the development of a new cell container and furnace setup, which allows us to collect the scattered light in the same direction as the incident laser beam. Figure 1 illustrates the cross section of the cell container. It is mainly composed of T-shaped quartz tubing whose bottom part is a cylinder of 3.5 cm in length and 1.5 cm in diameter where the glassy carbon crucible containing the melt is deposited. Several clips (not drawn) are pressing the quartz tubing tightly against a brass lid which serves as cover. The center of the lid is fitted with a quartz window for the laser beam and for collecting the Raman light. The air-tightness of the cell and the window is ensured through silicone joints. The window is partially protected from vapor deposition by a tangential argon flow and remains reasonably clean and transparent

for a couple of hours. Pipes in the brass lid were provided to allow an air or water flow to ensure the cooling of the lid. The temperature is measured at the level of the crucible with a Pt–Pt 10% Rh thermocouple. The connection to the thermocouple is made by contacts with insulated links passing through the lid.

Because the transparency of the window can be ensured only for a limited time, the duration of the experiments is also limited (about 2 h). For a full temperature scan, the temperature of the sample is increased stepwise from 25 to 1050 °C. Due to limited experimental time, the Raman spectra were recorded without waiting for a complete temperature stabilization. The temperature is thus only known with an accuracy of ± 10 °C. However, in the temperature ranges where the major changes occurred, all the experiments were repeated several times with new melts by increasing the temperature first quickly close to the temperature of interest, and then slowly. The spectra were obtained with a Dilor Labram using the 514.5 nm line of an argon ion laser with a power of 150 mW for the FLiNaK samples and the 488 and 514.5 nm lines with the same power for the samples made with cesium and potassium fluorides.

Solubility Measurements. The solubility measurements were carried out in an argon-filled glovebox, with a water and oxygen content < 1 ppm, tightly connected to the furnace. The graphite radiation shields, sampling tubes, stirrer, and glassy carbon crucible were dried under vacuum at 900 °C for 6–8 h. The glassy carbon crucible was filled with weighed amounts of sodium, potassium, and lithium fluorides giving the FLiNaK composition, and placed at the bottom of a quartz container. Radiation shields of glassy carbon fitted above the crucible had holes to accommodate the thermocouple, graphite stirring rod, quartz tube for additions, and graphite sampling tube. The thermocouple was contained in an alumina case with platinum sheets and placed just above the melt. The graphite sampling tube had a graphite filter of porosity 3 (15–40 μm). The measurements were performed with about 70 g of FLiNaK and about 3.7 mol % of cryolite in the crucible. The molten salt mixture was stirred and equilibrated at the required temperature from 750 to 500 °C for 7–22 h, and then sampled through the graphite filter. Inductive coupled plasma emission spectroscopy (ICP) was used to determine the aluminum concentration in the filtered samples. Solutions for ICP analysis were prepared as follows: about 0.5 g of sample was crushed in an agate mortar, weighed, and placed in a glassy carbon crucible, and then 10 g of NaOH was added. The crucible containing the mixture was kept under argon flow at 470–480 °C for 3–4 h. The cooled melt was transferred to a plastic container, and distilled, deionized water was added up to 200 g.

Results

The Raman spectrum of 3 mol % AlF_3 in FLiNaK at room temperature (Figure 2) reveals two main bands located at 328 and 560 cm^{-1} . When the temperature is increased, the following observations can be made: (1) The bands shift gradually to lower wavenumber, and their half-widths increase. The temperature effect is more pronounced for the 560 cm^{-1} peak. The location of its maximum intensity shifts down 25 cm^{-1} when the temperature reaches 740 °C. (2) At about 740 °C, the intensity of the bands drops and the spectra are very noisy. But already at 750 °C, the intensity increases again, and the band shape changes. The main band is split into two peaks, one located at about 515 cm^{-1} and the other one at 560 cm^{-1} . Both bands are fully polarized and can

