Supporting information

$Na_{(1-x)}Li_x(Gd_{0.39}Y_{0.39}Yb_{0.2}Er_{0.02})F_4$ ($0 \leq x \leq 1$) solid solution microcrystals: Li/Na ratio-induced transition of crystalline phase and morphology, and their enhanced upconversion emission

Ran Luo[a], Tao Li[a], Yang Chen[a], Zhanglei Ning[a], Yan Zhao[a*], Mengjiao Liu[a], Xin Lai[a], Cheng Zhong[b], Chao Wang[c], Jian Bi[a], Daojiang Gao[a*]

[a] *College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610068, China*

[b] *Department of Basic Education, Dazhou Vocational and Technical College, Dazhou 635001, China*

[c] *Clean Energy Materials and Engineering Center, State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, 611731, P.R. China*

Corresponding author: Yan Zhao and Daojiang Gao

E-mail address: zhaoyan@sicnu.edu.cn;

daojianggao@sicnu.edu.cn; daojianggao@126.com

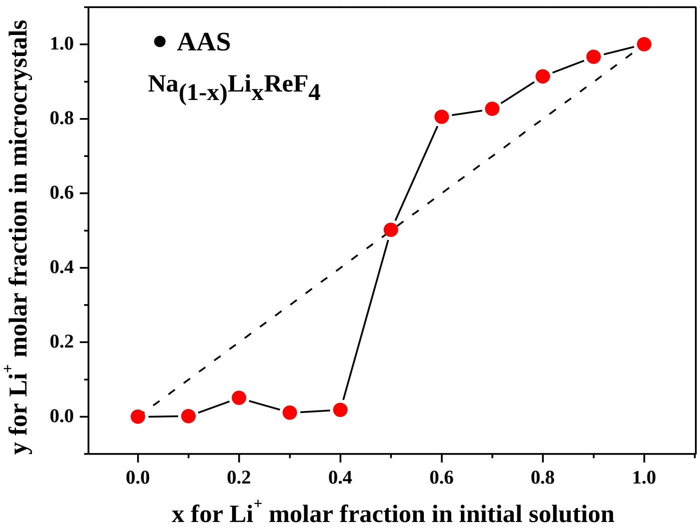

Figure S1. Molar fraction of Li^+ ions in $Na_{(1-x)}Li_xReF_4$ microcrystals depending on the molar fraction of Li^+ in the initial solution,

x= [Li^+ molar content in initial solution]/ ([Li^+ molar content in initial solution] + [Na^+ molar content in initial solution), y= [Li^+ molar content in microcrystals]/ ([Li^+ molar content in microcrystals] + [Na^+ molar content in microcrystals]).

Table S1. Molar fraction of Li^+ in the initial solution and the $Na_{(1-x)}Li_xReF_4$ microcrystals

Ideal molar fraction of Li^+ in initial solution	**Molar content of Li^+ and Na^+ in microcrystals**		**Molar fraction of Li^+ in microcrystals**
	Li^+ %	Na^+ %	
x=0	0	0.38	0
x=0.1	0.00034	0.38	0.00091
x=0.2	0.021	0.40	0.050
x=0.3	0.0055	0.51	0.011
x=0.4	0.0057	0.31	0.018
x=0.5	0.18	0.18	0.50
x=0.6	0.19	0.045	0.81
x=0.7	0.45	0.095	0.83
x=0.8	0.44	0.042	0.91
x=0.9	0.81	0.028	0.97
x=1.0	0.46	0	1.0

