

## Supporting information

### **LiF-Doped Sulfide Solid Electrolytes with Stabilized $\alpha$ -Li<sub>3</sub>PS<sub>4</sub> Analog Phase for All-Solid-State Li Metal Batteries**

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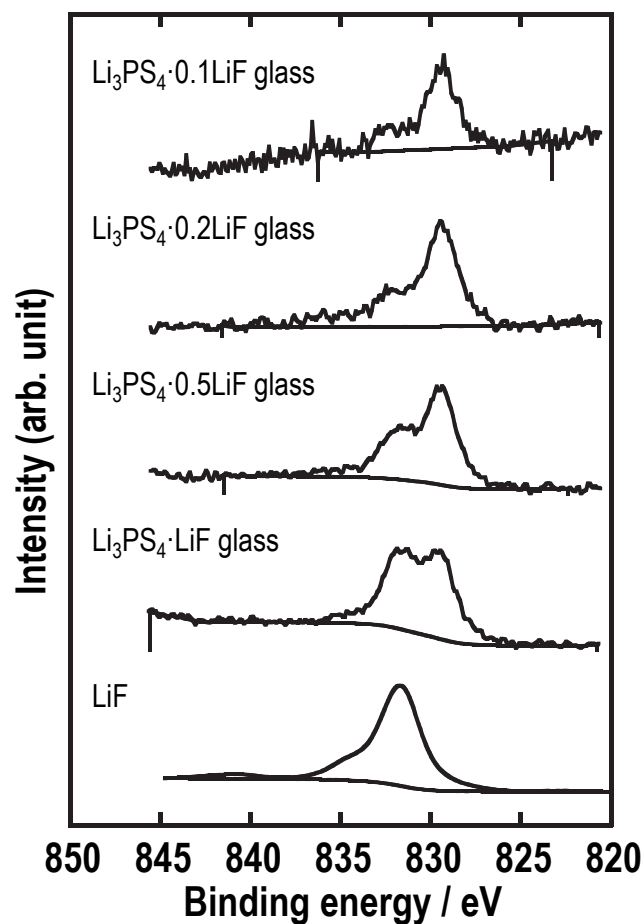


Figure S1 F KLL XPS spectra of  $\text{Li}_3\text{PS}_4 \cdot x\text{LiF}$  glasses.

