

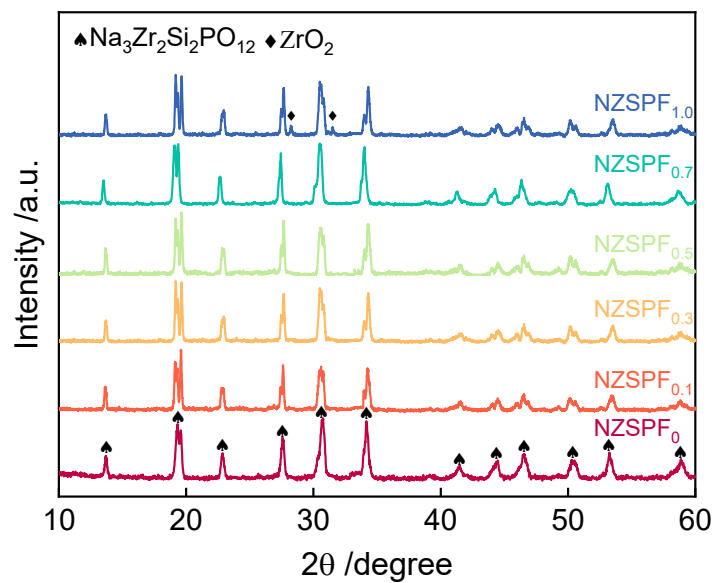
## **Supporting Information**

### **Epoxy resin reinforced F-assisted Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> solid electrolyte for solid-state sodium batteries**

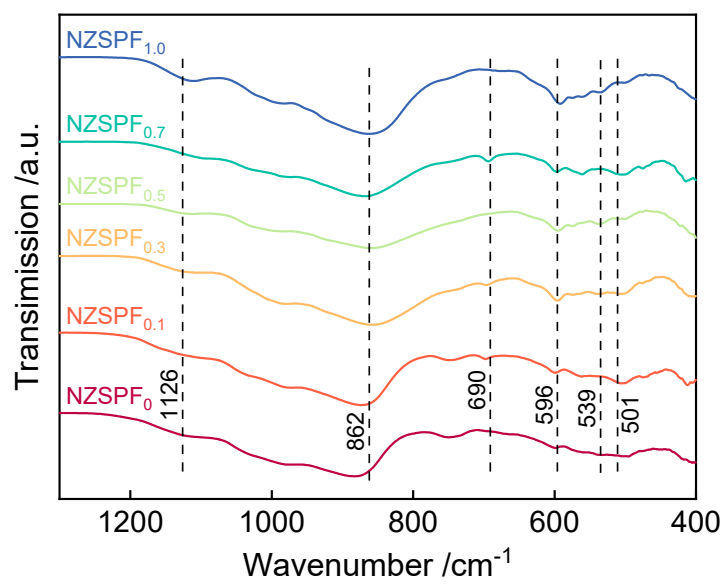
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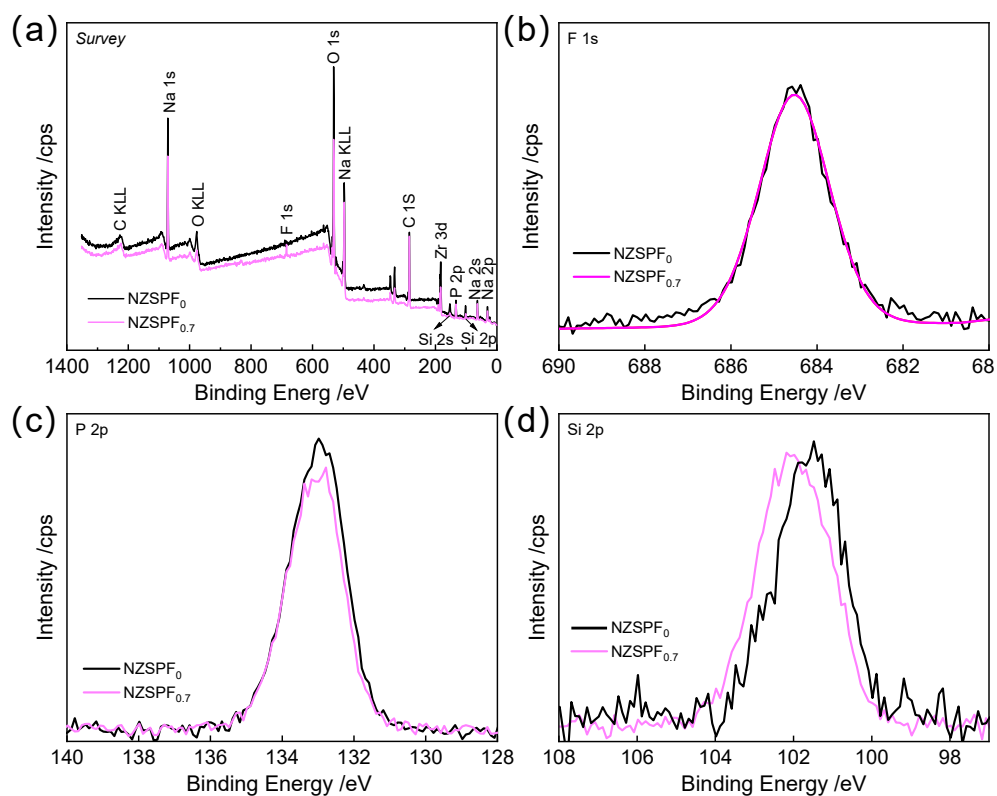
E-mail: guohong@ynu.edu.cn (H.G.)



