In situ NMR approach of the local structure of molten materials at high temperature

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Abstract

The developments of NMR spectroscopy at high temperature now allow us to study in situ a great number of molten materials. This technique is sensitive to local environment around the nucleus, and gives selective and quantitative information not limited by the disorder existing in liquids. NMR can thus provide a microscopic approach of the structure and dynamics of molten compounds by means of knowledge of different species existing in the melt, the average coordination, or nature of the first neighbors. We present high temperature NMR approach of molten fluoride systems of nuclear interest and description of the local structure around each nucleus, and its evolution with the composition. ***To cite this article: C. Bessada et al., C. R. Chimie 9 (2006)***.
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Résumé

Les développements de la spectroscopie RMN dans le domaine des hautes températures permettent d'étudier in situ un grand nombre de milieux fondus. Cette technique est sensible à l'environnement local autour du noyau et ce, de manière sélective et quantitative, sans être limitée par le désordre existant dans les liquides. Elle permet donc une approche microscopique de la structure et de la dynamique du bain fondu à travers la connaissance des espèces en présence, des coordinences moyennes ou de la nature des premiers voisins. Nous présentons ici une approche par RMN haute température de systèmes fluorés fondus d'intérêt nucléaire et la description de la structure locale autour de tous les noyaux du système, ainsi que son évolution avec la composition. ***Pour citer cet article : C. Bessada et al., C. R. Chimie 9 (2006)***.
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1. Introduction

This paper is centered on NMR spectroscopy approach of high temperature materials. Two main aspects can be described. The first one concerns the characterization of the solidified materials at room temperature, or up to 300 °C that corresponds to the classical 'commercial' temperature range for NMR measurements. In this temperature range, we can focus on the description of the different phases present in the material, on the structural disorder, on the effect of doping agents, or cooling procedure. This is the aim of high-resolution solid state NMR, and of the very latest development of new pulse sequences, and recent very high field technology. The other approach is more focused on the in situ characterization at high temperature of the real state of the system during industrial processes: structural modifications on heating, phase transitions, liquid phase formation, or the nature of the ionic species in the melt. That is the domain of high temperature NMR up to 2500 °C [1–3]. Such very high temperatures give rise to specific technical problems: the use of a superconducting magnet implying cryogenic liquids, the radiofrequency fields that can be strongly perturbed by the heating system, the geometry and the available space or the problems linked to the sample itself. Chemically inert solid materials can become very corrosive and difficult to handle in the molten state at high temperature. Up to now, different solutions have been proposed including gas heating, or furnaces, but implying a very efficient water-cooling device [4]. In our laboratory, the heating system is based on a CO_2 laser heating. The principle is rather simple and involves a modified axial probe associated with a CO_2 power laser (120 W), a mirror directing the laser beam on the sample inside the NMR probe and a computer that controls the power of the laser and thus the temperature of the sample. Depending on the temperature range, two designs have been adapted [1]. For the very high temperatures from 1500 to 2500 °C, the sample is compacted in a small droplet of few millimeters and sustained on a gas flow, and is then directly heated by the laser without any contact with a container. This system has been successfully applied for molten oxides, aluminates or silico-aluminates [2,3]. For lower temperatures up to 1300 °C, and for corrosive and reactive liquids, a container in pure boron nitride tight to air and moisture has been designed in order to avoid any evaporation and interaction with the surrounding atmosphere. A ceramic tube is added for thermal protection of the coil, and is also associated with the circulation of an airflow at room temperature. It's this latter domain of temperature that will be illustrated in this paper, with the description of molten fluorides, for which any experimental study is extremely difficult because of their reactivity at high temperature. These systems are involved as solvent in a number of metallurgical processes based on electrolysis, as in the industry of aluminum, or for refractory metals such as niobium and tantalum. They are also currently implied in the pyrochemical extracting processes for nuclear waste treatments. The principle can be schematized as a series of operations starting from the dissolution of the irradiated elements in a eutectic mixture of alkali or alkaline earth halides up to 900 °C, followed by the more or less selective separation of elements for their recycling or conditioning. The optimization of such processes implies a good knowledge of the physico-chemical properties of the molten baths, and their structure in terms of ionic species distribution, coordination, charge, and oxidation number. The formation of complexes in the melt can be predicted by molecular dynamics, quantum chemical or thermo-statistic calculations but the direct experimental description is crucial for testing the validity of models and species distribution proposed in the liquid phase. Because of their corrosive and aggressive nature towards a great number of materials, and their sensitivity to moisture and oxygen, their NMR analysis was very difficult up to now and it can explain the scarcity of such kind of study in the literature.

