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ARTICLE TYPE

In-situ spectroscopic study of the local structure of oxyfluoride melts: I. A NMR insight into the speciation LiF-LaF_3 containing oxides Supplementary Information

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1. X-Ray diffraction and MAS NMR characterization of the samples after HT NMR experiments

To identify the phases coexisting in the sample after NMR measurement, X-ray diffraction analysis on some samples have been also performed. The fig. S1 presents the X-Ray diffractograms of LiF-LaF_3 (x_{LaF3} = 0.20) + Li_2O (x_{Li2O} = 0.20) and of LiF-LaF_3 (x_{LaF3} = 0.20) + Li_2O (x_{Li2O} = 0.50) after High Temperature NMR experiments.

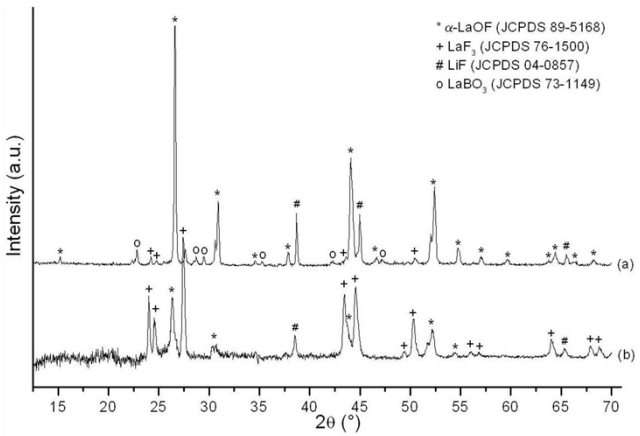

Fig. S1. X-ray diffraction patterns of the solidified compounds after high temperature NMR experiments: (a) LiF-LaF_3 (x_{LaF3} = 0.20) + Li_2O (x_{Li2O} = 0.50) and (b) LiF-LaF_3 (x_{LaF3} = 0.20) + Li_2O (x_{Li2O} = 0.20)

No Li_2O is observed in the diffractograms whatever its concentration. It has completely reacted with LaF_3 to form LaOF. No La_2O_3 is either observed. However in the case of x_{Li2O} = 0.50, the sample was heated for approximately 40 minutes at temperature up to 1400K and small amount of LaOF has reacted with the boron nitride (coming from the crucible) to form $LaBO_3$.

The ^{19}F MAS NMR spectra are displayed in figure S2. At x_{Li2O} = 0, the peak of LiF at -201ppm and the three peaks of LaF_3 can be observed. At x_{Li2O} = 1, the peak of LaOF at -35ppm is clearly visible along the one of LiF. This value is close to the value of rhombohedral-LaOF at room temperature obtained by Woo et al. by thermal decomposition of $LaFCO_3$.[1]

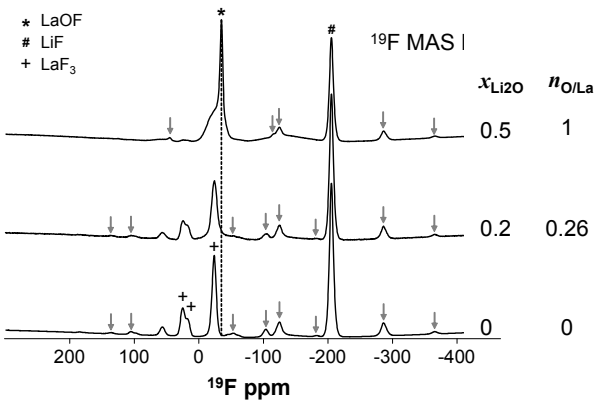

Fig. S2. ^{19}F MAS NMR of the solidified compounds after high temperature NMR experiments for several amount of Li_2O. The arrows indicate the spinning side bands.

2. Behaviour during heating

In the following figures are presented the NMR spectra of ^{19}F and ^{139}La from 790K to 1393 K in the mixture of LiF-LaF_3 (x_{LaF3} = 0.2, x_{LiF} = 0.8) + Li_2O:

- x_{Li2O} = 0 figure S3
- x_{Li2O} = 0.1 figure S4 and S5
- x_{Li2O} = 0.3 figure S6 and S7
- x_{Li2O} = 0.5 figure S8 and S9

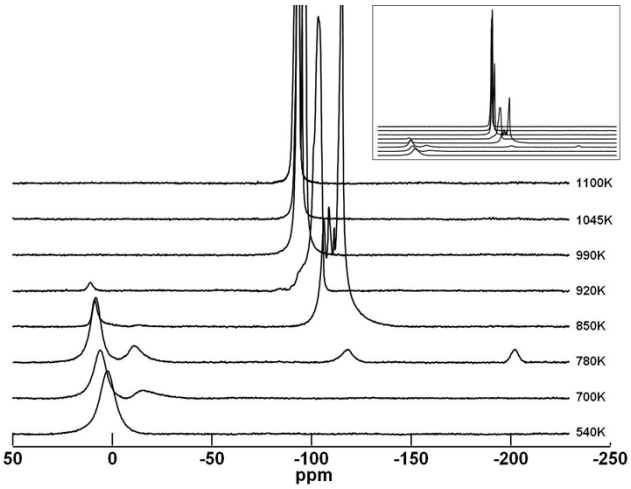

Fig. S3. ^{19}F NMR spectra of $LaLi_4F_7$ without Li_2O for increasing temperature. The liquid peak is not fully represented to allow us to see the LaOF, LaF_3 and LiF solid peaks. In the encart is shown the full spectra.