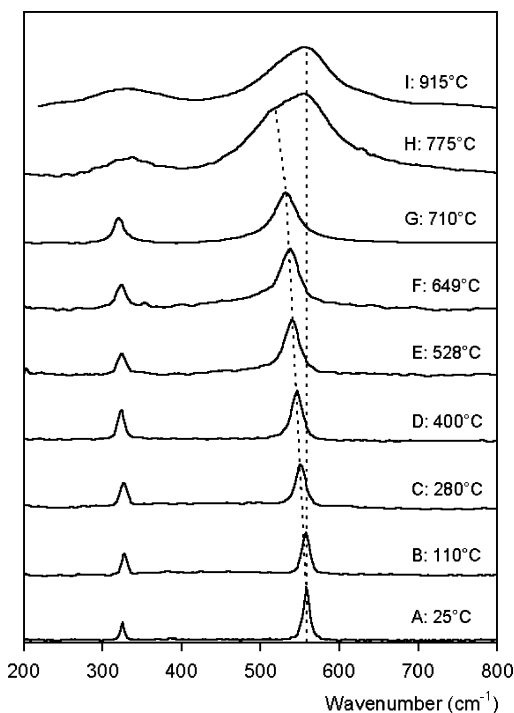


Figure 2. Raman spectra of mixture made of 3 mol % AlF_3 in FLiNaK at different temperatures. The spectra noted H and I are recorded on fully molten mixtures.

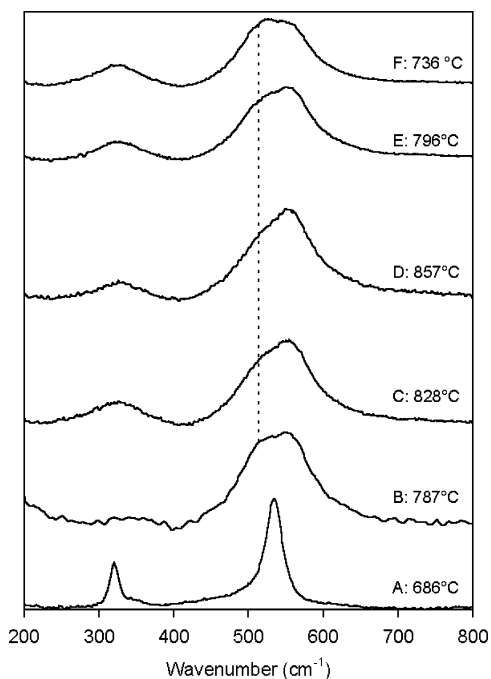


Figure 3. Details of spectra recorded when the 3 mol % AlF_3 in FLiNaK system started to melt. Spectrum A belongs to a sample where the fluoroaluminate is still mainly solid. The other recordings are from liquids. The temperature was increased from A to D and then decreased from D to F. The change of the intensity ratio of the two main peaks is shown to be reversible.

then be assigned to symmetrical vibrations. (3) The intensity ratio of these two peaks changes with temperature. The intensity at 515 cm^{-1} decreases with temperature while the other one increases. This process is reversible as shown in Figure 3. The same experiment has also been done with FLiNaK + 10% AlF_3 . The full melting occurs at about 800

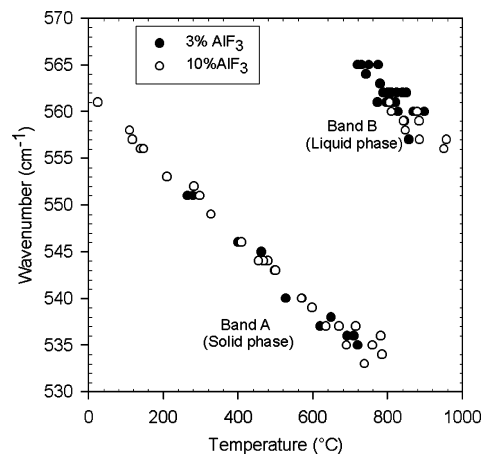


Figure 4. Variation of the location of (A) the main band observed from room temperature and (B) the new band appearing after full melting for the AlF_3 -FLiNaK mixtures; full circles (\bullet), 3 mol % AlF_3 ; empty circles (\circ), 10 mol % AlF_3 .

$^{\circ}\text{C}$; the observations are identical except that the spectra are less noisy since the relative amount of scattering species is larger. Figure 4 shows in more detail the variation, with temperature, of the location of the main bands around $500\text{--}550\text{ cm}^{-1}$ for both mixtures. The indicated frequencies are the location of (i) the main band observed from room temperature (band A) and (ii) the new band appearing after full melting (band B). The data show clearly a decrease in frequency when the temperature is increased, both in the solid and liquid phases.