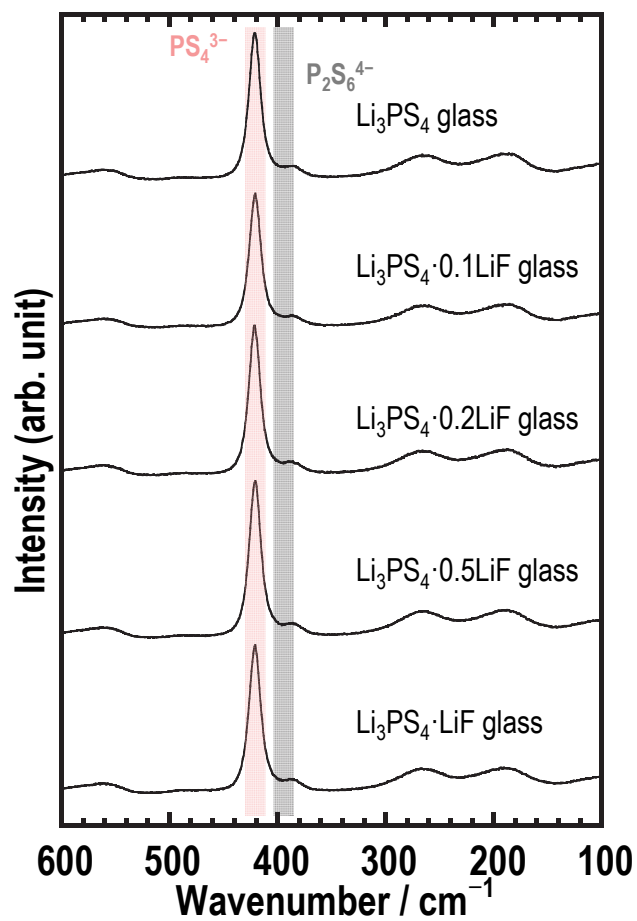
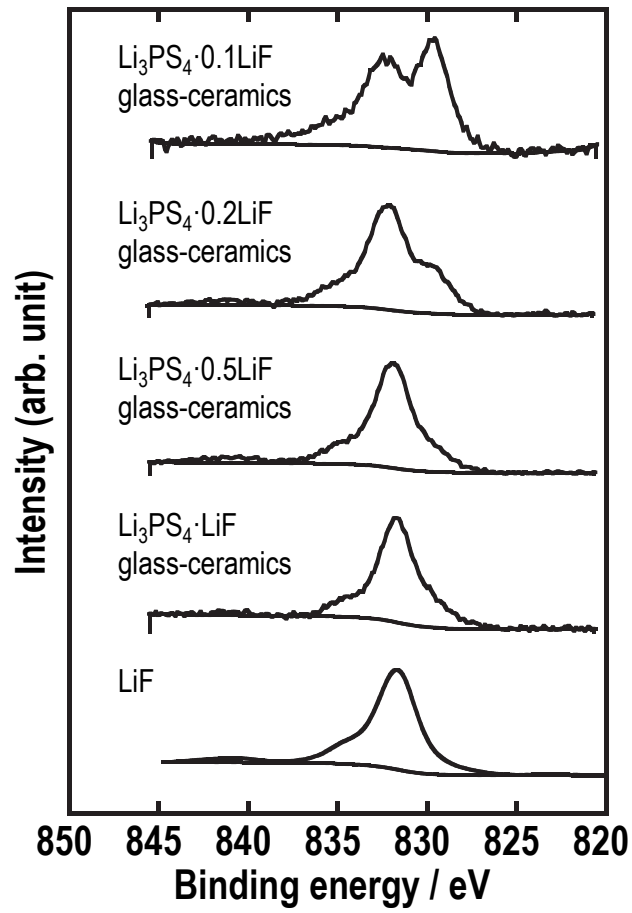
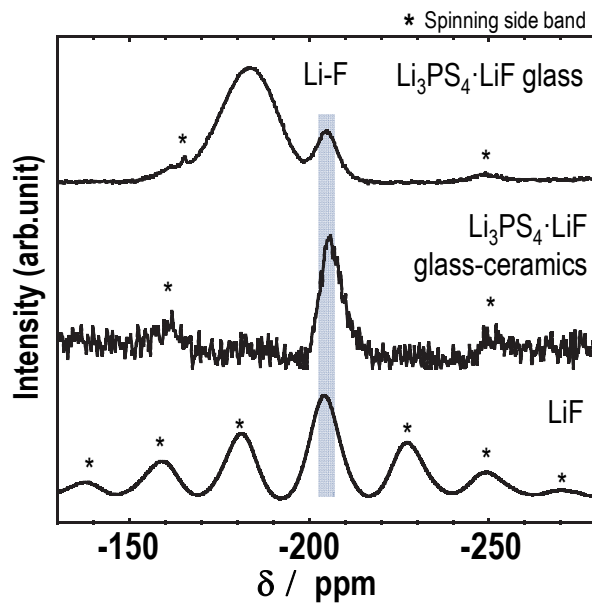