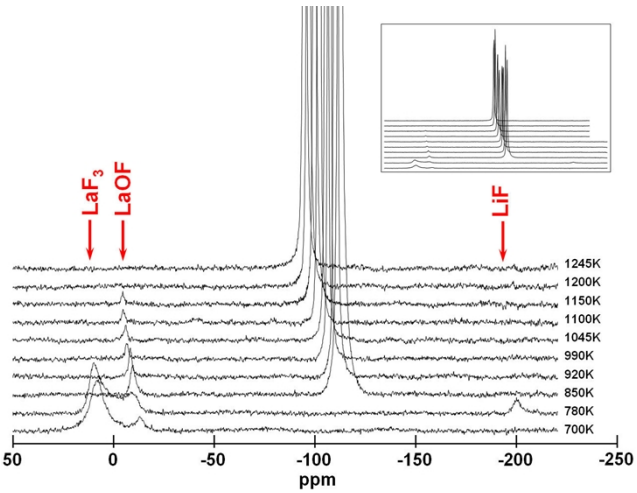

Fig. S4. ^{19}F NMR spectra of $LaLi_4F_7$+ Li_2O (x_{Li2O} = 0.10) for increasing temperature. The liquid peak is not fully represented to allow us to see the LaOF, LaF_3 and LiF solid peaks. In the encart is shown the full spectra.

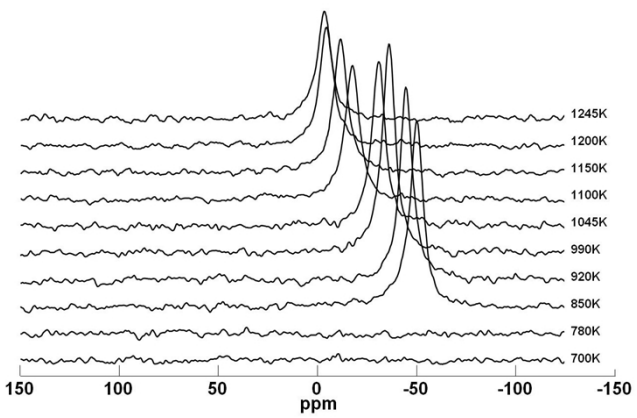

Fig. S5. ^{139}La NMR spectra of $LaLi_4F_7$+ Li_2O (x_{Li2O} = 0.10) for increasing temperature.

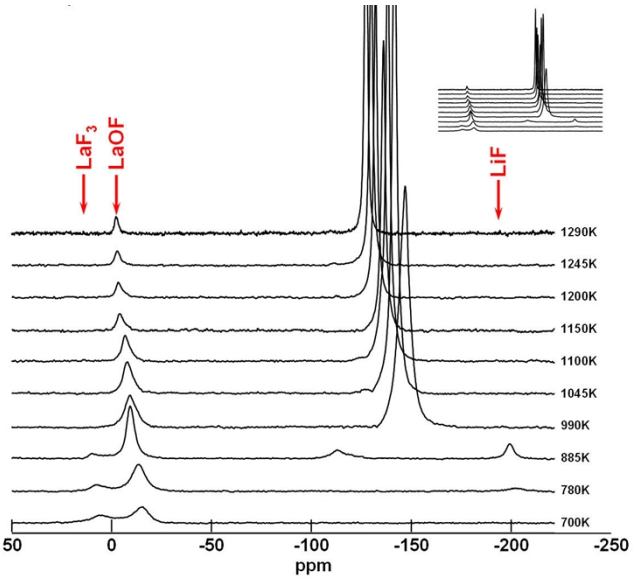

Fig. S6. ^{19}F NMR spectra of $LaLi_4F_7$+ Li_2O (x_{Li2O} = 0.30) for increasing temperature.

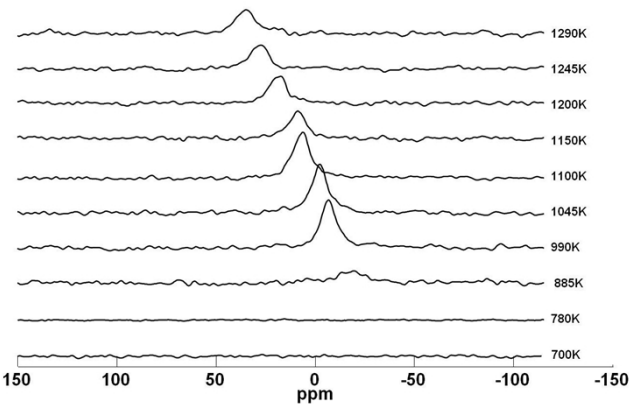

Fig. S7. ^{139}La NMR spectra of $LaLi_4F_7$+ Li_2O (x_{Li2O} = 0.30) for increasing temperature.