Among the different experimental parameters that can be extracted from a spectrum, chemical shifts provide a significant source of structural information including the nature of first neighbors, the coordination numbers, bond lengths and angles. Chemical shift results from a perturbation of the resonance frequency due to small changes in the electronic configuration around the observed nucleus. In solids, this interaction is more precisely described by the Chemical Shift Anisotropy (CSA) tensor with its principal components δ_1, δ_2 and δ_3, the average of which is the isotropic chemical shift, δ_{iso}. Using high resolution developments based on the Magic Angle Spinning (MAS) technique, the resolution is considerably enhanced by a rapid rotation of the sample at the Magic Angle ($\theta = 54.7°$) with respect to the external magnetic field.

The chemical shift can be then accurately measured. In the case of a non integer quadrupolar nucleus sensitive to EFGs (electric field gradient) like ^{27}Al ($I = (5/2)$), the effects of the quadrupolar interaction can give rise to a very complex resonance pattern (Fig. 1) and the peak positions are generally shifted towards values lower than δ_{iso} and broadened by the second order quadrupolar interaction.

In liquids, due to rapid isotropic rotation of molecules the electric field gradient experienced by the nucleus and hence the quadrupolar interaction average to zero. δ_{iso} is then the actual position of the peak. Moreover, the rapid exchange between the different bonding configurations results in a fully averaged local environment giving a single narrow lorentzian line. The signal position, or the isotropic chemical shift, is the weighted averaged chemical shift of the different components in the melt. Knowing the chemical shift of the individual species, we can extract their distributions depending on the composition.

In oxides, ^{27}Al isotropic chemical shifts are known to strongly depend on the coordination number. For tetrahedral sites, AlO_4^{5-}, δ values fall in the range of 55–90 ppm and in the range of –20 to +20 ppm for octahedral ones. AlO_5^{7-} groups have been characterized in a few structures with δ values of about 30–40 ppm. In melts, based on these chemical shifts ranges, the position of the single line is correlated to an average coordination around the aluminum atoms. For example, in YAG ($Y_3Al_5O_{12}$), the ^{27}Al chemical shift measured in the melt, 68 ppm at 2000 °C, is interpreted as a mixture of Al_{IV}, Al_V and Al_{VI} species undergoing
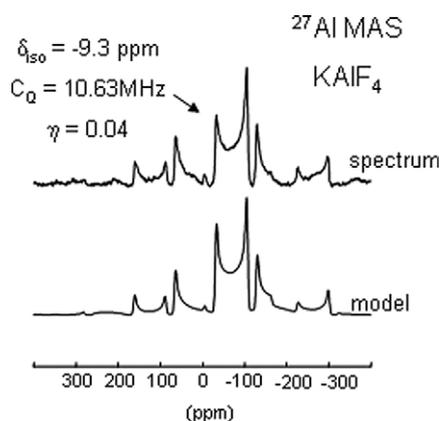
rapid exchange [3]. Combining Molecular Dynamics simulations and chemical shift measurements in such melts, it is then possible to reach a quantitative description of the anionic distribution.

In solid alkali fluoroaluminates, aluminum atoms are essentially octahedrally coordinated with F, and the ^{27}Al chemical shifts range reported lies between –15 and +1.4 ppm, at least 20 ppm more shielded than AlO_6 octahedra in aluminum oxides. The more ionic character of the Al–F bond compared to the Al–O bonds could explain this difference. Some authors have tried to correlate chemical shift data and structural features for AlF_6^{3-} octahedra with different connectivity, symmetry or cationic second sphere [6–8]. They conclude that the Al nucleus is more effectively shielded by its surroundings and less sensitive to the cationic substitutions in the second sphere. S. Kohn et al. [9], have reported the existence of V and VI coordinated aluminum in glasses of jadeite mixed with Cryolithe, associated with chemical shifts at 22 and –5 ppm, respectively. N. Herron et al. [10] demonstrated the existence of tetrahedral AlF_4^- anion in organic solvents and associated to a δ_{iso} at 49 ppm. In preview studies, we have performed high-temperature ^{27}Al, ^{23}Na and ^{19}F NMR measurements in the NaF–AlF$_3$ binary system [5,11]. We reported experimental chemical shifts, measured at 1010 °C, in melts of compositions ranging from 20% to 50 mol% AlF$_3$. The chemical shift evolution over the whole composition range coincided well with the structural description proposed by Gilbert et al. [12], on the basis of Raman spectroscopy and thermodynamic data. The anionic proportions given by Raman, for a dissociation scheme involving three fluoroaluminate species AlF_4^-, AlF_5^{2-} and AlF_6^{3-}, was clearly confirmed by the NMR chemical shift measured experimentally. From the collected ^{27}Al chemical shift values, we were able to propose, as for aluminum oxides, significantly separate chemical shifts ranges for the AlF_4^-, AlF_5^{2-} and AlF_6^{3-} configurations (Fig. 2) that can be used further for the interpretation of high temperature spectra in fluoroaluminates.