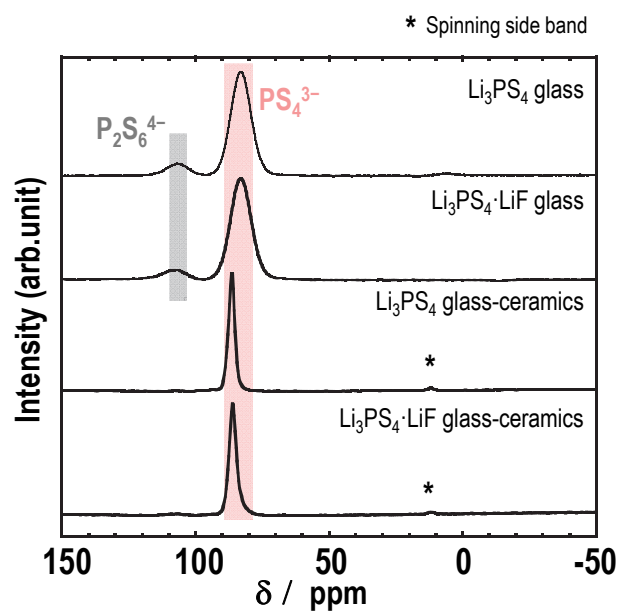
Figure S2 Raman spectra of  $\text{Li}_3\text{PS}_4 \cdot x\text{LiF}$  glasses.



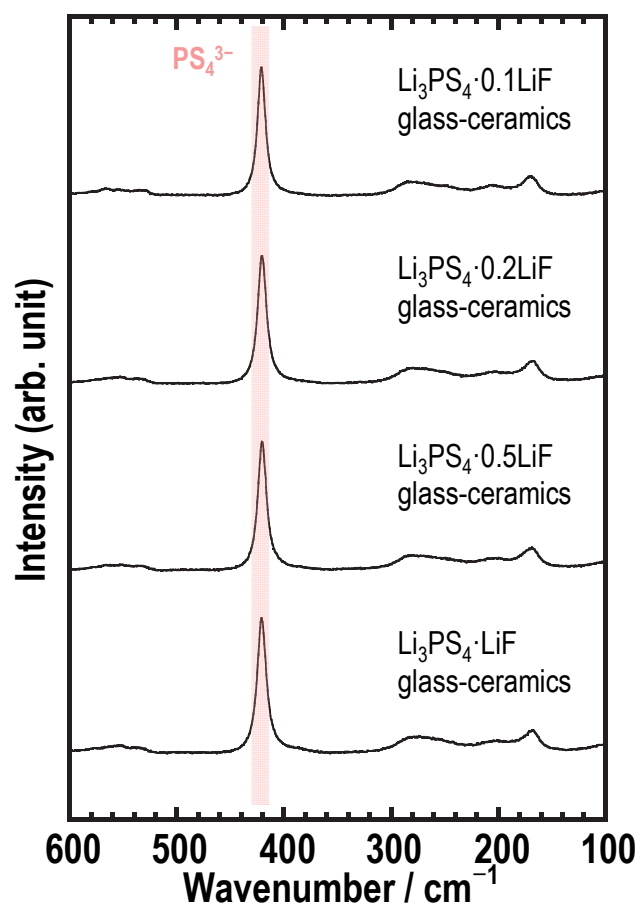
**Figure S3** F KLL XPS spectra of  $\text{Li}_3\text{PS}_4 \cdot x\text{LiF}$  glass-ceramic samples.



