# LiF – Rare Earth Fluoride Systems — Potential Novel Polaritonic Materials: Material Preparation and Phase Diagram Studies

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**Abstract**— Most systems consisting of LiF and $REF_3$ (RE: rare earth) possess a eutectic between LiF and an intermediate compound $RELiF_4$. This eutectic shows upon crystallization ordering that could be useful for its application as metamaterial. Aspects of material preparation, phase diagram studies, and the growth of self-organized eutectic structures are reported.

Thoma [1] reported that some systems $LiF–REF_3$ (RE = rare earth element from La to Lu, or Y, respectively) contain one intermediate compound $LiREF_4$ which melts congruently for RE = Er, Tm, Yb, Lu, and possibly Y. For RE = Eu, Gd, Tb, Dy, Ho the $LiREF_4$ undergo peritectic melting under the formation of $REF_3$. LiF (melting point $T_f = 848\,^{\circ}C$) and $LiREF_4$ ($690\,^{\circ}C \leq T_f \leq 819\,^{\circ}C$) are in equilibrium with the melt at one eutectic point. Crystallized eutectics are known as prospective metamaterials [2] and the preparation of such eutectics will be in the focus of this study. The intermediate compounds crystallize in the tetragonal scheelite crystal structure type and could rather be written as $RE^{[8]}[Li^{[4]}F_4]$ because $Li^+$ (73 pm) is much smaller than e.g. $Y^{3+}$ (116 pm). However, the radii are differing less than in the eponym mineral scheelite ($CaWO_4$) and the formation of complex anions is not so pronounced. $Bi^{3+\,[8]}$ (131 pm) is considerably larger compared to the $RE^{3+\,[8]}$ and $BiLiF_4$ crystals possessing scheelite structure were grown by Schultheiss et al. [3]. The different $RE^{3+}$ ions can replace each other and consequently $(RE,RE')LiF_4$ crystals are interesting for laser hosts or scintillators. Single crystals of $Nd_xY_{1-x}LiF_4$ (YLF) are offered commercially. It turns out, however, that material preparation and phase relations in such pseudo-binary ($LiF–REF_3$) or pseudo-ternary ($LiF–REF_3–RE'F_3$) systems are not straightforward.

Depending on the cation, fluorides are more or less sensitive against moisture. If water is present in the environment, reactions such as

$$F^- + H_2O \rightleftarrows OH^- + HF \tag{1}$$

$$2\,F^- + H_2O \rightleftarrows O^{2-} + 2\,HF \tag{2}$$
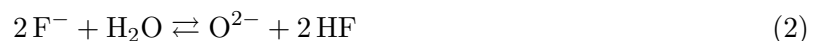
can destroy the material. If 1 mol LiF is heated in 1 mol Ar with $10^{-6}$ mol (1 ppm) water to $700\,^{\circ}C$ (close to the $LiF/YLiF_4$ eutectic temperature), $6 \times 10^{-9}$ mol HF are created by (1). For $YF_3$ the situation is worse: Here $1.5 \times 10^{-6}$ mol HF are created by (2) and only 25% of the water is unchanged. As water is ubiquitous, many commercial fluorides are contaminated by oxides. On the other hand, the back reaction (2) is a good possibility to prepare fluorides of superior quality. The process works as follows [4]: (i) starting material (typically oxide, if not available carbonate) is heated in flowing Ar ($\geq 99.99\%$ purity) to $\approx 850\,^{\circ}C$; (ii) HF gas is added to the Ar flow approximately 1:1 for several hours (depending on mass); (iii) the product is cooled to room temperature in the Ar/HF flow; (iv) the HF is removed either by rinsing with HF, or by pumping. Conversion rates $> 99.95\%$ are typically obtained with such treatment, and the quality of the $REF_3$ can be checked by thermal analysis that shows sharp peaks for melting and (if appropriate) the solid state phase transformation. It should be noted that not only the melting behavior of the $REF_3$ depends on the chemical purity of the chemicals and the atmosphere, but also the behavior of the scheelites: Pastor et al. [5] showed that only the hydrolysis of yttrium fluoride is responsible for the often claimed incongruent melting of $YLiF_4$ — instead it is "borderline peritectic" (Fig. 1 left).