It is the same kind of analysis we want to present in the case of lanthanide fluorides. Lanthanide fluorides are known for their wide range of technological uses: in solid state as materials for electrodes, lasers, and superionic conductors, or in the molten state in electrolytic processes for metallurgy, and in pyrochemical processes for nuclear wastes recycling. In addition, their
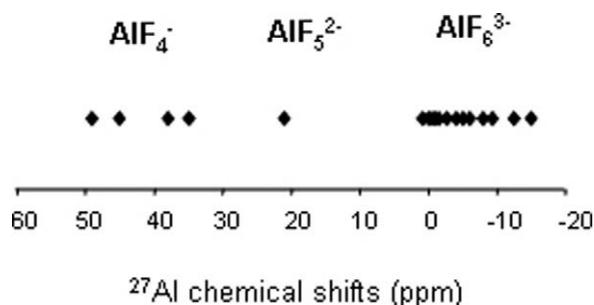

Fig. 1. ^{27}Al MAS NMR spectrum of solid KAlF$_4$ at room temperature (B_o = 9 T, spinning rate = 15 kHz).

AlF$_4^-$ AlF$_5^{2-}$ AlF$_6^{3-}$

Fig. 2. ^{27}Al chemical shifts range for fluoroaluminates [5–10] [13].

chemical properties and similarities with actinides make them particularly useful as models for the study of speciation of radioactive actinides. Pyrochemical methods for the treatment of irradiated nuclear fuel have stimulated number of research programs and developments [14,15]. Separations would be based on the possibility of modifying the oxidation state of an element by electrolysis or by addition of a chemical agent. In a molten salt this process is complicated by different complexation phenomena and by the influence of temperature. It is of primary importance to identify the nature and the structure of the chemical species that could be involved in the reactive medium. Up to now, the experimental determination of lanthanide speciation in molten fluorides has been extremely limited because of the strong technical difficulties inherent to these melts.

We present in this paper ^{19}F NMR chemical shifts measurements performed in situ in molten LnF$_3$–LiF mixtures at temperature ranging from 850 to 1200 °C. We combine these measurements with ^{139}La and ^{89}Y data obtained for specific compositions in order to draw some first description of the local structure existing in such molten fluorides.

2. Experimental

Samples have been prepared in a glove box under dried argon by mixing suitable proportions of LnF$_3$, Ln = La, Y, Lu, Ce, Sm (Aldrich, 99.99%) and LiF (Aldrich, 99.9%) without further purification. The composition range extends from 0% to 100 mol% of LnF$_3$.

The NMR experiments have been carried out on a Bruker DSX 400 NMR spectrometer with a magnetic field of 9.4 T, operating at frequencies of 376.3 MHz for ^{19}F and 19.6 MHz for ^{89}Y and on a very high field

spectrometer (17.61 T) for the ^{139}La observation at 105.9 MHz. High temperature (HT) NMR experiments were acquired using the previously described laser heated system developed at CRMHT (Orléans, France) [5,16]. Each sample was contained in a high purity boron nitride (BN AX05 from Carborundum) crucible, tightly closed by a screwed BN cap. The crucible was placed inside the RF coil, in the center of the cryomagnet, and heated by a continuous CO$_2$ laser beam (λ = 10.6 μm). A ceramic shield thermally isolated the axial saddle coil. The high temperature NMR spectra were obtained using single pulse excitation (π/2 = 20 μs) and recycle delays of 500 ms to 15 s, depending on the nucleus. Up to 256 scans were accumulated to obtain a reliable signal-to-noise ratio. All HT NMR spectra were recorded at temperatures corresponding to 10–20 degrees above the melting temperature of the corresponding composition.

Solid-state MAS NMR spectra of ^{19}F, ^{89}Y and ^{139}La have been acquired at room temperature on pure compounds YF$_3$, LaF$_3$, LiYF$_4$, and on solidified compositions after high temperature measurements, to correlate the experimental chemical shifts and the structural features given by crystallographic data. The experimental conditions are summarized in Table 1.

