Supporting Information

High-Temperature MAS NMR Reveals a Sodium Ion Doped Crystal Phase Formation in FLiNaK Eutectic Salt Solidification

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- **Figure S1.** ¹⁹F solid-state NMR spectra of LiF, NaF, KF and FLiNaK eutectic salt at room temperature.
- **Figure S2.** ⁷Li and ²³Na solid-state NMR spectra of LiF, NaF and FLiNaK eutectic salt at room temperature.
- Figure S3. XRD patterns of LiF, NaF, KF and FLiNaK eutectic salt at room temperature.
- **Figure S4.** Quantitative ²³Na spectrum of FLiNaK eutectic salt at room temperature.
- **Figure S5.** The binary NaF-KF phase diagram.
- **Figure S6.** ¹⁹F-²³Na CP/MAS spectrum of FLiNaK eutectic salt with different spinlock time.
- **Figure S7.** ²³Na T₁ relaxation curves at different temperature.
- Table S1.
 Chemical shift calculating results of different ionic structures of NaF-KF systems.

Figure S1. ¹⁹F solid-state NMR spectra of LiF, NaF, KF and FLiNaK eutectic salt at room temperature.



Figure S2. ⁷Li and ²³Na solid-state NMR spectra of LiF, NaF and FLiNaK eutectic salt at room temperature.



Figure S3. XRD patterns of LiF, NaF, KF and FLiNaK eutectic salt at room temperature.



Figure S4. Quantitative ²³Na spectrum of FLiNaK eutectic salt at room temperature. (D1 was set to 100 s to ensure complete relaxation of ²³Na spins)



Figure S5 The binary NaF-KF phase diagram.



Figure S6. ¹⁹F-²³Na CP/MAS spectrum of FLiNaK eutectic salt with different spinlock time.





Figure S7. ²³Na T₁ relaxation curves at different temperature.

Table S1. ²³Na chemical shift calculating results of different ionic structures of NaF-KF systems.

	Calculated shielding	Reference shielding	Calculated chemical
	tensor (ppm)	tensor (ppm)	shift (ppm)
NaF crystal	546.57	553.67	7.1
Na-K doped crystal	564.94	553.67	-11.27
NaF-KF 100-100 phase	539.33	553.67	14.34
NaF-KF 110-110 phase	534.08	553.67	19.59