The exact amount of Li^{+}/Na^{+} ratios in $Na_{(1-x)}Li_{x}ReF_4$ microcrystals is important for working out the effect of substitution on the properties of materials. Atomic absorption spectroscopy (AAS) is used to determine the amount of Li^{+} doped in the $Na_{(1-x)}Li_{x}ReF_4$ microcrystals (molar fraction y) and are compared with the molar fraction of Li^{+} in initial solution (x). Table S1 shows the ideal molar fraction of Li^{+} in initial solution and the exact molar fraction of Li^{+} (*i. e.* the actual fraction of Li^{+}) in the obtained $Na_{(1-x)}Li_{x}ReF_4$ microcrystals, respectively. Fig. S1 also gives the molar fraction of Li^{+} ions in the $Na_{(1-x)}Li_{x}ReF_4$ microcrystals depending on the molar fraction of Li^{+} in the initial solution, in which, the dashed line represents the ideal molar fraction of Li^{+} in initial solution and the solid line represents the actual molar fraction of Li^{+} in the obtained $Na_{(1-x)}Li_{x}ReF_4$ microcrystals. It can be seen that when the molar fraction of Li^{+} in the initial solution is less than 0.4, the fraction of Li^{+} in the obtained $Na_{(1-x)}Li_{x}ReF_4$ microcrystals is much lower than its ideal one in the initial solution, whereas the fraction of Li^{+} in the obtained $Na_{(1-x)}Li_{x}ReF_4$ microcrystals is slight higher than that one in the initial solution when $x \geq 0.6$. Most importantly, the fraction of Li^{+} in obtained $Na_{(1-x)}Li_{x}ReF_4$ microcrystals is almost same to that one in the initial solution when $x = 0.5$. The detailed explanations are given in the section of Supporting Information. This change trend may be explained through the principle of hard and soft acids and bases (HSAB) and solubility product rule as follows. According to HSAB, hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases [1, 2], where hard acids are defined as the acceptor atoms with high positive charge, small size and no easily polarized outer electrons, whereas hard bases are the donor atom hardly oxidized with high electronegativity, low polarizability and only high energy empty orbitals. In aqueous solution, H_2O and $[ReF_4]^-$ can be regarded as a Lewis base. Since $[ReF_4]^-$ (Re = Gd, Y) has a larger volume than H_2O molecule and has a negative charge, it is a softer base than H_2O. As a Lewis acid, Li^+ has much larger ion potential than that of Na^+, hence its hardness is greater than that of Na^+. Therefore, Li^+ tends to bond to H_2O to form a hydrated ion instead of forming $LiReF_4$ precipitate with $[ReF_4]^-$, resulting in a larger solubility of $LiReF_4$ crystal in aqueous solution. Combination with the solubility product rule, the relationship between the molar fraction of Li^+ in the $Na_{(1-x)}Li_xReF_4$ microcrystals and the molar fraction of Li^+ in the initial solution can be easily understood. At the lower x (Li^+ molar fraction in solution), it will have a much lower degree of supersaturation for $LiReF_4$ than that of $NaReF_4$ owing to the lower Li^+ ion concentration in the initial solution and the larger solubility of $LiReF_4$. Therefore, there are most of Na^+ ions and part of Li^+ ions can combine with $[ReF_4]^-$ to stable $Na_{(1-x)}Li_xReF_4$ in solution, leading to the larger negative deviation in Li^+ molar fraction in the final $Na_{(1-x)}Li_xReF_4$ microcrystals. Whereas at the higher x ($x \geq 0.6$), it will have the higher degree of supersaturation for $LiReF_4$ than that of $NaReF_4$ owing to the higher Li^+ ion concentration in the initial solution. Hence, the majority of Li^+ ions and part of Na^+ ions can be incorporated in the final $Na_{(1-x)}Li_xReF_4$ microcrystals, resulting in the relative smaller positive deviation in Li^+ molar fraction in the final $Na_{(1-x)}Li_xReF_4$ microcrystals. As for the case at x=0.5, there are both higher degree of supersaturation for $LiReF_4$ and $NaReF_4$ due to the both higher concentrations of Li^+ ion and Na^+ ion in the initial solution, it can ensure that the most of Li^+ ions and the most of Na^+ ions both be incorporated in the final $Na_{(1-x)}Li_xReF_4$ microcrystals. As a result, the molar fraction of Li^+ ions in the $Na_{(1-x)}Li_xReF_4$ microcrystals is almost to the same that one in the initial solution.

References

[1] Pearson, R. G. Hard and soft acids and bases -the evolution of a chemical concept. *Coord. Chem. Rev*. **1990**, 100, 403-425.

[2]Pearson, R. G. Hard and soft acids and bases, HSAB, part 1: fundamental principles. *J. Chem. Educ*. **1968**, 45, 581-587.

Table S2. Fitting parameters of the $^4S_{3/2}$ state of Er^{3+} ions (542 nm) for the $Na_{(1-x)}Li_xReF_4$ samples with x=0, 0.5 and 1.

Li^+ concentration (molar fraction)	**Fitting Parameters**			
	A_1	τ_1 /μs	A_2	τ_2/μs
x = 0	554.96	89.85	554.95	89.85
x = 0.5	3182.99	181.03	867.29	647.93
x = 1	293.41	345.61	24108.32	66.54