Supplemental Information for

Modulation of Defects and Electrical Behaviors in Cu-Doped KNN Ceramics by Fluorine-Oxygen Substitution

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Table S1 The ionic radii of K^+, Na^+, Nb^{5+}, Cu^{2+}, O^{2-}, and F^- ions.

| Ion species	Coordination Number	Ionic Radius/Å
K^+	12	1.64
Na^+	12	1.39
Nb^{5+}	6	0.64
Cu^{2+}	6	0.73
O^{2-}	6	1.40
F^-	6	1.33

Table S2. The theoretical tolerance factor t of KNCNF-x ceramics.

| Composition (x)	Average ionic radius (Å)			Tolerance factor t
	$R_{\text{A-site}}^{\text{a}}$	$R_{\text{B-site}}^{\text{b}}$	$R_{\text{O-site}}^{\text{c}}$	
0	1.515	0.6409	1.4	1.00996425
0.04	1.515	0.6409	1.3972	1.01038031
0.12	1.515	0.6409	1.3916	1.01121588
0.20	1.515	0.6409	1.386	1.01205607
0.28	1.515	0.6409	1.3804	1.01290091

[a] Indicates the average ionic radius of K^+ and Na^+.

[b] Indicates the weighted average ionic radius of Nb^{5+} and Cu^{2+}.