All $REF_3$ are melting considerable higher compared to LiF. Consequently it turns out that in the case of peritectic decomposition of the $RELiF_4$ the rare earth fluoride remains as solid. This is
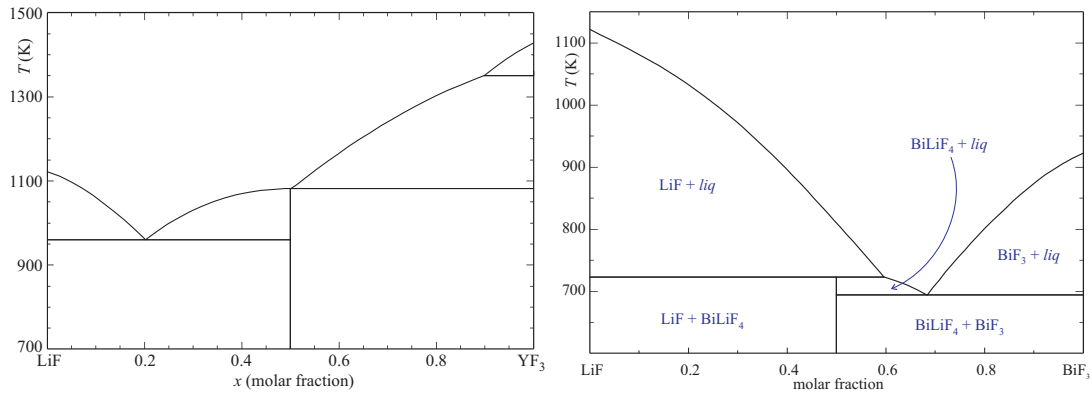
Figure 1: The binary phase diagrams LiF–YF$_3$ (left panel, [6]) and LiF–BiF$_3$ (right panel).

not the case for the system LiF–BiF$_3$ where bismuth fluoride melts 200 K below LiF. Consequently LiF remains upon the peritectic decomposition of BiLiF$_4$ at 725 K (Fig. 1 right). In contrast to the LiF-REF$_3$ systems, both phases forming the eutectic in LiF-BiF$_3$ contain the heavy metal.
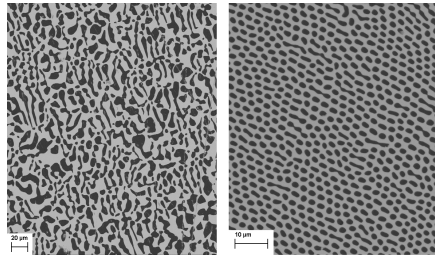


Figure 2: SEM micrographs of cross sections of LiF–YLiF$_4$ (left) and LiF–YLiF$_4$ doped with 1 mol% ErF$_3$ (right) growth by Bridgman at 4 mm/h and 40 mm/h respectively. The images show the most frequently found microstructure on the samples. The dark phase is LiF.

First growth experiments of undoped and Er-doped LiF–YLiF$_4$ show some degree of ordering by self organization that improves with higher pulling rate (Fig. 2). It is clear that further studies with doped samples will require better understanding of the LiF–REF$_3$–RE´F$_3$ systems, because the eutectic point degenerates there to a eutectic line. For LiF–LuF$_3$–GdF$_3$, with a crossover from congruently to peritectically melting scheelites, a complete thermodynamic assessment is demonstrated for the first time [7].

**ACKNOWLEDGMENT**

**REFERENCES**

1. R. E. Thoma, G. D. Brunton, Equilibrium dimorphism of the lanthanide trifluorides, Inorg. Chem. 5 (1966) 1937–1939, doi:10.1021/ic50045a022.
2. D. A. Pawlak, Metamaterials and photonic crystals – potential applications for self-organized eutectic micro- and nanostructures, Scientia Plena 4 (2008) 14801.
3. E. Schultheiss, A. Scharmann, D. Schwabe, Single crystal growth and structure analysis of BiLiF$_4$, J. Crystal Growth 80 (1987) 261–269.
4. H. Guggenheim, Growth of highly perfect fluoride single crystals for optical masers, J. Appl. Phys. 34 (1963) 2482–2485.
5. R. C. Pastor, M. Robinson, W. M. Akutagawa, Congruent melting and crystal growth of LiRF$_4$, Mat. Res. Bull. 10 (1975) 501–510.
6. I. A. D. Santos, D. Klimm, S. L. Baldochi, I. M. Ranieri, Thermodynamic modeling of the LiF–YF$_3$ phase diagram, J. Crystal Growth (accepted).
7. I. A. dos Santos et al., to be published.