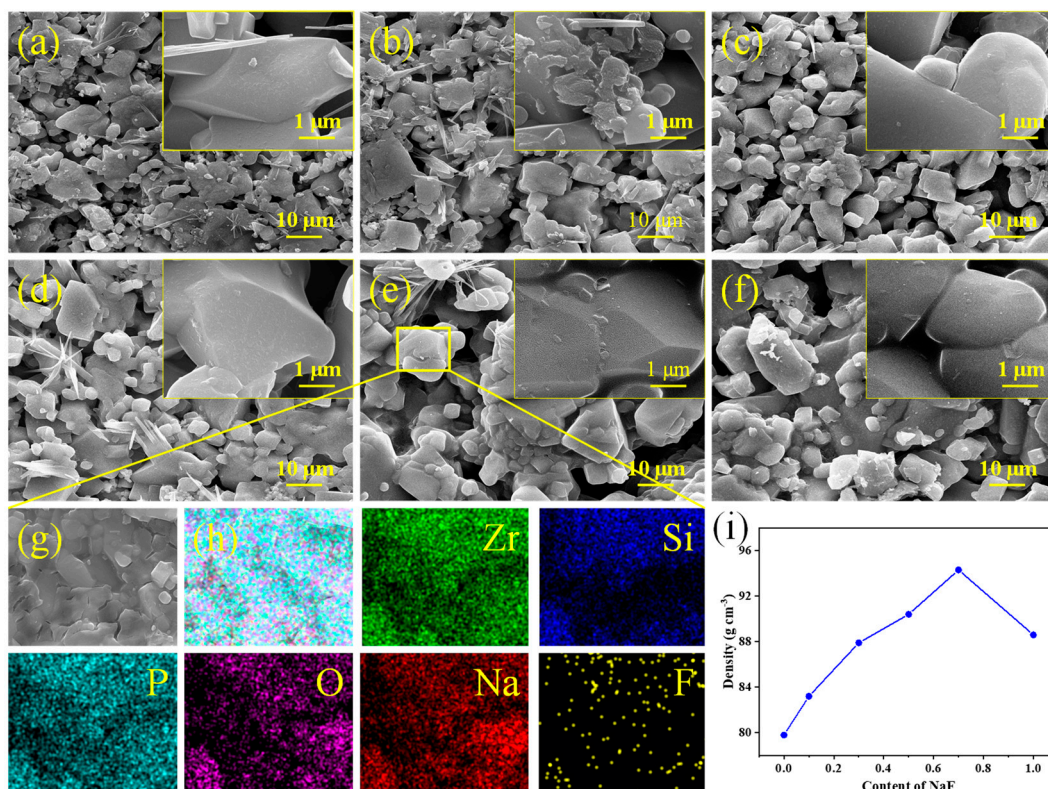
**Figure S1.** (a) XRD patterns of  $\text{NZSPF}_x$  ( $x = 0, 0.1, 0.3, 0.5, 0.7$ , and  $1.0$ ).



