Supporting Information

Structure, Magnetism, and Electrochemistry of $LiMg_{1-x}Zn_xVO_4$ Spinels with $0 \leq x \leq 1$

Takeshi Uyama,[†] Kazuhiko Mukai,[*,†] and Ikuya Yamada[‡]

Toyota Central Research and Development Laboratories, Inc., 41–1 Yokomichi, Nagakute, Aichi 480–1192, Japan, and Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1–2 Gakuen-cho, Sakai, Osaka 599–8570, Japan

*E-mail: e1089@mosk.tytlabs.co.jp

Phone: +81-561-71-7698. Fax: +81-561-63-6119

[*]To whom correspondence should be addressed

[†]Toyota Central Research and Development Laboratories, Inc., 41–1 Yokomichi, Nagakute, Aichi 480–1192, Japan

[‡]Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1–2 Gakuen-cho, Sakai, Osaka 599–8570, Japan

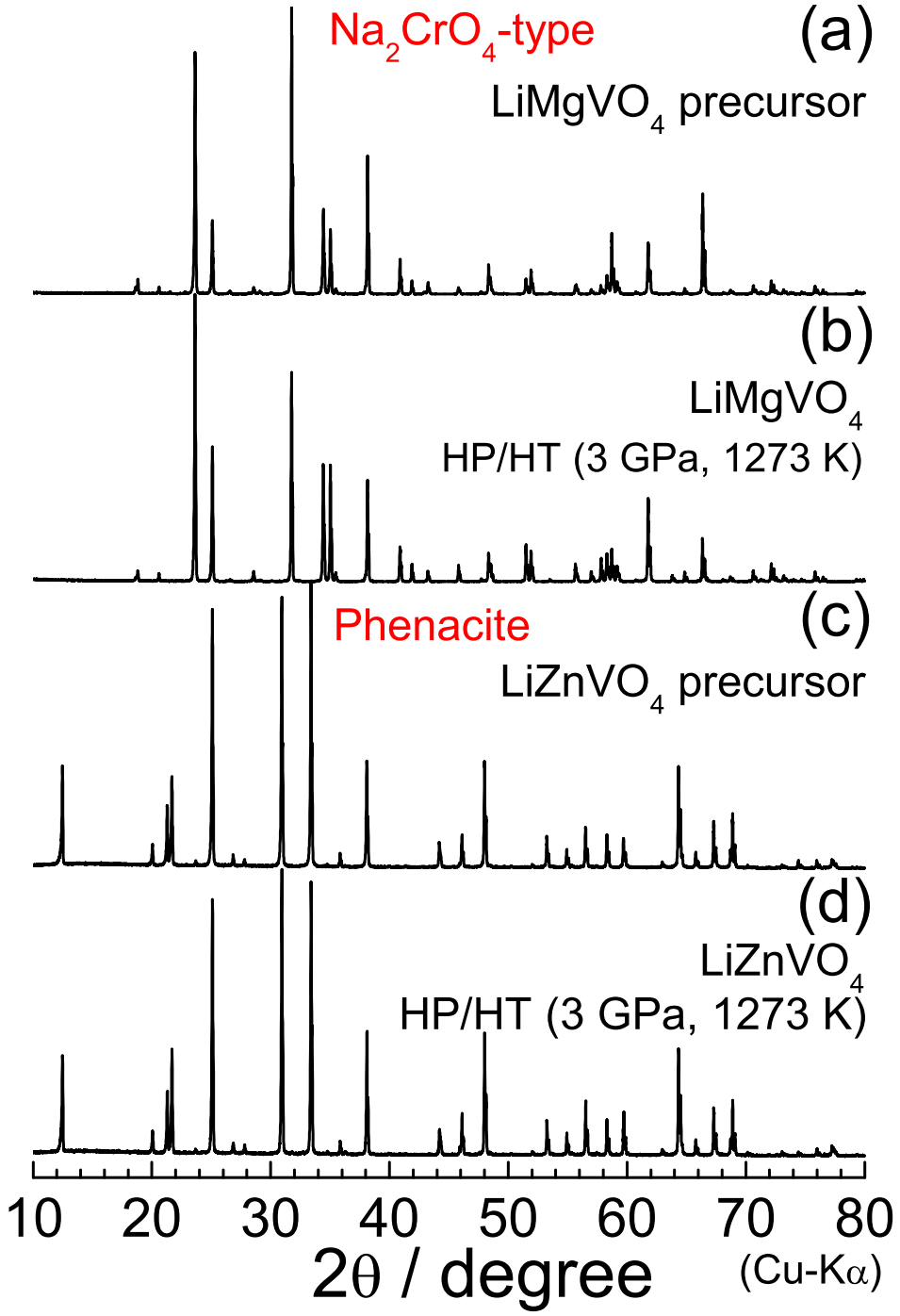

Figure S1: XRD patterns of the (a) $LiMgVO_4$ precursor, (b) the $LiMgVO_4$ sample HP/HT-treated at 3 GPa and 1273 K, (c) $LiZnVO_4$ precursor, and (d) the $LiZnVO_4$ sample HP/HT-treated at 3 GPa and 1273 K. The $LiMgVO_4$ and $LiZnVO_4$ precursors possess Na_2CrO_4-type and phenacite structures, respectively.

