In Situ High Temperature NMR And EXAFS Experiments In Laf_3-Lif Melts

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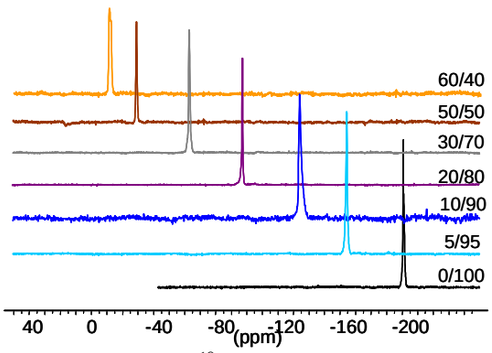
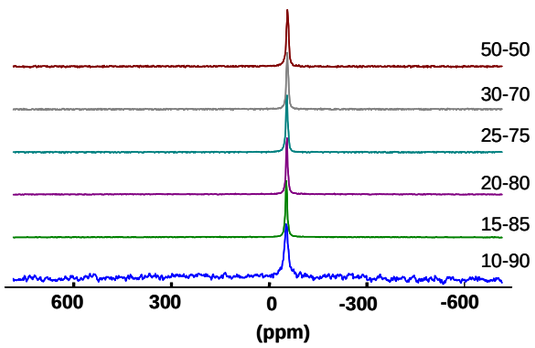
The properties as solvent of the high temperature molten salts have been the key point of many industrial applications: metal treatment (extraction, purification, recycling…), production of halogens in particular fluorine, production of glasses and ceramics, heat transfer, molten salt fuel cells, solar energy conversion, molten salt nuclear reactor… Some of their particular physico-chemical properties can be recalled: high thermal conductivity and capacity, moderate viscosity, high electrical conductivity, mutual miscibility, wide range of thermochemical stability, good solvents and non aqueous media, good electrochemical stability, corrosive, low dielectric constants, hygroscopic… Moreover, the molten salts are highly associated liquids. However, their local structure (nature of neighbors, coordination and distances around the cation…) is still matter of debate, particularly in the case of fluorides. Indeed, manipulation hindrances caused by relatively elevated melting points (500-1500°C) and high corrosiveness, have generated scarcity in experimental data for molten fluoride salts.

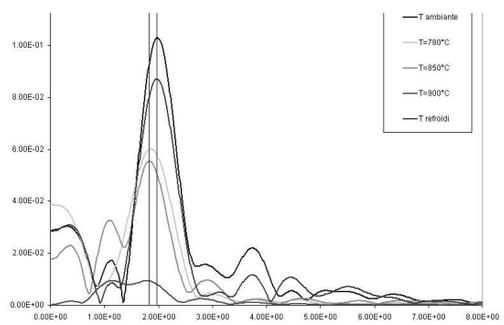
This presentation will deal with our recent results on binary mixtures of lanthanum fluoride and lithium. Different structural information has been collected using NMR and EXAFS techniques. These studies have required an important preliminary development in order to adapt these techniques to the high temperature, corrosiveness and volatility of the samples. We have investigated the influence of the composition of the salt on the local structure of the cations and the anion. The NMR results indicate that the local environment is not modified around the cation. The EXAFS results on the Lanthanum indicate that the distance La-F is decreased in the melt compared with the corresponding solid. These results give a local view on the character of “highly associated liquids” of these systems.



High temperature ^{19}F NMR spectra evolution in LaF_3 –LiF melts (850-1250°C)



High temperature ^{139}La NMR spectra evolution in LaF3-LiF melts (850-1250°C)



Fourier transform of EXAFS spectra of 20-80 mol% LaF3-LiF