It is well-known that the bandwidths of some symmetrical vibrations are strongly affected when the cation is changed.¹⁹ The bandwidth increases when the size of the cation decreases, and this observation has been interpreted as a much stronger interaction between cations and anions in the melt in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. Using an eutectic based on the binary CsF-KF, the expected bandwidth decrease should allow for a better separation of the overlapping peaks, and measurements on such systems were then initiated. The behavior of AlF_3 in the eutectic CsF-KF was found to be similar to the one in FLiNaK. Figure 5 shows the Raman spectra obtained during heating of the CsF-KF + 7.5% AlF_3 sample. At room temperature, the main peak is located at 533 cm^{-1} . The relative intensities of all the bands and their frequency interrelation indicate that the solid formed is mostly in “elpasolite” Cs_2KAlF_6 -like structure, as also confirmed from an X-ray diffraction analysis. Upon increasing the temperature, the main band shifts down to 510 cm^{-1} . At about $670\text{ }^{\circ}\text{C}$, the mixture melts, and a new peak appears at 554 cm^{-1} , which replaces progressively the one at 510 cm^{-1} . As expected, it is indeed found that the widths of the bands are narrower, and the existence of two peaks is indisputable.

Finally, in order to confirm the present observations and since the new furnace setup allows it, measurements have also been made with samples of pure M_3AlF_6 (with $\text{M} = \text{Na}, \text{K}, \text{Cs}$) (Figures 6–8).

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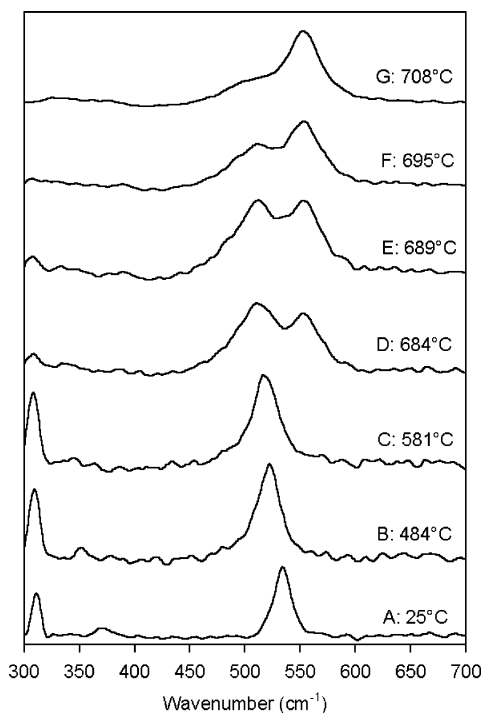


Figure 5. Raman spectra of a 7.5 mol % AlF_3 in CsF-KF mixture at different temperatures from the solid to the fully liquid state.

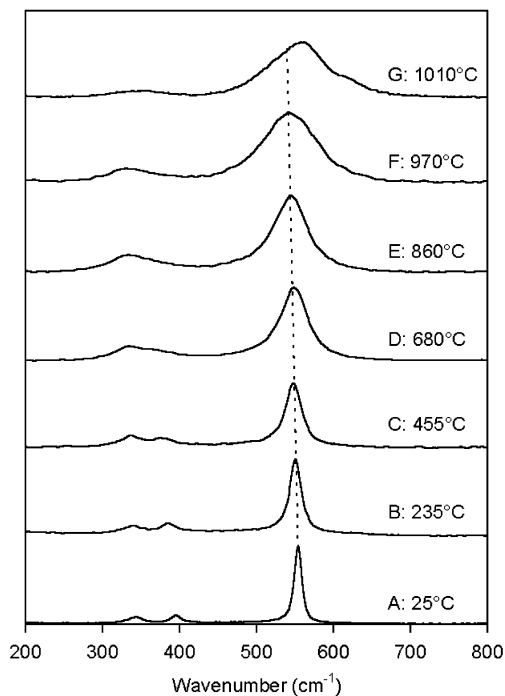


Figure 6. Raman spectra of Na_3AlF_6 at different temperatures from the solid to the liquid state.

