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Lanthanide and actinide speciation in molten fluorides: A structural approach by NMR and EXAFS spectroscopies

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Abstract

The objective of this paper is to describe the local structure in fluoride melts of nuclear interest. Our experimental approach combines NMR and EXAFS spectroscopies both sensitive to the microstructure of solid and liquid materials. These techniques allow identifying the complex formation in molten media. Thanks to the development of specific cells adapted to molten fluorides up to 1300 °C, we give some structural description of LiF–LnF_3 systems ($Ln = Y, Lu, Ce$) and discuss the evolution of ^{19}F spectra in terms of different fluorine configurations depending on the composition. This approach is further extended to the characterization of LiF–ThF_4 system by ^{19}F NMR in melts from 0 to 100 mol% ThF_4 at temperatures ranging from 600 to 1100 °C. We report also very first EXAFS spectra obtained *in situ* at high temperature, at the Thorium LIII edge, in LiF–ThF_4 molten mixtures.

1. Introduction

The problems of energy management in terms of pollution and production lead to the renewal of the interest in nuclear energy, through the Generation IV initiative. Among the six selected GenIV concepts, the thorium based molten salts reactor (MSR) would provide a series of attractive advantages on safety requirements, nuclear source extension and proliferation resistance [1,2]. The radiotoxicity of the inventory of these reactors could be considerably lower than that of uranium reactor with fast spectrum, with an efficient separation of minor actinides and fission products. The choice of the salt is of primary importance and will be based on neutronic, stability, reactivity criteria but also on the chemical reprocessing ability and the selective extraction of the different components in the spent fuel: uranium, thorium, minor actinides and lanthanides. The knowledge of the different ionic species existing in these baths in terms of their distribution, coordination and oxidation number is one of the unavoidable stages toward a better understanding of physical and chemical properties of the molten salts proposed for the MSR. In one of the scenario, the carrier salt would be a mixture of fluorides based on LiF, ThF_4, possibly BeF_2 and

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small additions of $^{233}UF_4$ at temperatures up to 800 °C.

Because of the strong reactivity of molten fluorides at high temperature towards a great number of materials, and their sensitivity to moisture and oxygen, their experimental analysis is extremely difficult and needs specific developments. Our approach is based on *in situ* characterization at high temperature by two complementary spectroscopic techniques that we have adapted for high temperature measurements in molten salts up to 1300 °C: nuclear magnetic resonance (NMR) and extended X-ray absorption fine structure (EXAFS) [3–5]. These two spectroscopies are both sensitive to the local structure around a selected element. NMR is better adapted for the structural description of the lightest elements, such as ^{19}F, ^{17}O, ^{27}Al, ^{23}Na, ^{7}Li,..., while EXAFS gives the description of the environment for the heaviest (lanthanides, thorium,...). More precisely, NMR spectroscopy probes the local environment around a nucleus in solid or liquid materials, and can provide information about its coordination, the nature of the first neighbours around the anions and cations of the system, and then the nature of the chemical complexes formed in the melt. A laser heated system associated with a tightly closed boron nitride crucible was developed and adapted to the NMR spectrometer, at the CRMHT laboratory few years ago and has been successfully used in the study of different molten fluorides [5–7].

EXAFS analysis provides direct information on the first shell of neighbours around the observed element by mean of its coordination number, and the interatomic distances. We have built a new cell compatible with molten fluorides and X-ray spectroscopy requirements that we have successfully tested on molten LiF–LaF_3, YF_3 and LuF_3 binaries [3–5]. The spectra obtained are difficult to model because of the disorder existing in the melt and the rapid decrease of the EXAFS oscillations. Nevertheless, the data confirmed that the first shell remains unchanged with composition around the lanthanide in these melts and evidence a decrease of the coordination between the solid and the liquid phase.

We describe in this paper our in situ approach of the LiF–LnF_3mixtures at temperature ranging from 850 to 1250 °C. We focus on the ^{19}F NMR study of LiF–YF_3, CeF_3 and ThF_4 systems and present our preliminary EXAFS spectra at the Thorium LIII edge on LiF–ThF_4 mixtures.