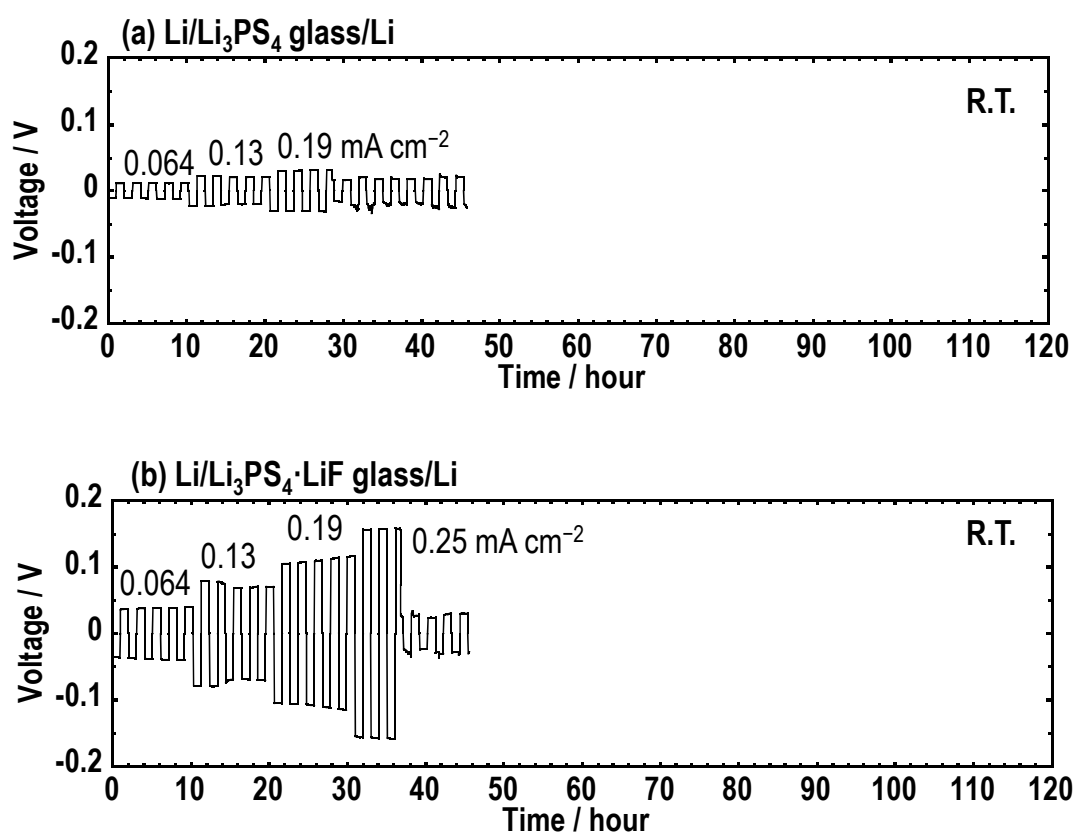
**Figure S4**  $^{19}\text{F}$  MAS-NMR spectra of  $\text{Li}_3\text{PS}_4 \cdot \text{LiF}$  glass and glass-ceramic samples.



**Figure S5**  $^{31}\text{P}$  MAS- NMR spectra of  $\text{Li}_3\text{PS}_4 \cdot \text{LiF}$  glass and glass-ceramic samples.



**Figure S6** Raman spectra of  $\text{Li}_3\text{PS}_4 \cdot x\text{LiF}$  glass-ceramics samples.



**Figure S7** Galvanostatic cycling tests of (a)  $\text{Li}/\text{Li}_3\text{PS}_4$  glass/ $\text{Li}$  and (b)  $\text{Li}/\text{Li}_3\text{PS}_4 \cdot \text{LiF}$  glass/ $\text{Li}$  cells at room temperature. The applied current densities are shown in the figure.

**Table S1** The result of intensity decomposition for XRD pattern of  $\text{Li}_3\text{PS}_4$  glass-ceramic sample.

Crystal system	Orthorhombic	Lattice parameter	$a = 12.457 (3) / \text{\AA}$ $b = 8.2968 (15) / \text{\AA}$ $c = 6.1439 (10) / \text{\AA}$	$\alpha = \beta = \gamma = 90^\circ$
Space group	<i>Pnma</i> (No. 62)	Volume	$V = 635.014 / \text{\AA}^3$	$Z = 4$
$R_{\text{wp}} = 4.63 \%$ , $S = 2.1775$				

**Table S2** The result of intensity decomposition for XRD pattern of  $\text{Li}_3\text{PS}_4 \cdot \text{LiF}$  glass-ceramic sample.

Crystal system	Orthorhombic	Lattice parameter	$a = 12.486 (4) / \text{\AA}$ $b = 8.2710 (15) / \text{\AA}$ $c = 6.1414 (10) / \text{\AA}$	$\alpha = \beta = \gamma = 90^\circ$
Space group	<i>Pnma</i> (No. 62)	Volume	$V = 635.997 / \text{\AA}^3$	$Z = 4$
$R_{\text{wp}} = 3.58 \%$ , $S = 1.6435$				