Discussion

According to the results presented in the literature,^{12,17–18} we can clearly assign the bands observed in the frozen melt to the AlF_6^{3-} anion with its ν_1 symmetrical band being located around 560 cm^{-1} . In addition, since the solid is a mixture of fluoroaluminate diluted and finely dispersed into FLiNaK , the ν_1 band was found polarized even at room temperature. Upon increasing the temperature, the downward

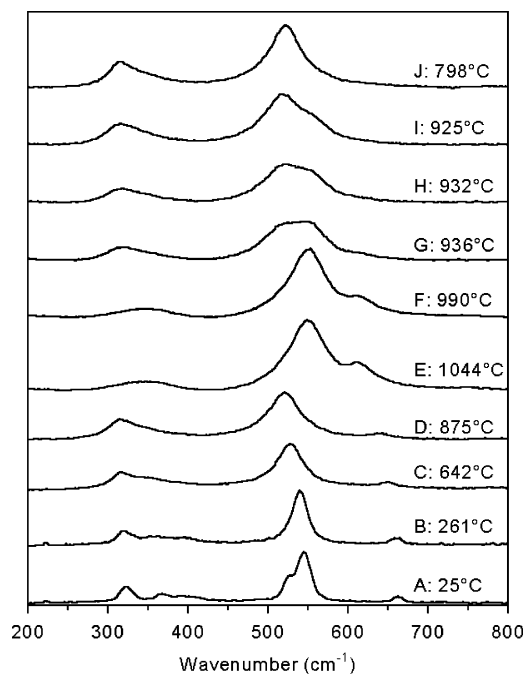


Figure 7. Raman spectra of K_3AlF_6 at different temperatures from the solid to the liquid state. The temperature was increased from A to E and then decreased from E to J.

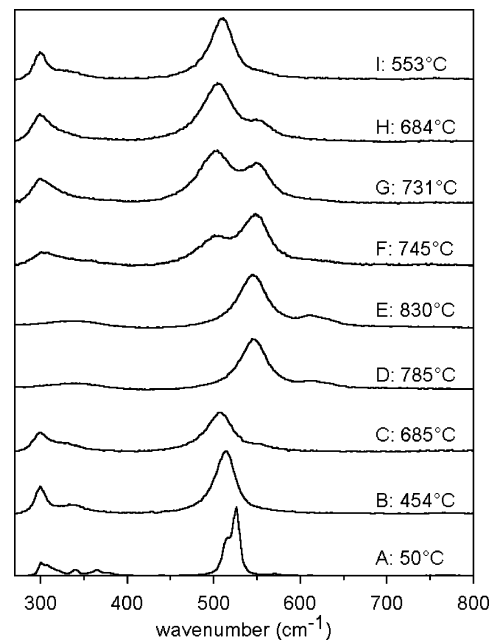


Figure 8. Raman spectra of Cs_3AlF_6 at different temperatures from the solid to the liquid state. The temperature was increased from A to E and then decreased from E to I.

shift of this band is explained by the gradual lattice expansion, in agreement with the propositions made by Brooker et al.¹² At about $450\text{ }^\circ\text{C}$, the melting point of FLiNaK , no discontinuity appears in the spectra shown in Figure 2. At this temperature, however, it is important to note that the mixture is not fully molten. This was very easy to observe when the windowless graphite cell with a 90° scattering geometry was used, since the melt was milky white and not transparent. For a mixture made of 3 mol % AlF_3 in FLiNaK , the temperature must reach at least $720\text{ }^\circ\text{C}$ before the melt starts clearing up. If the AlF_3 content is increased,

Table 1. Solubility^a of Na₃AlF₆ in FLiNaK at Equilibrium in the Temperature Interval 500–750 °C

T (°C)	weight of melt (g)	weight of Al (mg) in the melt ^b	mole fraction of K ₂ NaAlF ₆
750	0.4716	7.508	0.02764
700	0.4961	3.809	0.01246
650	0.5113	1.746	0.00536
600	0.4714	0.499	0.00163
550	0.5117	0.19	0.00057
500	0.4739	0.077	0.00025

^a The solid phase in equilibrium with the melt was not known during the measurements; it has been assumed to be K₂NaAlF₆. ^b As determined by emission spectrometry (ICP).

the required temperature was even higher before complete melting was observed. Clearly, there is a solubility problem.

The solubility of cryolite in FLiNaK has therefore been measured as a function of temperature, as described in the Experimental Section. The results are listed in Table 1. From the measured total aluminum content in the equilibrium melt, the cryolite solubility could be calculated. However, experiments made after full melting of an AlF₃–FLiNaK solution followed by cooling showed that the solid formed after the freezing process is actually not cryolite but K₂NaAlF₆, as confirmed by X-ray diffraction and in agreement with Brooker et al.¹² Since we do not know the exact form of the solid fluoroaluminate in equilibrium with the melt, the solubility has then been expressed in terms of K₂NaAlF₆, the compound which is formed upon cooling. The temperature dependence of the solubility in FLiNaK can be described by the equation

$$\ln x_{(\text{K}_2\text{NaAlF}_6)} = -15254/T(\text{K}) + 11.241 \quad (5)$$

in the temperature interval 773–1023 K. x is the mole fraction of K₂NaAlF₆ in the melt.