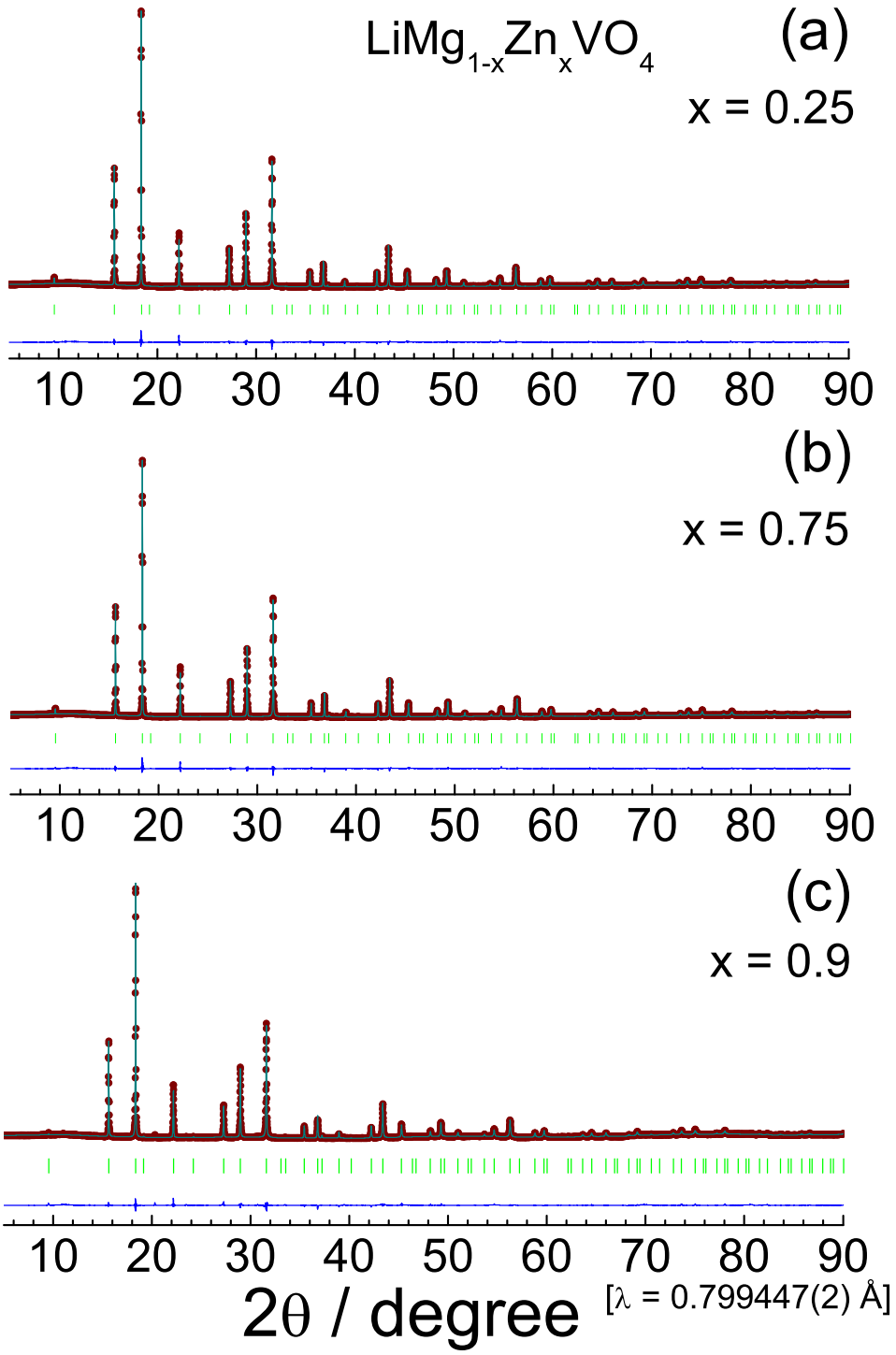

Figure S2: Rietveld refinement results of the (a) $x = 0.25$, (b) $x = 0.75$, and (c) $x = 0.9$ samples.

Table S1: Structural Parameters of the $x = 0.25$, 0.75, and 0.9 Samples Determined by Rietveld Refinements

Sample	Atom	Wyckoff position	Occupancy[a] (g)	x	y	z	B_{iso} / Å^2
$x = 0.25$	Li1	8a	0.024(2)	0.125	0.125	0.125	0.3(1)
	V1	8a	0.976(2)	0.125	0.125	0.125	0.3(1)
	Li2	16d	0.488(2)	0.5	0.5	0.5	0.8(1)
	V2	16d	0.012(2)	0.5	0.5	0.5	0.8(1)
	Mg	16d	0.375	0.5	0.5	0.5	0.8(1)
	Zn	16d	0.125	0.5	0.5	0.5	0.8(1)
	O	32e	0.997(2)	0.246(1)	0.246(1)	0.246(1)	0.4(1)
$x = 0.75$	Li1	8a	0.040(2)	0.125	0.125	0.125	0.3(1)
