

## Lanthanide additional effect on the local structure of zirconium cation in molten LiF – ZrF<sub>4</sub> eutectic

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### Introduction

Researches on the Generation IV nuclear reactors have been focused on respecting a series of criteria in terms of sustainability, safety and reliability, economics, proliferation resistance and physical protection. For example, fast reactors offer the possibility of burning actinides to further reduce waste and of being able to breed more fuel than they consume. Molten salts fast reactors current researches imagine the possibility of treating nuclear waste *in situ* in a loop dedicated for this purpose. Pyrochemical reprocessing consists of a reductive extraction of lanthanides from minor actinides. In order to simulate the pyrochemical treatment process it is mandatory to acquire a good knowledge of the ion speciation present on the molten. It is especially important to extract lanthanides from the fuel for avoiding neutronic poisoning of reactor. For this purpose we have studied the impact on the structure and speciation on M<sup>IV</sup>F<sub>4</sub>-LiF-M<sup>III</sup>F<sub>3</sub> systems by coupling XAFS measurements to molecular dynamics calculations. For synchrotron measurements we have added Ce<sup>III</sup>, Nd<sup>III</sup>, Sm<sup>III</sup> and Eu<sup>III</sup> to an initial eutectic mixture of 21%ZrF<sub>4</sub>-79%LiF mol (where Zr<sup>IV</sup> is used for modelling Th<sup>IV</sup>, main component of molten salts fuel). Preliminary experiments were carried out at PF / KEK and compared with the results by high temperature NMR on ZrF<sub>4</sub>-LiF-LaF<sub>3</sub>.

### Experimental

The Zr K-edge XAFS spectra have been collected with fixed time scan method by the X-ray from a double Si (111) crystals monochromator in transmission mode. Mixtures of (1-x)(ZrF<sub>4</sub>-LiF)-xLnF<sub>3</sub> (Ln = Ce, Sm, Eu and Nd at x=0.025; 0.05 and 0.075) were mixed with boron nitride powder, and pressed into pellets in 8 mm diameter and 1 mm thickness. The mixing weight ratio of sample to BN was ca. 1: 2. To prevent chemical reaction of samples with oxygen during heating process in EXAFS measurements, these pellets were installed in a cell made with pyrolytic boron nitride and the electric furnace was filled with He gas. Experiments were done at room temperature (before and after heating) and at different temperatures in the melt (mainly 650, 750 and 850°C), using a typical heating rate of 10°C/min. XAFS data were analysed by using the Athena software version 0.8.056.

### Results and discussion

Local structure of Zr<sup>IV</sup> has been evaluated on the ternary mixtures as function of temperature of the molten, trivalent element nature and molar content of this element. The impact of the nature of trivalent cations on the Zr coordination have been investigated and is compared in the next figure for a same content (7.5% molar of LnF<sub>3</sub> and 92.5% eutectic composition ZrF<sub>4</sub>-LiF) at 850°C of temperature. As we are measuring in liquid media short-range order of atoms leads to an only contribution on XAFS spectra, compared to fluoride solids where large-range order shows two kinds of contributions corresponding to 1<sup>st</sup> and 2<sup>nd</sup> coordination shell. Surface of this first shell contribution is more important on a binary mixture than a ternary one, which means that coordination number of fluorines around a zirconium decreases and Zr-F distance varies when lanthanides are added. Whatever the nature of lanthanide, the amplitude of the FT first peak does not drastically change.

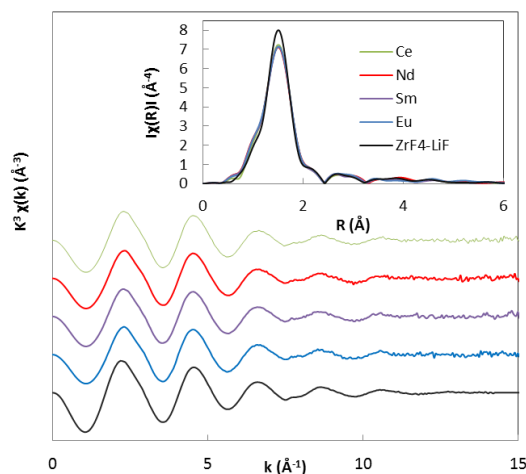


Fig. 1. Zr K-edge XAFS and FT spectra of (LiF-ZrF<sub>4</sub>)-LnF<sub>3</sub> (Ln=Nd, Eu, Ce, Sm 7.5% molar) at 850°C

Further XAFS studies on compositions closer to real composition of molten TMSR fuel on ThF<sub>4</sub>-LiF-LnF<sub>3</sub> must be carried out on L<sub>III</sub> edge of Th and must confirm the influence of adding trivalent cations on the local structure of main component of the molten fuel, i.e., thorium. Publication about this study is in progress.

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