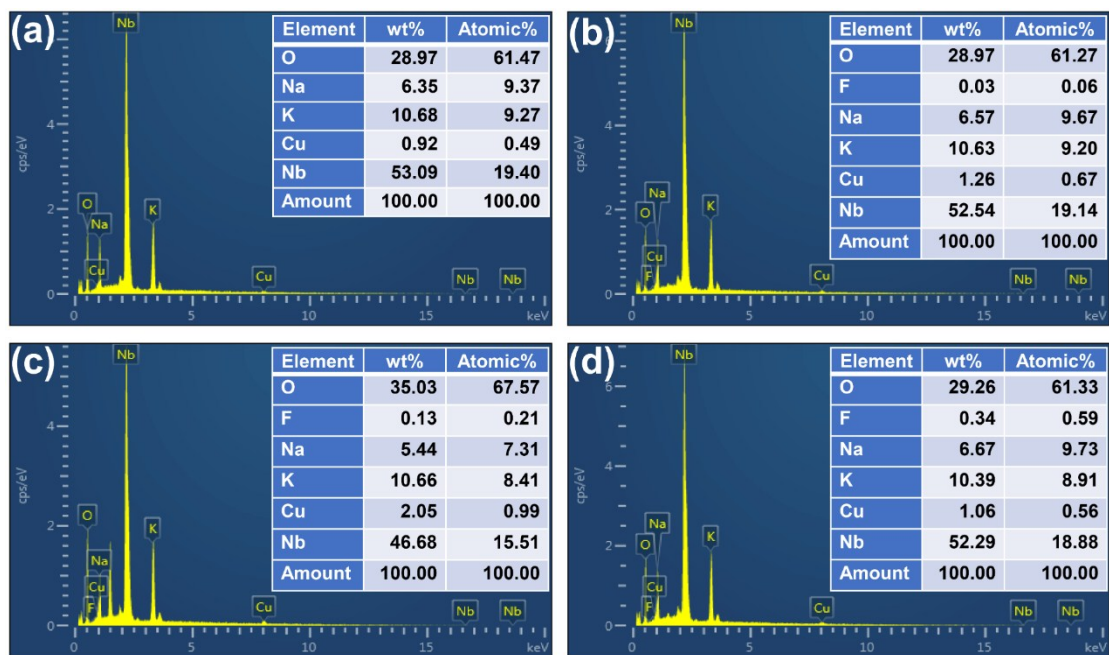[c] Indicates the weighted average ionic radius of O^{2-} and F^-.
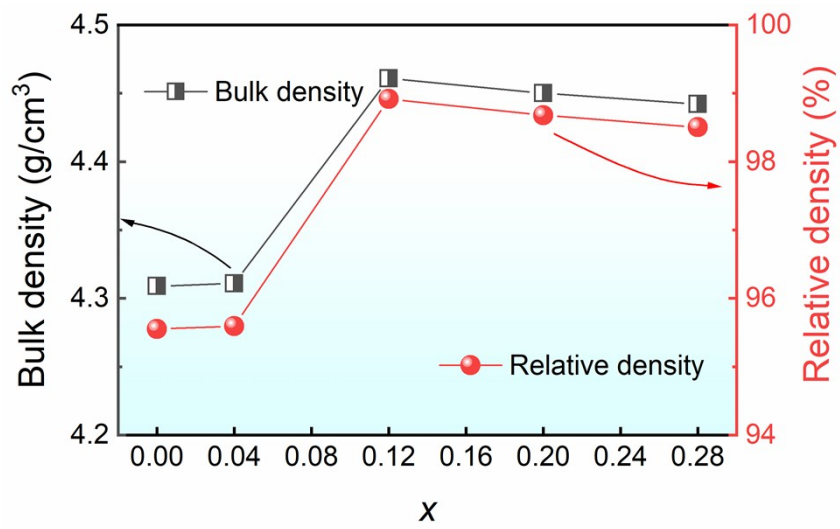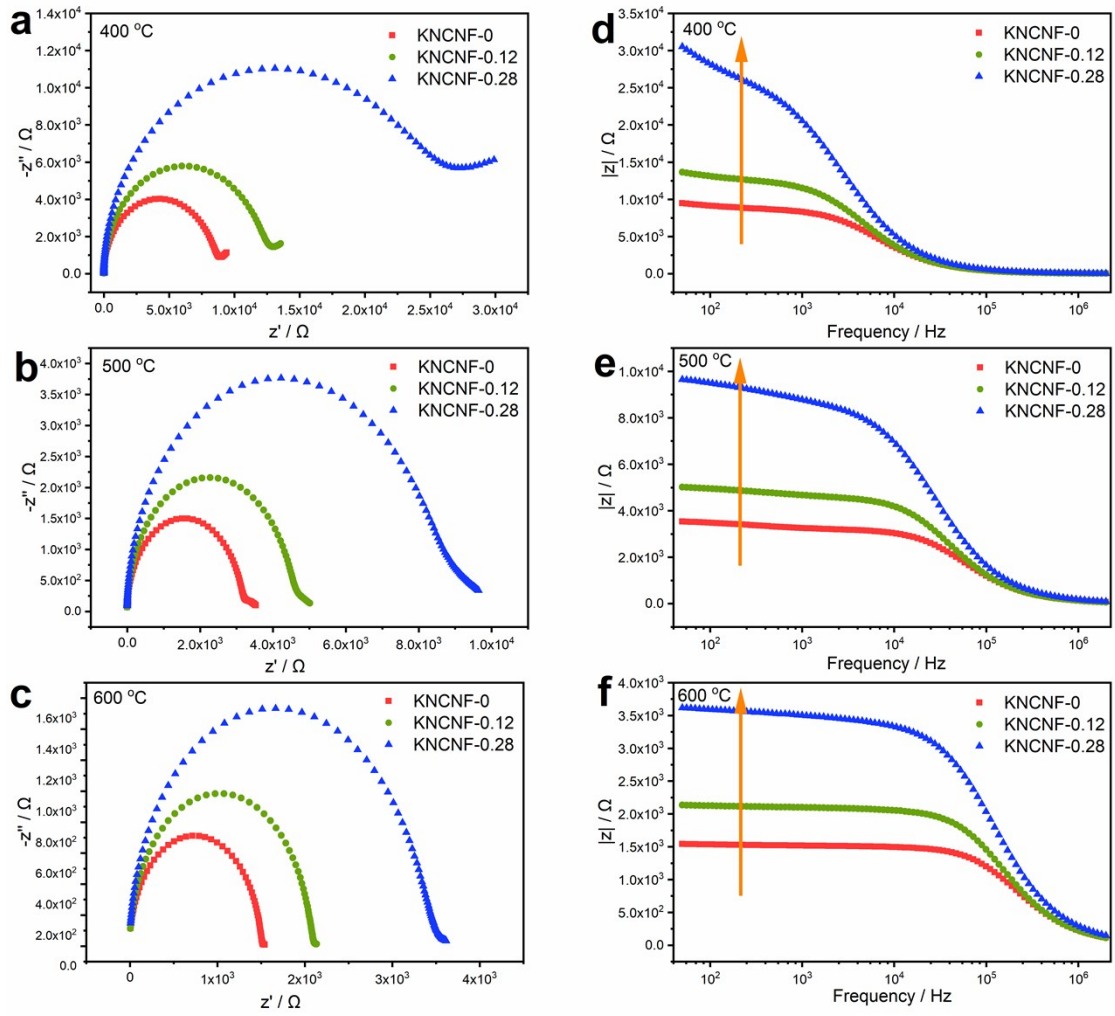
**Figure S1.** Component dependence of density for KNCNF-*x* ceramics.
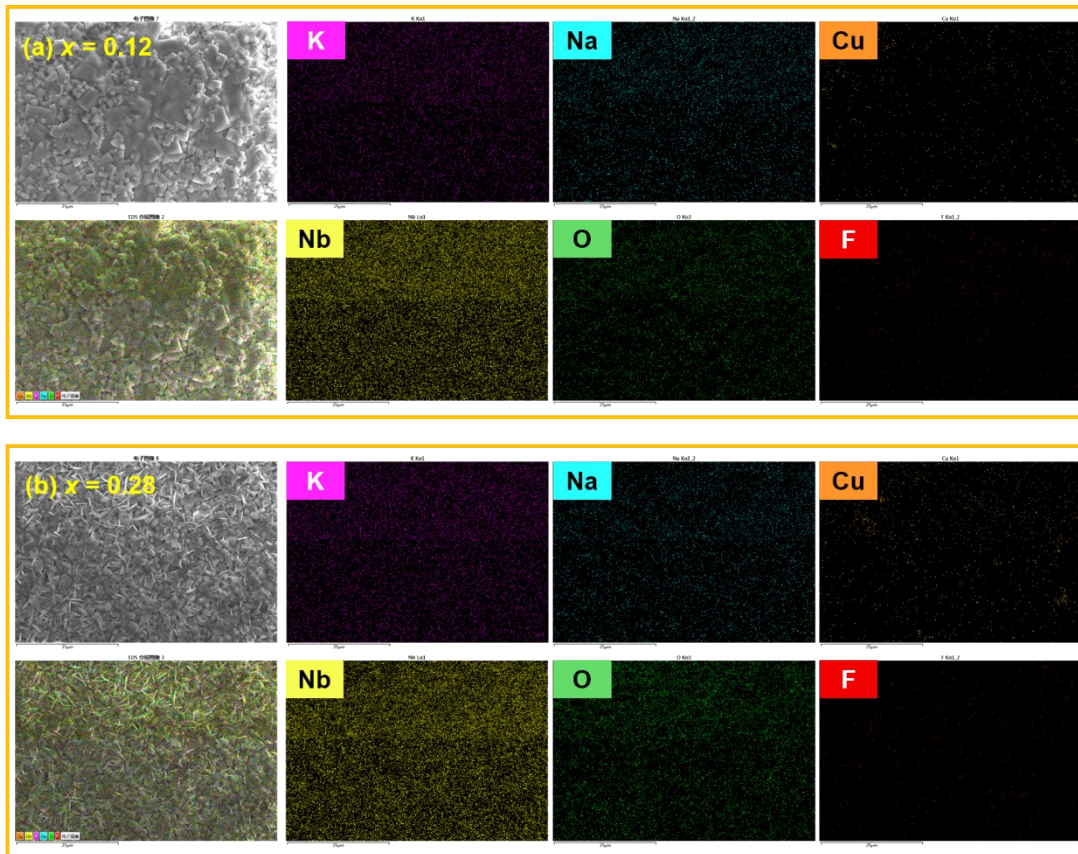
Figure S2. Element area profile of the surface for KNCNF-*x* ceramics: (a) *x* = 0.12
and (b) *x* = 0.28.