According to these data, a melt to which 3 mol % of solid Na₃AlF₆ has been added should be totally molten above 750 °C which is in close agreement with the Raman observations. However, the solubility measurements and the Raman spectra are not made with strictly the same melt. In the Raman experiment, the fluoroaluminate was added to FLiNaK as solid AlF₃ and not as Na₃AlF₆. The melt did not have the same overall composition as the Na₃AlF₆–FLiNaK salts used for the solubility study. The difference is small, however, at least when the two systems are fully melted. As explained in the Experimental Section, the time for a full Raman experiment (heating and cooling) was limited because of slow clouding of the quartz window despite the protecting argon flow. Since the experiment could not last for hours at each temperature, the system was probably not at complete equilibrium. This is the reason the measurements were made using a heating and cooling cycle, and the difference in liquidus temperature during heating and cooling is of the order of 20 °C. Considering these restrictions, the liquidus information obtained from the two sets of data agree very well. The main point, however, is that below a certain temperature, which depends on the mixture under investigation, there is a limit in the solubility of the fluoroaluminate and it must be taken into account.

Considering this limited solubility, the experimental observations made by Brooker et al.¹² as well as the present data can now be understood. In the temperature range where the melt is not fully molten, the bands of the undissolved material mainly characterize the Raman spectra. These bands are indeed narrower and more intense than those found in the fully liquid melt. By comparison with the literature data, they are assigned to the AlF₆³⁻ anion of the solid. In addition, due to the lattice expansion, the ν_1 band will shift downward with increasing temperature as observed in Figures 2–8 and in good agreement with the results obtained by Booker et al. As a matter of fact, for temperatures below 650 °C, the dissolved part of the fluoroaluminate is too low to be detected by Raman, and the spectra belong essentially to the AlF₆³⁻ anion in the solid state.

In the intermediate temperature range 700–800 °C, the solubility has increased enough so that the spectrum of the liquid gradually begins to be observed. For the dilute solutions of AlF₃, the main band is now made of two peaks located at 560 and 515 cm⁻¹ for the FLiNaK, and at 554 and 510 cm⁻¹ for the CsF–KF eutectic solvents. This is clearly shown in Figures 3 and 5.

An interpretation of the preceding observations can now be made. The band situated at 515 cm⁻¹ (in FLiNaK) or 510 cm⁻¹ (in CsF–KF), even when the mixture is fully molten, is still due to the AlF₆³⁻ anion, since its location is in the continuation of the downward shift of the band of AlF₆³⁻ in the solid state upon raising the temperature. For a comparison, measurements with the system K₃YF₆ were made. This system is considered to contain *only* octahedral YF₆³⁻ anions in both the solid and liquid phases.²⁰ Upon heating, the ν_1 band initially located at 461 cm⁻¹ in the solid state at room temperature shifted gradually to 441 cm⁻¹, its position in the molten state. This shift was monotonic, and nothing happened at the melting point. As there is no reason AlF₆³⁻ and YF₆³⁻ would behave differently when they melt, the peaks at (515, 510) cm⁻¹ can be assigned to AlF₆³⁻ in the liquid state. If these bands (515, 510) cm⁻¹ belong to AlF₆³⁻ in the molten state, the bands at (560, 554) cm⁻¹ should indicate that there is another species in these melts. Indeed, the intensity ratio of the two bands is clearly modified with temperature, the bands at (560, 554) cm⁻¹ being favored at higher temperatures. In addition, the present measurements show that this variation in band intensity with temperature is reversible. On the other hand, we know that the location of the main frequency of the AlF₄⁻ ion is found at 622 cm⁻¹ and is almost independent of cation type and temperature.²¹ The new species should therefore be AlF₅²⁻ in agreement with the dissociation model given by eqs 3–4 proposed earlier.^{7–11}

The present results fit very well with our previous propositions: (1) An increase of temperature shifts the equilibria toward a dissociation of AlF₆³⁻ into AlF₅²⁻ and

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AlF_4^- in agreement with the positive ΔH° values²² for both reactions 3 and 4. (2) The main species in the liquid state is AlF_5^{2-} . (3) In order to observe the AlF_6^{3-} species in the liquid state, several conditions must be fulfilled: (a) the ratio alkali fluoride/aluminum fluoride, called the cryolite ratio in the industry, must be very high, i.e., AlF_3 must be diluted, and (b) the temperature should be kept as low as possible, but high enough to ensure a sufficient solubility of AlF_3 in the solvent.