**Figure S2.** FTIR spectra of  $\text{NZSPF}_x$  ( $x = 0, 0.1, 0.3, 0.5, 0.7$ , and  $1.0$ ).

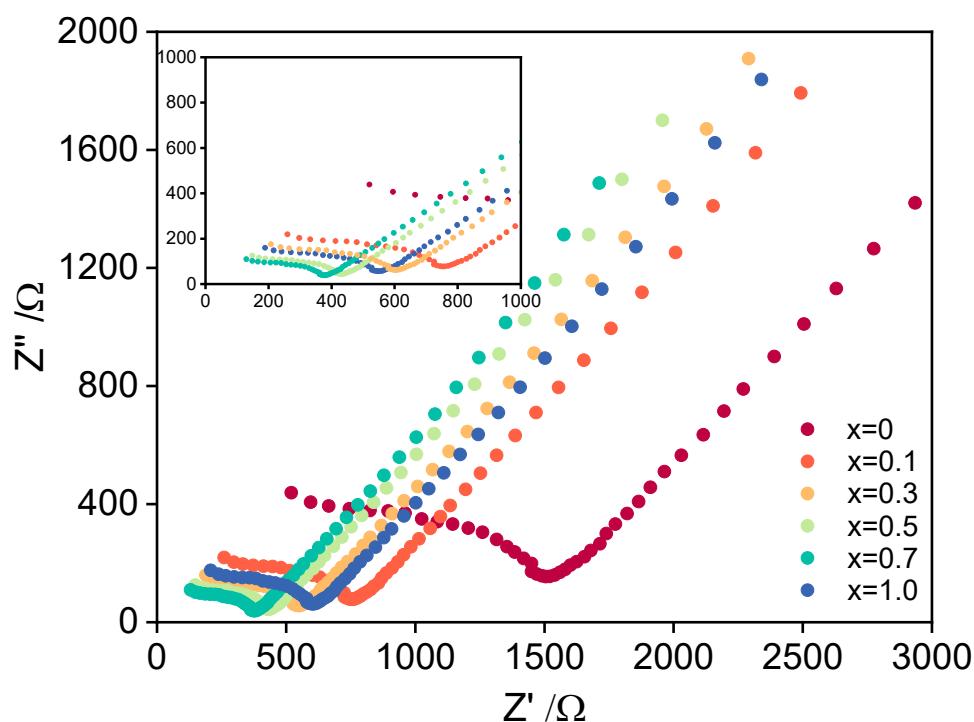


**Figure S3.** XPS spectra of (a) survey spectra, (b) F 1s, (c) P 2p and (d) Si 2p of NZSPF<sub>0.7</sub>.

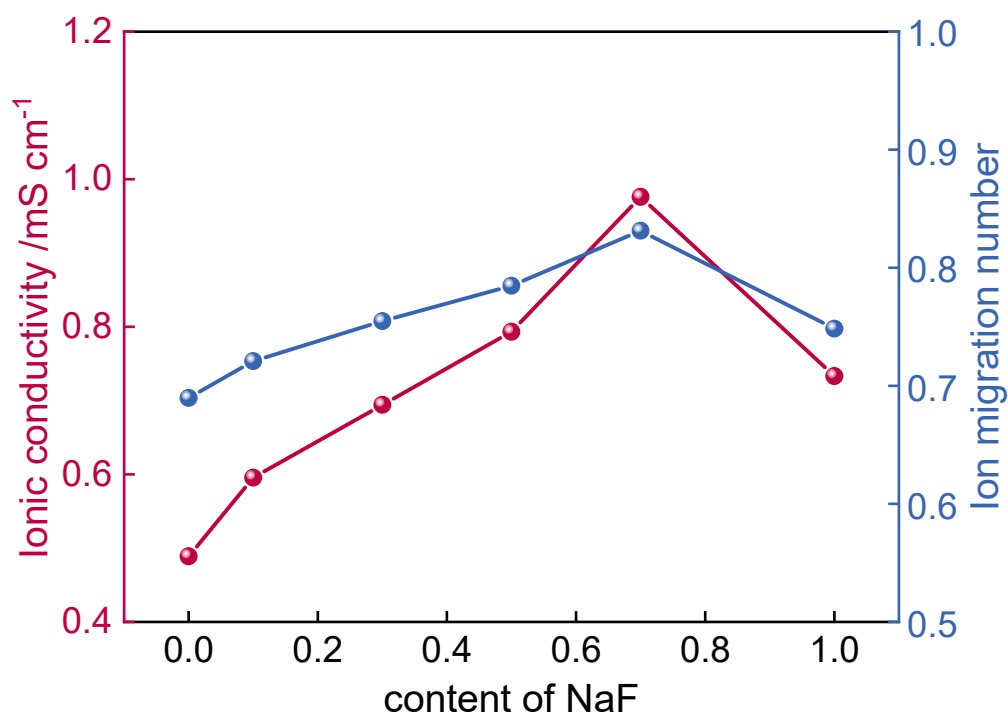


**Figure S4.** SEM images of NZSPF<sub>x</sub> ceramic pellets, (a) x = 0, (b) x = 0.1, (c) x = 0.3,

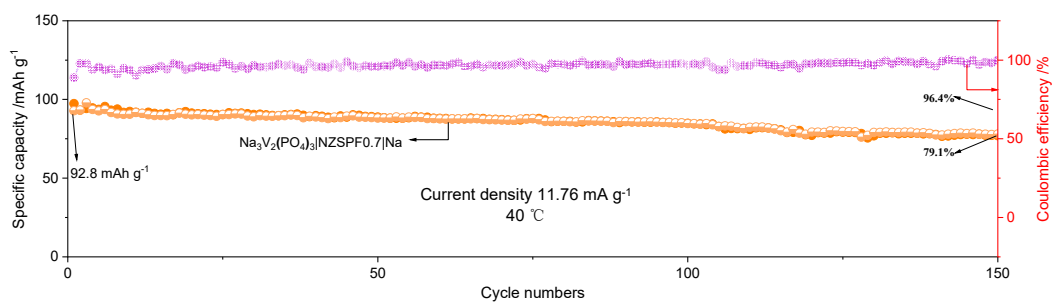