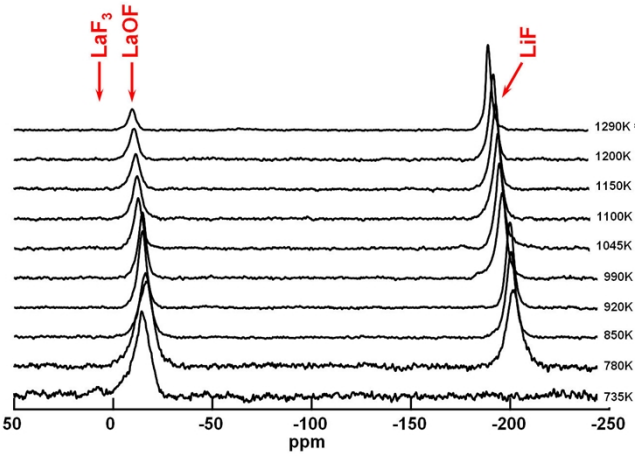

Fig. S8. ^{19}F NMR spectra of $LaLi_4F_7$+ Li_2O (x_{Li2O} = 0.50) for increasing temperature.

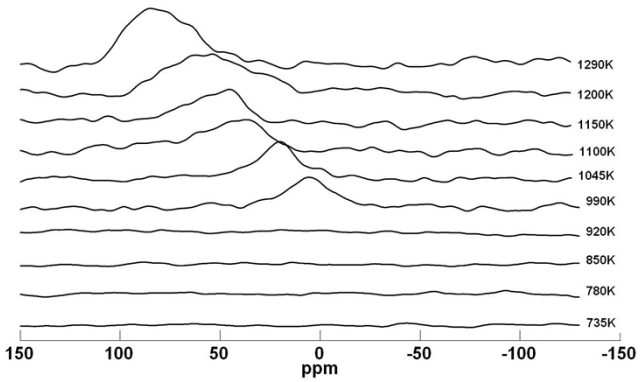

Fig. S9. ^{139}La NMR spectra of $LaLi_4F_7$+ Li_2O (x_{Li2O} = 0.50) for increasing temperature.

3. HT NMR experiments on the LaF_3-LiF phase diagram

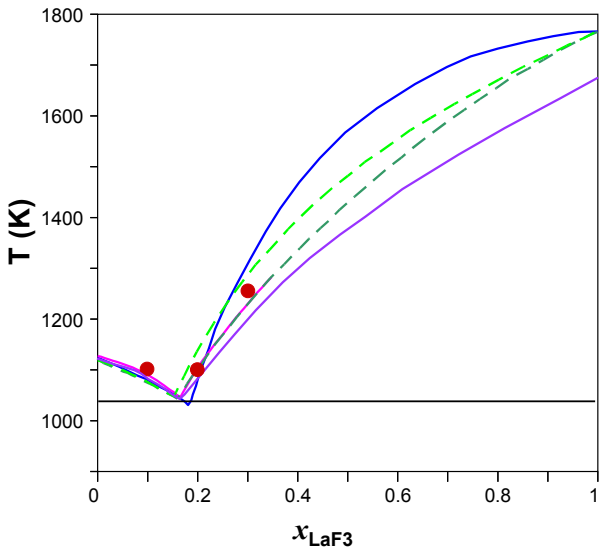

Fig. S10. LiF-LaF_3 phase diagram from Fedorov[2] (blue line), Beilmann et al.[3] (dashed dark green line), F. Abdoun et al. (pink line)[4], Van der Meer et al.[5] (dashed light green line), A. I. Agulyanskii and V. A. Bessonova[6] (purple line). The red points indicate the position of the experiments made in this paper.

If LaOF precipitation occurs when Li_2O is added to the system, it induces a shift in the phase diagram toward poorer composition in LaF_3 as shown in figure S11. For LaF_3-LiF 30-70mol%, the experimental temperature then becomes much higher than the liquidus temperature. The consequence in our experiments is a vaporization of LiF, we have therefore kept the experiment duration short and we haven't investigated the effect of temperature on this system. For LaF_3-LiF 10-90mol%, we had to increase the temperature to reach the liquidus.

Notes and references

1 D. C. Woo, M.-H. Lee, W.-S. Jung, *Ceram. Int.*, 2013, **39**, 1533.
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4 F. Abdoun, M. Gaune-Escard, G. Hatem, *J. Phase Equilib*., 1997, **18**, 6.
5 J. P. M. van der Meer, R. J. M. Konings, K. Hack, H. A. J. Oonk, *Chem. Mater*., 2006, **18**, 510.
6 A. I. Agulyanskii and V. A. Bessonova, *Zh. Neorg. Khim*., 1982, **27 [4]**, 1029-1032; *Russ. J. Inorg. Chem*. (Engl. Transl.), 1982, **27 [4]** 579-581.