2. Experimental

Samples have been prepared in a glove box under dried argon by mixing suitable proportions of LnF_3, $Ln = Y, Lu, Ce$ (Aldrich, 99.99%), ThF_4 (CERAC) and LiF (Aldrich, 99.9%) without further purification. The composition range extends from 0 to 100 mol% of LnF_3 or ThF_4.

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. High temperature (HT) NMR experiments were acquired using the previously described laser heated system developed at CRMHT (Orleans, France) [7]. Each sample was contained in a high purity boron nitride (BN AX05 from Carborundum) crucible, tightly closed by a screwed BN cap and placed inside the RF coil in the centre of the cryomagnet.

The sample is heated by a CO_2 laser ($\lambda = 10.6$ μm) 10–20° above the melting temperature of the corresponding composition. The NMR signal of the different nuclei in the molten state is sharp and Lorentzian shaped, corresponding to the average signature of the different species present in the melt. The high temperature NMR conditions were tuned in order to obtain reliable signal to noise ratio: single pulse excitation, 20 μs, recycle delays of 500 ms–15 s and up to 256 scans.

^{19}F solid-state MAS NMR spectra have been acquired at room temperature on pure compounds YF_3, CeF_3 and ThF_4 and on solidified compositions after high temperature measurements, to correlate the experimental chemical shifts and the structural details given by crystallographic data. The solid state NMR data were collected with the same spectrometer (9.4 T) using a 2.5 mm MAS probe and a 35 kHz spinning rate with short pulse lengths (0.5 μs), and recycle times of 1–5 s. ^{19}F chemical shifts were referenced to 1 M $CFCl_3$ solution at room temperature.

The EXAFS spectra presented in this paper were obtained at the Thorium L_{III} edge (16.3 keV) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France), on the D2AM French CRG Beamline. The LiF–ThF_4 compositions were chosen around the eutectic composition: 22.5, 25 and 28.5 mol% ThF_4. The cell is made by two plates of pyrolitic boron nitride maintained fixed by screws and has been previously described elsewhere [3,4]. The heating system has been optimized in order to fit with the limited space available on ESRF beam lines, and is now based on two ceramic elements with geometry adapted with the transmission mode for absorption measurements.

3. Results and discussion

3.1. LiF–LnF$_3$

The ^{19}F MAS NMR spectra of solid lanthanide trifluorides, at room temperature are generally very broad and difficult to interpret because of the strong paramagnetic effect of the lanthanide cation, while the major part of the lanthanides are not observable by NMR. In the melts, this effect is averaged and the signal of the fluorine is much less influenced by the lanthanide. Our approach has been first focused on the LiF–LaF$_3$ and LiF–YF$_3$ systems [5,6]: La and Y are diamagnetic and do not influence the NMR observation, even in the solid, and secondly they are both observable by NMR, providing the description of the different elements of the binary system. In addition due to their chemical and structural properties, these systems have been shown to be good models for the whole series of lanthanides fluorides [8,9]. It is currently accepted that yttrium behaves as the prototype of heaviest lanthanides, as a consequence of its ionic size and chemical behaviour, while the Lanthanum represents the lightest, from La to Nd. In molten compounds, the peak position indicates that the local structure around fluorine ions is preserved and close to that existing in the solid. We present in Fig. 1(a) the ^{19}F NMR spectra measured in molten LiF–YF$_3$ mixtures from 0 to 100 mol%YF$_3$, at temperatures ranging from 800 to 1300 °C, depending on the composition. The signal is sharp and well resolved. Its position corresponds to the isotropic chemical shift and is the average value of the different contributions. In pure LiF, the ^{19}F signal lies at -200 ppm, corresponding to free fluorines that are not embedded into any [YF$_x$] complex [10], while in molten YF$_3$, the chemical shift measured is -28 ppm, which has to be compared with the solid spectrum reported in Fig. 1(b). In solid YF$_3$, the crystallographic structure is made of [YF$_9^{6-}$] polyhedra connected by bridging fluorines. The ^{19}F NMR spectrum at room temperature exhibits two different signals at -56 and -67 ppm corresponding to the two inequivalent fluorine sites of the structure only different by the F–Y bond lengths. The difference between the chemical shifts measured in the solid and the liquid express the disorder in the liquid: the coordination around the yttrium atom is lowered, and a non negligible part of the connections between YF$_x$ polyhedra are broken.