^{139}La NMR spectrum of solid LaF$_3$ has been obtained under static conditions at 17.6 T. ^{139}La NMR spectroscopy is rather difficult in solids because of the large quadrupolar interaction for lanthanum nucleus (I = 7/2) that strongly broadens the NMR lines. For the high-temperature experiments, these interactions are averaged to zero and the signal obtained is sharp and well defined. At room temperature, ^{139}La, ^{89}Y and ^{19}F chemical shifts were referenced to 1 M aqueous solutions at room temperature of La(NO$_3$)$_3$, YCl$_3$ and CFCl$_3$, respectively.

3. Results and discussion

Even in very high-speed conditions, the ^{19}F MAS spectra at room temperature on solid phases are governed by the strong paramagnetic effect of the lanthanide. This effect depends on the element and is different from one cation to another. The resulting broadening can be very important such as in the case of NdF$_3$, with a line width extending over more than 400 KHz, much larger than the available spinning rates.

We focus first on the LaF_3–LiF and YF_3–LiF systems in order to overcome these problems and to show that these systems are really good models for the whole series of lanthanides fluorides.

At room temperature (Fig. 3) the ^{19}F MAS spectrum of LaF_3 exhibits three components at –25.2, 12.4 and 19.7 ppm corresponding to the three fluorine sites of the structure, in good agreement with the work of F. Wang et al. [18].

The ^{19}F MAS spectrum of solid YF_3 exhibits the signature of the two different fluorine sites (F1 and F2) at –56 and –67 ppm. Only one fluorine site is described in the scheelite structure of $LiYF_4$ and $LiLnF_4$ compounds [19] in agreement with the obtained spectra.

The comparison of the ^{19}F MAS NMR spectra obtained at room temperature with the sharp line obtained in the melt, for LaF_3, YF_3, $LiYF_4$, and LiF compounds shows that the fluorine signal position is slightly modified on melting, and shifted of up to 40 ppm in the case of YF_3. If we consider simply the solid compounds of the YF_3–LiF system, we can remark that the chemical shifts are different, and depend on the nature of fluorine atoms local environment. For LiF, the fluorine atoms are free fluorines not embedded into any $[YF_x]$ unit [20]. In solid YF_3, the structure is made
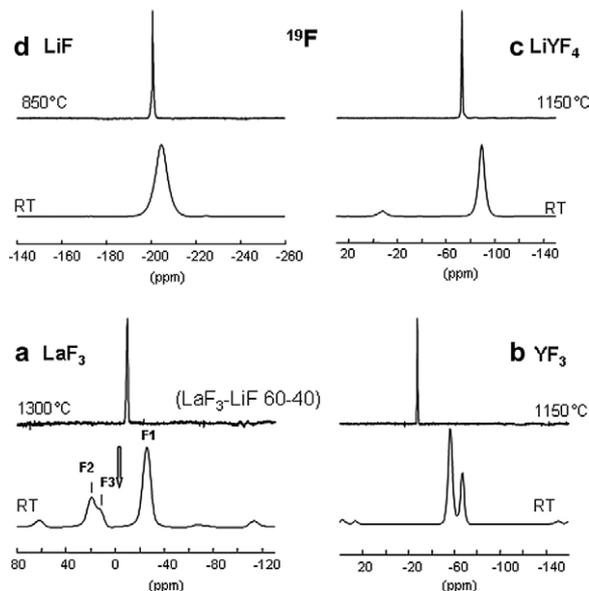
of $[YF_9{}^{6-}]$ polyhedra connected by bridging fluorines, as in $LiYF_4$, for $[YF_8{}^{5-}]$ polyhedra [19]. We have also performed ^{19}F NMR measurements in the YF_3–KF binary system. In this system, the crystallographic structure of the K_3YF_6 compound (25 mol% YF_3), is characterized by isolated octahedra $[YF_6{}^{3-}]$ where the fluorine atoms are non-bridging. The Fig. 4 represents the ^{19}F NMR spectra of the high-temperature solid phase (α) at 910 °C and of the molten phase at 990 °C. The position of the peak is just slightly modified ($\Delta\delta = 4$ ppm) on melting, and indicates that the fluorine configuration is preserved in the melt. We can then deduce that at this composition the major part of the fluorine atoms are non-bridging.