(d)  $x = 0.5$ , (e)  $x = 0.7$ , and (f)  $x = 1.0$ ; (g,h) the corresponding elemental mapping in the square of (e) image; (h) densities and relative densities of NZSPF<sub>x</sub>.



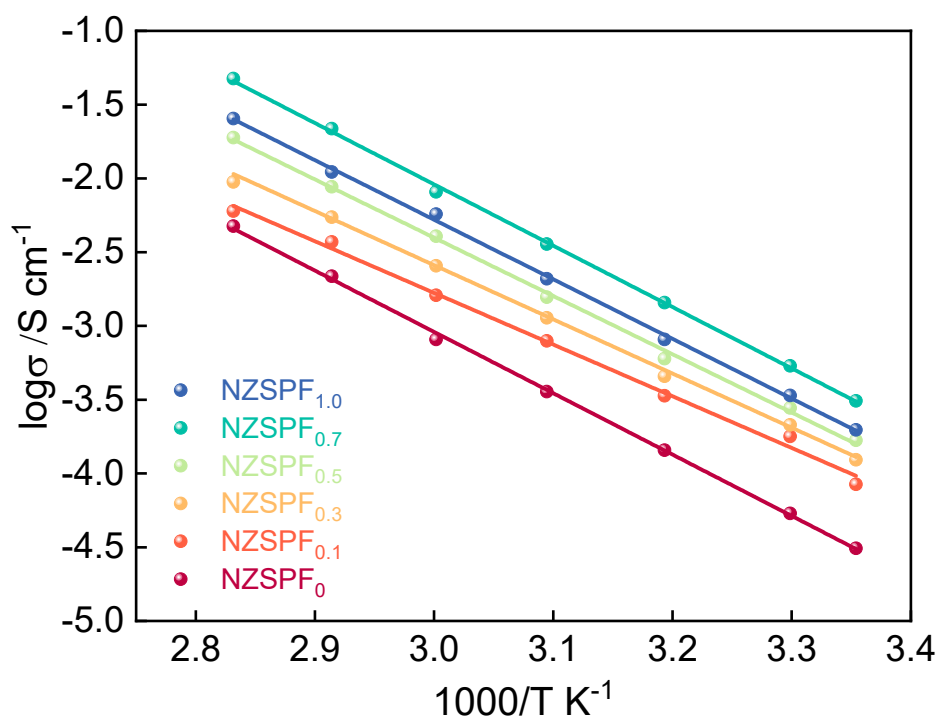
**Figure S5.** EIS measurements performed of NZSPF<sub>x</sub> ( $x = 0, 0.1, 0.3, 0.5, 0.7$ , and  $1.0$ ) solid electrolytes.