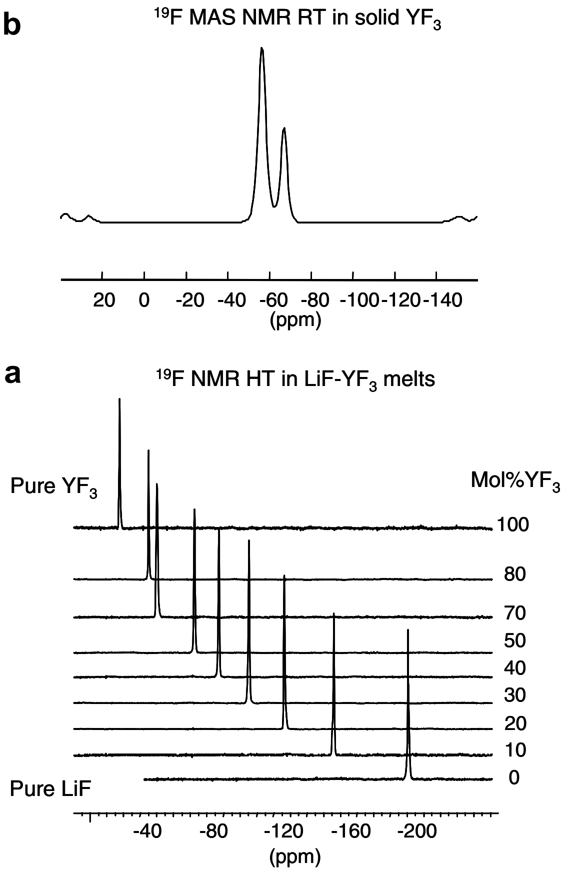

Fig. 1. ^{19}F NMR spectra at high temperature in LiF–YF$_3$ (0–100 mol% YF$_3$) melts (a) (The temperature range extended from 800 °C to 1100 °C depending on the melting temperature.) and in solid YF$_3$ at room temperature (b).

The evolution of ^{19}F signals with the YF$_3$ content in the melt is continuous with a progressive shift from -200 ppm in pure LiF towards -28 ppm in pure YF$_3$. We have attributed this evolution to the existence of three kinds of fluorines [6]: free fluorines, non bridging fluorines involved in complexes around the lanthanide cation for low LnF$_3$ content, and bridging fluorines between LnF$_x$ polyhedra for high LnF$_3$ content, corresponding to strongly associated liquids or network-like liquids as described by Dracopoulos et al. [11,12].

The same trends have been observed in the LiF-LuF$_3$ system (Fig. 2). The ^{19}F MAS NMR spectrum at room temperature, of the solidified 90 mol% LuF$_3$ composition, shows two contributions corresponding to fluorine in LuF$_3$ and LuLiF$_4$ phases,