From these considerations, one has to note that the molar ratios $\text{F}^-/\text{Al}^{3+}$ in the FLiNaK and the CsF–KF eutectic solutions are such that the AlF_4^- ion is not observed in the present melts as expected, and therefore, this species has not been discussed here.

As far as the pure M_3AlF_6 compounds are concerned, their behavior as a function of temperature is more complex.

At first, they exist under allotropic forms varying with temperature. Na_3AlF_6 undergoes a monoclinic–cubic transition at about 550 °C¹⁸ which can be seen in the Raman spectrum as an increase of the ν_1 frequency from 543 to 546 cm^{-1} in the transition temperature range. K_3AlF_6 exhibits a tetragonal–cubic transition at about 320 °C,²³ whereas Cs_3AlF_6 seems to be cubic at room temperature.²⁴ It is also believed that, for the latter compounds, superstructures complicate the overall picture.²⁵ The precise interpretation of the spectra upon heating the solid samples from room temperature is thus not simple and is outside the scope of this paper. Nevertheless, the spectra present, as a general feature, a main band characteristic of AlF_6^{3-} octahedra of the solid phase, which shifts more or less gradually toward lower frequencies.

Second, the pure M_3AlF_6 samples melt at much higher temperature, respectively, 1009 °C ($\text{M} = \text{Na}$)¹, 985 °C ($\text{M} = \text{K}$)¹ and 790 °C ($\text{M} = \text{Cs}$)²⁴ and the melt is more concentrated in AlF_3 than in the described mixtures. Thus, the formation of AlF_6^{3-} in the liquid is less favored, and the corresponding AlF_6^{3-} peak is weak. For Na_3AlF_6 , only a very weak shoulder can barely be recognized in the liquid under the most favorable experimental conditions, as shown in Figure 6. In addition, it is found that, upon cooling from the melt, K_3AlF_6 and Cs_3AlF_6 stay liquid below their melting temperature mainly as a result of a supercooling effect. Only in that case and since they are characterized by narrower peaks than cryolite, one can clearly observe from Figures 7

(curves F, G, H, I) and 8 (curves F, G, H) that, during cooling, the AlF_5^{2-} bands are progressively replaced by the one of AlF_6^{3-} in the supercooled liquids. Since evaporation is unavoidable especially for samples made with CsF, one has to recognize that the sample composition could probably change from its initial value, considering the time required for stabilization at a given temperature and recording all the preceding spectra. As a consequence, the observation of a liquid phase upon cooling from and below the melting point may also be partially attributed to this change in composition. However, full heating–cooling–heating cycles have been performed on the same mixture; after such cycles, the melting point indeed decreased but not much (about 10–20 °C), indicating that the supercooling effect is the main reason for this observation.

In any case, when the samples are molten, all the spectra point to the equilibria proposed as described.

Conclusions

The present results indicate a large structural transition between solid and liquid fluoroaluminates mixtures. From 25 °C and up to temperatures close to the liquidus, the spectra of M_3AlF_6 ($\text{M} = \text{Na}, \text{K}$ and Cs), and of various mixtures of AlF_3 in the FLiNaK and CsF–KF eutectic systems, exhibit only bands of the AlF_6^{3-} anion in agreement with the propositions made by Brooker et al.¹² However, when the mixture is close to full melting or fully molten, the picture is different. Now the AlF_6^{3-} ν_1 band located at about 515 cm^{-1} (depending on the cation's nature) is progressively replaced by a band appearing at 560 cm^{-1} . This result leads us to conclude that these mixtures are characterized by a dissociation of AlF_6^{3-} into AlF_5^{2-} in the liquid state. This dissociation is reversible with respect to temperature and composition changes.

Actually, there is no discrepancy between the experimental results presented by Brooker et al.¹² and the present work, provided it is recognized that the mixtures are not totally molten at certain temperatures. This paper has clearly shown that the interpretation of the experimental Raman spectra of AlF_3 in fluoride melts can only be made when both the “solubility” of AlF_3 and a large temperature window are considered in the experimental matrix. The construction of a new furnace design allowing the recording of spectra (i) on a large temperature range and (ii) despite the evaporation of the melt thus gives new perspectives in the structural understanding of very corrosive molten salts.

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