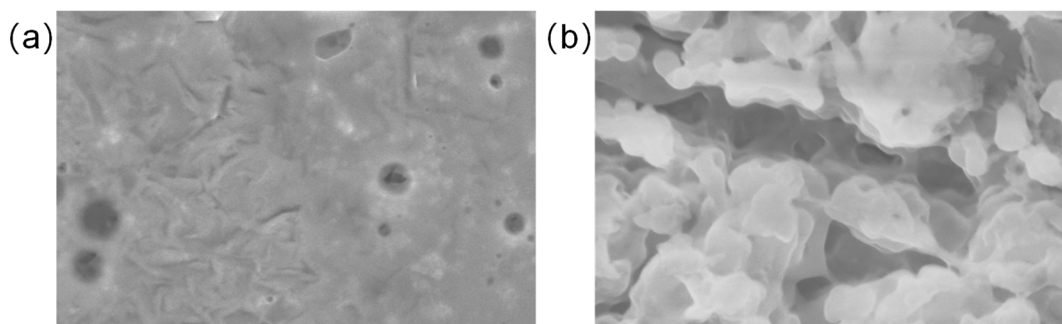
**Figure S6.** Ion conductivity (red) and ion transfer number (blue) of NZSPF<sub>x</sub> ( $x = 0, 0.1, 0.3, 0.5, 0.7$ , and  $1.0$ ) solid electrolytes.



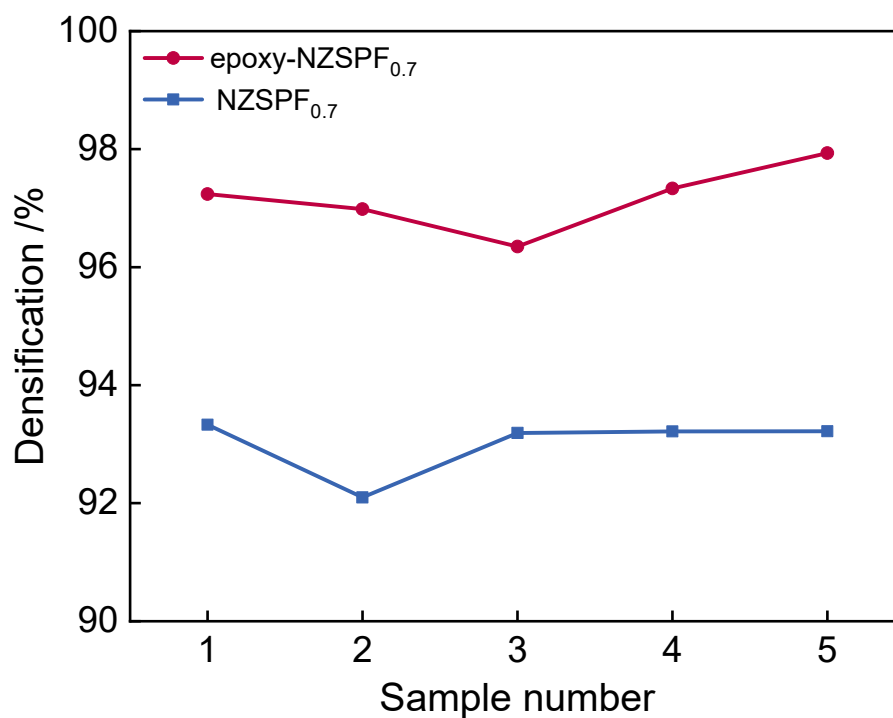
**Figure S7.** cycling performance of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3|\text{NZSPF}_{0.7}|\text{Na}$  battery.



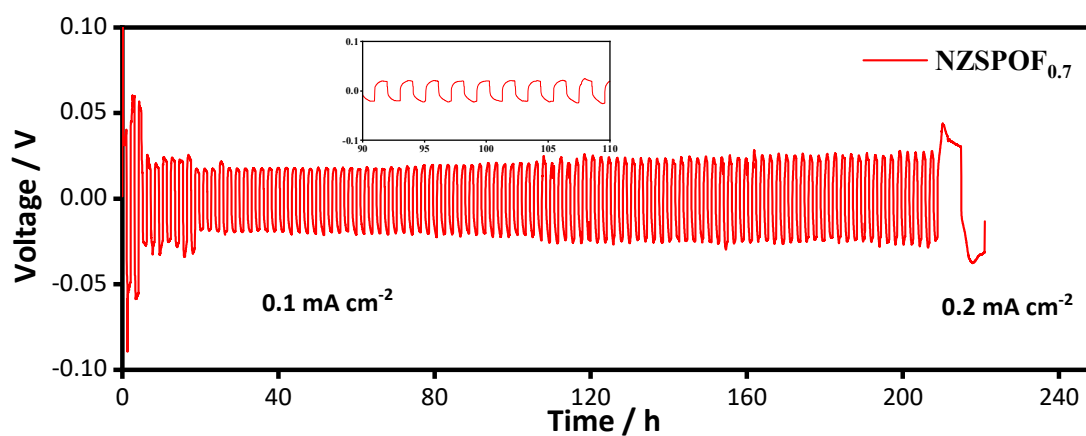
**Figure S8.** Arrhenius plots of  $\text{NZSPF}_x$  ( $x = 0, 0.1, 0.3, 0.5, 0.7$ , and  $1.0$ ) solid electrolytes.