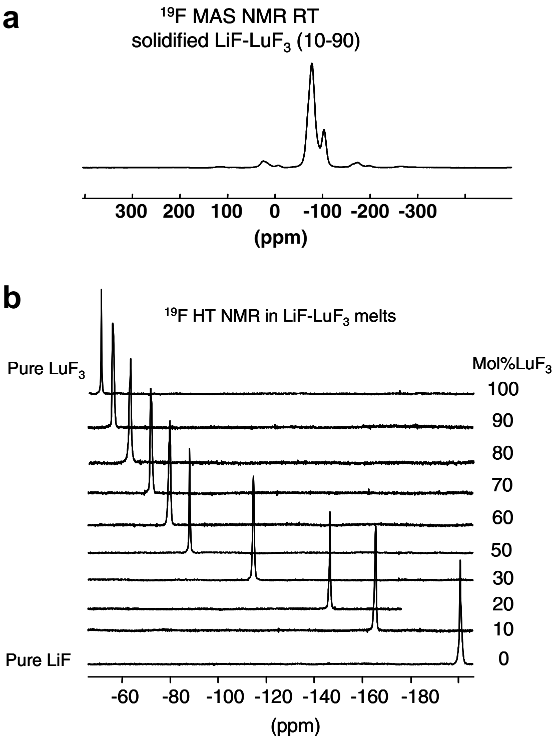

Fig. 2. ^{19}F NMR spectra at high temperature in LiF–LuF$_3$ (0–100 mol% LuF$_3$) melts in temperature range extended from 800 °C to 1250 °C(a) and in solidified LiF–LuF$_3$ (10–90) composition at room temperature. The asterisks (*) define spinning side bands of the signals (b).

at −77 and −103 ppm respectively. The evolution of the ^{19}F signal in LiF–LuF$_3$ melts with increasing the LuF$_3$ content is quite similar with what has been observed in the LiF–YF$_3$ system.

We report also in Fig. 3 the same kind of result in the LiF–CeF$_3$ system with a shift of the peak from −168 ppm (5 mol% CeF$_3$) to −21 ppm for 50 mol% CeF$_3$. This value can be compared with the ^{19}F chemical shifts measured on the MAS NMR spectrum of CeF$_3$ solid at room temperature (Fig. 3(a)). This spectrum consists in two sets of spinning side bands, originated from the MAS rotation and extended over more than 1000 ppm, due to the high paramagnetic influence of Ce^{3+} over the ^{19}F chemical shift anisotropy. By comparison of spectra obtained at different spinning rates, we can deduce the ^{19}F chemical shifts corresponding to the individual fluorine sites of the tysonite structure in solid CeF$_3$ i.e two contributions at 43.4 and 9.8 ppm. It indicates that the local structure around the fluorine atoms in molten 50–50 LiF–CeF$_3$ mixtures is rather different than the one present in solid CeF$_3$, and should involve the contribution of bridging fluorines that increase strongly the average chemical shift measured in the melt.

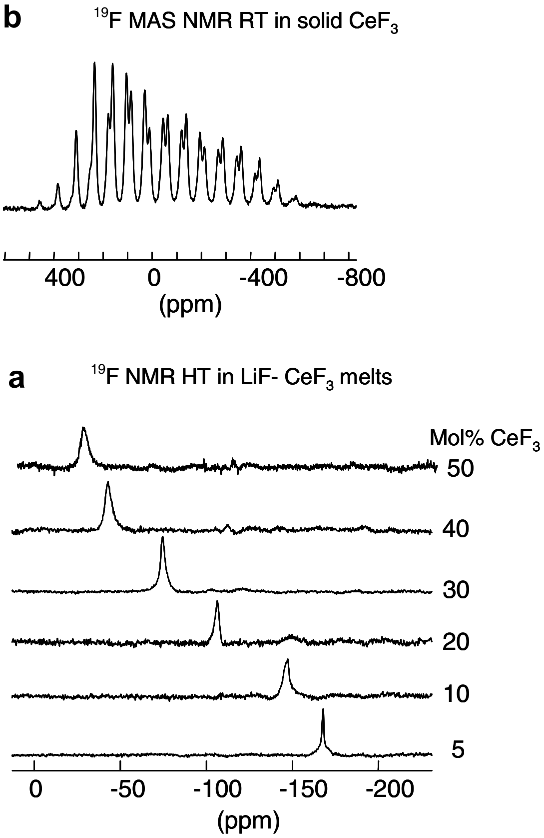

Fig. 3. ^{19}F NMR spectra at high temperature in LiF–CeF$_3$ (5–50 mol% CeF$_3$) melts in temperature range extended from 800 °C to 1200 °C(a) and in solid CeF$_3$ at room temperature (b).

3.2. LiF–ThF$_4$

We have reported in Fig. 4 the ^{19}F MAS NMR spectrum obtained at room temperature in solid ThF$_4$. The spectrum is rather complex and is made of different groups of bands regularly spaced by the spinning rate (35 kHz) and corresponding to the signals of different fluorine atoms existing in the crystallographic structure. The isotropic chemical shifts ‘group’ lies between 53 and 101 ppm, and is assigned to the seven different fluorine sites described in the literature [13]. The other groups of lines are spinning side bands of each isotropic component and are extended other more than 800 ppm drawing large chemical shift anisotropy.

