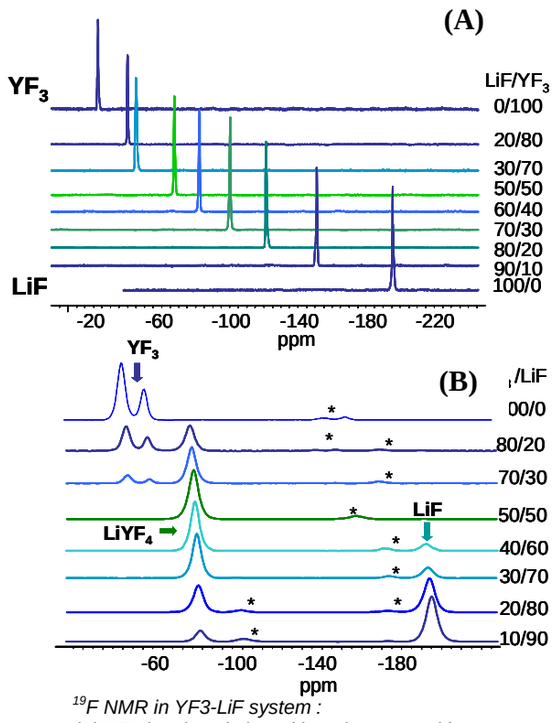
In Situ High Temperature NMR And EXAFS Experiments In Molten Lanthanide Fluorides: Application To Nuclear Wastes Recycling

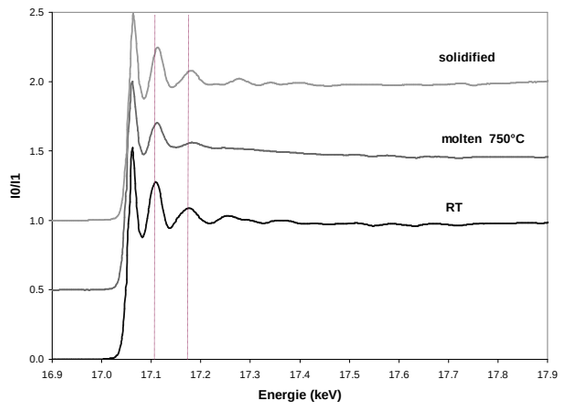
C. Bessada, A.L. Rollet, A. Rakhmatullin

CNRS-CRMHT, 45071 Orléans cedex 2, France,

The management of the nuclear reactor and the back-end of nuclear fuel cycle provide an extensive source of interests in the high temperature molten salts field. In particular, the mixtures of alkali-lanthanide fluoride and of alkali-actinide fluoride are of great importance for the molten salt reactor technology. Nevertheless, there is still an important need of physico-chemical data on these systems. Experimental study of molten fluorides is indeed extremely difficult because of their volatility and strong reactivity at high temperature (up to 1500°C for fluorides). Our laboratory, the CRMHT in Orléans, is mainly involved in the experimental study of solid and liquid materials from room temperature to very high temperature (3000°C) and thus in development of high temperature spectroscopy. High resolution NMR spectrometers have been combined to CO_2 laser heating in order to study the local structure of molten systems, including oxides and halide salts (fluorides, chlorides…). Recent developments of the heating system allow reaching the NMR signal (^{19}F, ^{7}Li, ^{23}Na, ^{35}Cl, ^{27}Al …) in situ in molten salts at high temperature. This research has been extended to molten lanthanide fluorides LnF_3 (Ln = Y, La, Ce, Pr, Nd, …) and binaries AkF-LnF_3 (Ak: alkali) with various compositions. In the same time, we have developed a specific cell for XAFS experiments in molten fluorides (up to 1400°C) to investigate the local environment, i.e. the first shells of neighbours, of the lanthanide ions in these mixtures. The combination of results obtained from in situ NMR and XAFS experiments for the different nuclei present in these high temperature melts gives the experimental evidence of complexes formation.



^{19}F NMR in YF3-LiF system :
(A) HT signal evolution with melts composition (800 to 1100°C)
(B) RT NMR MAS spectra of solidified mixtures



Yttrium EXAFS spectra in solid and molten LiF- YF3 (20-80mol%)