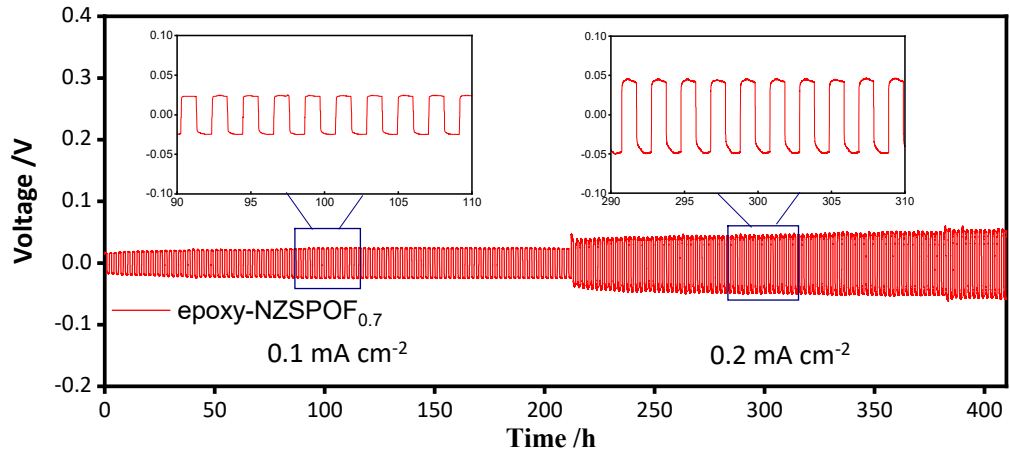
**Figure S9.** SEM images of the sodium metal surface of cell  $\text{Na}_3\text{V}_2(\text{PO}_4)_3|\text{NZSPF}_{0.7}|\text{Na}$  (a) before and (b) after cycling.



**Figure S10.** The densities of NZSPF<sub>0.7</sub> and epoxy- NZSPF<sub>0.7</sub>.



**Figure S11.** Variable current cycling of Na|NZSPF<sub>0.7</sub>|Na symmetric cells (the current density is 0.1 mA cm<sup>-2</sup> and becomes 0.2 mA cm<sup>-2</sup> after 200 h).



**Figure S12.** Variable current cycling of Na|epoxy-NZSPF<sub>0.7</sub>|Na symmetric cells (the current density is 0.1 mA cm<sup>-2</sup> and becomes 0.2 mA cm<sup>-2</sup> after 200 h).

**Table 1.** Chemical composition for NZSPF<sub>x</sub> (x=0, 0.1, 0.3, 0.5, 0.7, 1.0)

Sample	Chemical composition
NZSPF <sub>0</sub>	Na <sub>3.0060</sub> Zr <sub>2.0014</sub> Si <sub>2.0126</sub> P <sub>0.9869</sub> O <sub>12</sub>
NZSPF <sub>0.1</sub>	Na <sub>2.9950</sub> Zr <sub>2</sub> Si <sub>2.0054</sub> P <sub>0.9946</sub> O <sub>11.9894</sub> F <sub>0.0105</sub>
NZSPF <sub>0.3</sub>	Na <sub>2.9862</sub> Zr <sub>1.9986</sub> Si <sub>2.0094</sub> P <sub>0.9903</sub> O <sub>11.9712</sub> F <sub>0.0285</sub>
NZSPF <sub>0.5</sub>	Na <sub>2.9924</sub> Zr <sub>1.9942</sub> Si <sub>2.0105</sub> P <sub>0.9891</sub> O <sub>11.9586</sub> F <sub>0.0412</sub>
NZSPF <sub>0.7</sub>	Na <sub>2.9778</sub> Zr <sub>1.9952</sub> Si <sub>2.0091</sub> P <sub>0.9906</sub> O <sub>11.9503</sub> F <sub>0.0494</sub>
NZSPF <sub>1.0</sub>	Na <sub>2.9750</sub> Zr <sub>1.9949</sub> Si <sub>2.0083</sub> P <sub>0.9914</sub> O <sub>11.9458</sub> F <sub>0.0538</sub>