In Fig. 5, the high temperature ^{19}F NMR signals measured in LiF–ThF$_4$ melts, are reported from pure LiF up to molten ThF$_4$. We observe the same

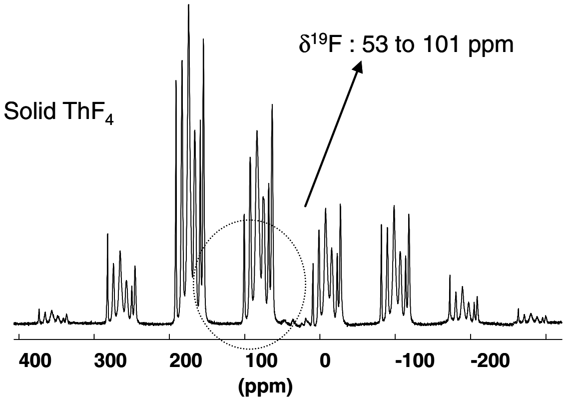

Fig. 4. ^{19}F MAS NMR spectrum of solid ThF_4 at room temperature.

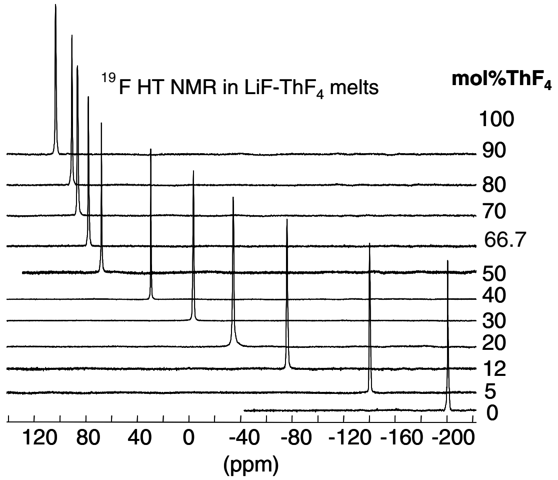

Fig. 5. ^{19}F NMR spectra evolution in molten LiF–ThF_4 mixtures in temperature range extended from 600 °C to 1200 °C.

variation than in LiF–LnF_3 mixtures with a progressive shift of the peak when ThF_4 content increases. This shift is clearly more pronounced from 0 to 50 mol% ThF_4 and signs a higher influence of the ThF_4 content in this domain of composition.

We have collected in Fig. 6, the variation of the ^{19}F chemical shifts measured in different MF–LnF_3 systems. We can remark the similar trend observed for the LiF–ThF_4 and the LiF–LnF_3 systems. From the conclusion drawn for the MF–LnF_3 (M = Li, Na, K) mixtures [6], we can deduce that in LiF–ThF_4 melts, the complexes formed can be described as polyhedra more or less connected depending on the ThF_4 concentration. The anion point of view given by the *in situ* NMR experiments confirms the important role of fluorine atoms in the melt.

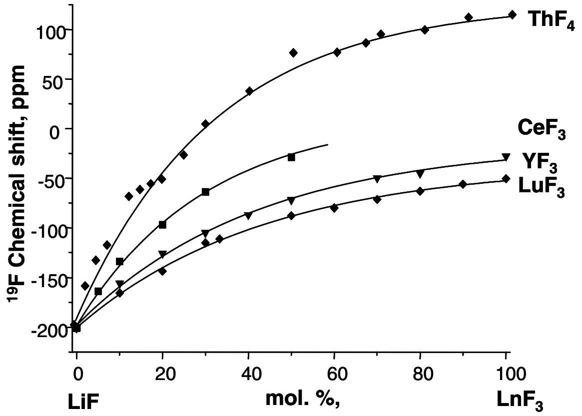

Fig. 6. ^{19}F chemical shifts evolution with LnF_3 content in LiF–LnF_3 binaries (Ln = Ce, Lu, and Y) at high temperature/comparison with LiF–ThF_4.