Figure S3. Energy dispersive spectroscopy (EDS) of surface morphology for KNCNF-*x* ceramics: (a) *x* = 0, (b) *x* = 0.04, (c) *x* = 0.12, and (d) *x* = 0.28.

(a)

Element	wt%	Atomic%
O	28.97	61.47
Na	6.35	9.37
K	10.68	9.27
Cu	0.92	0.49
Nb	53.09	19.40
Amount	100.00	100.00

(b)

Element	wt%	Atomic%
O	28.97	61.27
F	0.03	0.06
Na	6.57	9.67
K	10.63	9.20
Cu	1.26	0.67
Nb	52.54	19.14
Amount	100.00	100.00

(c)

Element	wt%	Atomic%
O	35.03	67.57
F	0.13	0.21
Na	5.44	7.31
K	10.66	8.41
Cu	2.05	0.99
Nb	46.68	15.51
Amount	100.00	100.00

(d)

Element	wt%	Atomic%
O	29.26	61.33
F	0.34	0.59
Na	6.67	9.73
K	10.39	8.91
Cu	1.06	0.56
Nb	52.29	18.88
Amount	100.00	100.00

Figure S4. (a-c) Original data of the impedance spectroscopies and (d-f) the impedance-frequency ($|Z|$-f) curves for KNCNF-x ceramics with $x = 0$, 0.12, and 0.28.
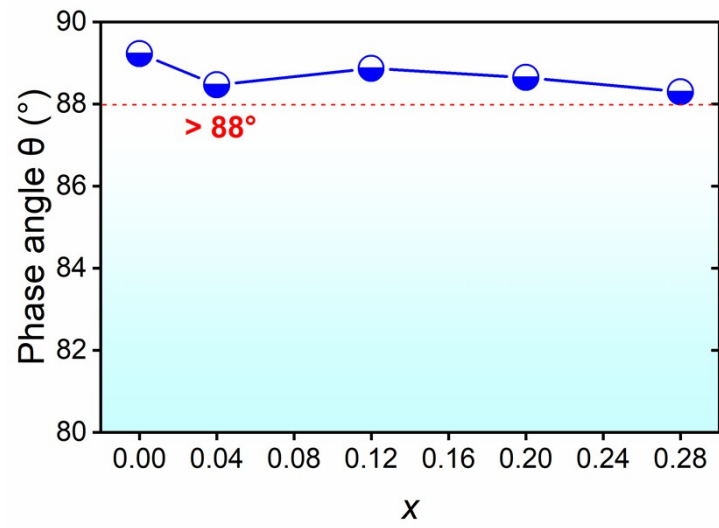
Figure S5. Component dependence of phase angle θ for the KNCNF-x ceramics.