These three kinds of fluorine environments have already described, by B. Bureau et al. in solid inorganic fluorides [21,22]. The authors have reported different chemical shifts range correlated to the different types of fluorine, free, bridging and non-bridging.

In molten compounds, the local structure around fluorine ions is preserved and from the peak position we can propose that the configuration around the fluorine is closer to that existing in the solid. The measured chemical shift in the melt being the weighted average value, we can validate that in the case of pure YF_3, the liquid contains a non negligible proportion of connected YF_x complexes, confirming the network-like structure proposed by G. Papatheodorou in the KF–YF_3 system, for YF_3 content higher than 25 mol% [23,24].

The ^{19}F spectra have been also recorded for LnF_3–LiF (Ln = La, Ce, Sm, Lu and Y) systems over the whole range of compositions. We have collected in the

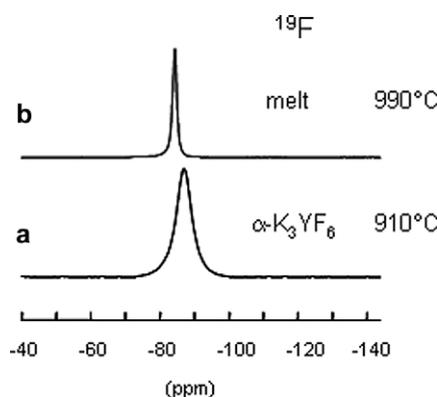Fig. 3. ^{19}F MAS NMR spectra of solid and molten compounds: (a) LaF_3 and molten 60–40 mol% LaF_3–LiF, YF_3 (b), $LiYF_4$ (c) and LiF (d).

Fig. 4. ^{19}F NMR spectra of K_3YF_6: (a) high temperature solid α-phase and (b) melt.

Fig. 5, the whole set of ^{19}F chemical shifts data measured for the different systems studied and over the whole range of compositions. When the LnF$_3$ content increases, we observe a systematic shift towards higher chemical shift values. More precisely, this evolution is not a linear function of the composition, but a smooth increase that indicates the presence of more than two different local environments for fluorine atoms in these melts, with proportions changing with composition. We can notice that the evolution is similar for all the lanthanides. Except in the case of SmF$_3$–LiF where the ^{19}F chemical shifts are rather constant at –200 ppm over the whole range of compositions might be correlated with the specific behavior of Samarium that seems to be not complexed. We can discuss the trends observed for the other systems with the existence of three kinds of fluorines: (1) in pure ionic LiF, all F anions are free fluorines (2) when low amount of LnF$_3$ is added to the melt, some of the fluorines are involved into LnF$_x$ complexes (3) for higher LnF$_3$ content (> 25%), some fluorine ions start to be connected, and shared between LnF$_x$ polyhedra. This evolution is continuous up to pure LnF$_3$ composition, where the local structure can be described as very similar to the solid one, with a 'network-like' arrangement.

In order to consider the nature of the LnF$_x$ polyhedra, we have followed in LaF$_3$–LiF and YF$_3$–LiF systems, the NMR signature of the ^{139}La and ^{89}Y nuclei. In LaF$_3$–LiF mixtures, the signal observed from 10% to 50 mol% of LaF$_3$, is a sharp and unique line at –53 ppm, which is not dependent on melt composition

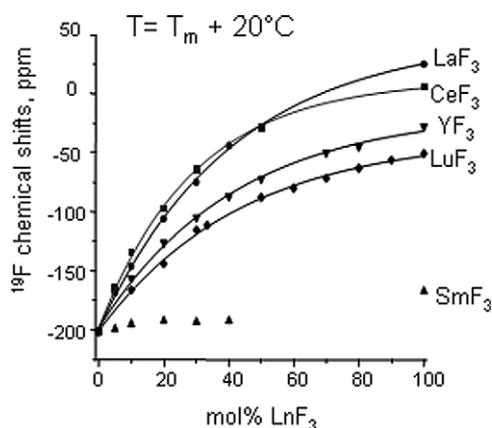(Fig. 6). The local environment around the La^{3+} is not modified. In order to decide the nature of the coordination polyhedra, we have registered the ^{139}La NMR spectrum in solid LaF$_3$ at room temperature. The signal is broad and characteristic of a strong quadrupolar interaction. We can define the chemical shift and quadrupolar coupling by modeling the experimental spectrum. The value extracted (δ = –123 ppm, C_Q = 15 MHz and η = 0.75) can be compared with the measured position in the melt. The lanthanum coordination in the solid phase at room temperature is known to be 11 [25,26]. The comparison of the chemical shift measured in melts at –53 ppm indicates that the important shift observed can be attributed to a change in coordination.