The thorium being not observable by NMR, these data have been combined with the approach of the cation point of view given by EXAFS measurements at the Thorium LIII edge *in situ* in solid and molten LiF–ThF_4 compositions. We report here the very first EXAFS spectra (Fig. 7(a)) obtained in these systems using our experimental set up and specific cells [4] developed for molten fluorides.

Fig. 7(b) shows the experimental *k*-weighted EXAFS spectra of LiF–ThF_4 (77.5–22.5%) at room temperature and at 576 °C in the solid and the molten phases respectively. The EXAFS oscillations are clearly visible in the *k*-range up to 9–10 $Å^{-1}$ for both temperatures. The decrease in oscillation amplitude at 576 °C is of the order of 30%. This damping reflects the thermal disorder increase at high temperature.

Fig. 7(c) shows the amplitude of the Fourier transform of the EXAFS spectra for the solid and the liquid samples. To obtain these Fourier transforms the *k* range from 1 to 10.9 $Å^{-1}$ was used and weighted with k^3. At both temperatures, we note a main peak around 1.9 Å corresponding to the nearest-neighbour distance (not corrected by the phase shift). For the liquid sample, in contrast to the solid, maxima related to more distant neighbours (characteristic of the medium-range order) are washed out. In the other hand, the main peak height of the liquid is reduced by a factor of 2.6 as compared to the solid at 25 °C and shifted to shorter Th–F distances (*R*). This reduction and broadening of the peak are typical of an asymmetric pair distribution function $g(r)$ characteristic of

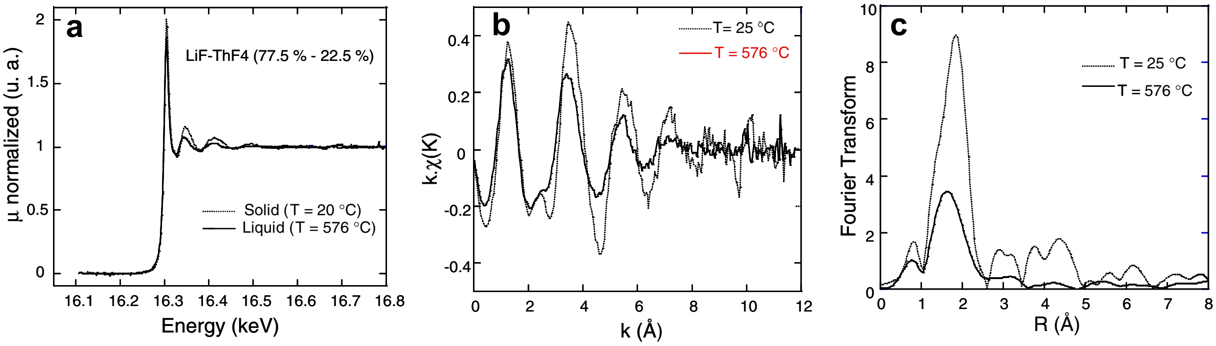

Fig. 7. (a) Absorption EXAFS spectra of thorium at the L_{III} edge for 77.5–22.5 mol% LiF–ThF_4 composition: solid 20 °C, molten 576 °C; (b) experimental *k*-weighted EXAFS spectra. The spectra are normalized to incident beam intensity and the background absorption is subtracted; (c) Fourier transform.

highly disordered systems. A quantitative analysis in terms of neighbours distance, number of neighbours and Debye–Waller factor is under progress and will be discussed in a next paper.

4. Conclusion

^{19}F high temperature NMR spectra evolution have been followed in different molten mixtures of LiF–LnF_3 ($Ln = Ce, Lu, Y$) binaries. Starting from pure LiF, the ^{19}F chemical shifts evidence an evolution from free to bridging fluorine between LnF_x polyhedra in melts rich in LnF_3. The same description has been applied to the LiF–ThF_4 binary, and shown that the ^{19}F evolution is rather similar and can be also described in terms of different kind of fluorines. First EXAFS spectra have been obtained *in situ* in molten LiF–ThF_4 mixtures, at the Thorium LIII edge and shown the availability of our high temperature device to study the compositions defined for the MSR concept.

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