In YF$_3$–LiF mixtures, the ^{89}Y signal has been obtained for three different compositions 30%, 50% and 70 mol% YF$_3$ at 1150 °C. ^{89}Y spectra suffer from long time relaxation and low sensitivity. Because of the limited duration of the high temperature experiments, the signal to noise ratio is poor, and the signals appear rather noisy. Nevertheless, the position of the line can be defined and is located at –50 ppm for all mixtures. In Fig. 7, we have reported the comparison between ^{89}Y spectra of the 50–50 mol% YF$_3$–LiF composition (a)
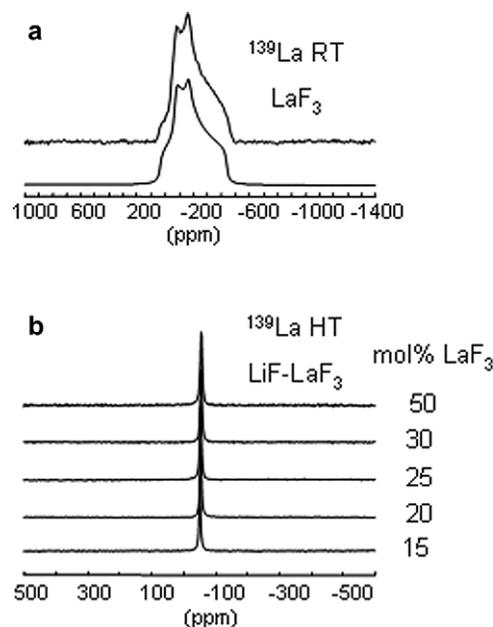

Fig. 6. ^{139}La NMR: (**a**) ^{139}La MAS NMR spectrum of LaF$_3$ at room temperature; (**b**) High-temperature ^{139}La NMR spectra evolution in LaF$_3$–LiF melts (850–1250 °C).

Fig. 5. ^{19}F chemical shifts evolution with LnF$_3$ content in LnF$_3$–LiF binaries (Ln = La, Ce, Sm, Lu, and Y) at high temperature.
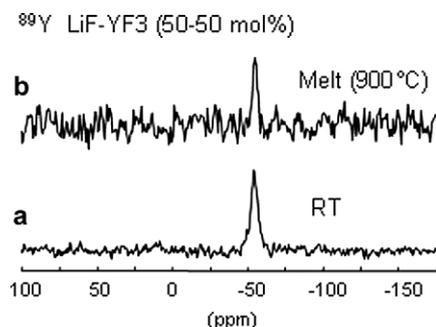
Fig. 7. ^{89}Y NMR: (**a**) ^{89}Y MAS NMR spectrum in LiYF$_4$ at room temperature; (**b**) high-temperature ^{89}Y NMR spectrum in 50–50 mol% YF$_3$–LiF melt at 900 °C.

in the solid at room temperature (LiYF4) and (b) in the melt. The identical positions indicate that the coordination around the yttrium atoms in melt is very close to what is described in the solid LiYF4 structure. In literature, for lanthanide trihalides–alkali halide mixtures, the coordination polyhedra proposed is LnF$_6{}^{3-}$ units more and more connected by sharing fluorine when LnF$_3$ content is increased in the melt. Our NMR results do not confirm this six coordination. From our first tentative empirical correlation, it should be higher and more likely seven or eight [17].

4. Conclusion

We have followed by high temperature NMR spectroscopy the evolution of ^{19}F, ^{139}La and ^{89}Y chemical shifts with the composition in YF$_3$–LiF, LaF$_3$–LiF binary systems. In YF$_3$–LiF, starting from pure LiF, the ^{19}F chemical shifts evidence an evolution from free to bridging fluorine between YFx polyhedra in melts rich in YF$_3$. Up to 25 mol% YF$_3$, the fluorines present in the melt are either free or included around the yttrium atom in its coordination polyhedron. When the YF$_3$ content is increased, some of these polyhedra start to be connected by bridging fluorines up to the YF$_3$ melts where the liquid has been described as a *network-like* liquid. This observation has been confirmed in other LnF$_3$–LiF systems for Ln = La, Ce, Lu. The ^{139}La and ^{89}Y signals confirmed that the coordination around the La and the Y atoms is independent of composition. From the first data reported here, it is difficult to conclude

towards the existence of six coordinated LnF$_6{}^{3-}$, while it seems to rather coincide with a higher coordination number 7 or 8.

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