	V1	8a	0.960(2)	0.125	0.125	0.125	0.3(1)
	Li2	16d	0.480(2)	0.5	0.5	0.5	0.7(1)
	V2	16d	0.020(2)	0.5	0.5	0.5	0.7(1)
	Mg	16d	0.125	0.5	0.5	0.5	0.7(1)
	Zn	16d	0.375	0.5	0.5	0.5	0.7(1)
	O	32e	0.995(2)	0.244(1)	0.244(1)	0.244(1)	0.4(1)
$x = 0.9$	Li1	8a	0.048(2)	0.125	0.125	0.125	0.1(1)
	V1	8a	0.952(2)	0.125	0.125	0.125	0.1(1)
	Li2	16d	0.476(2)	0.5	0.5	0.5	0.6(1)
	V2	16d	0.024(2)	0.5	0.5	0.5	0.6(1)
	Mg	16d	0.05	0.5	0.5	0.5	0.6(1)
	Zn	16d	0.45	0.5	0.5	0.5	0.6(1)
	O	32e	0.994(2)	0.246(1)	0.246(1)	0.246(1)	0.3(1)

[a]Constraints: g(V1) = 1 − g(Li1), g(Li2) = 0.5 − 0.5 × g(Li1), g(V2) = 0.5 × g(Li1), and g(O) = 1 − 0.125 × g(Li).

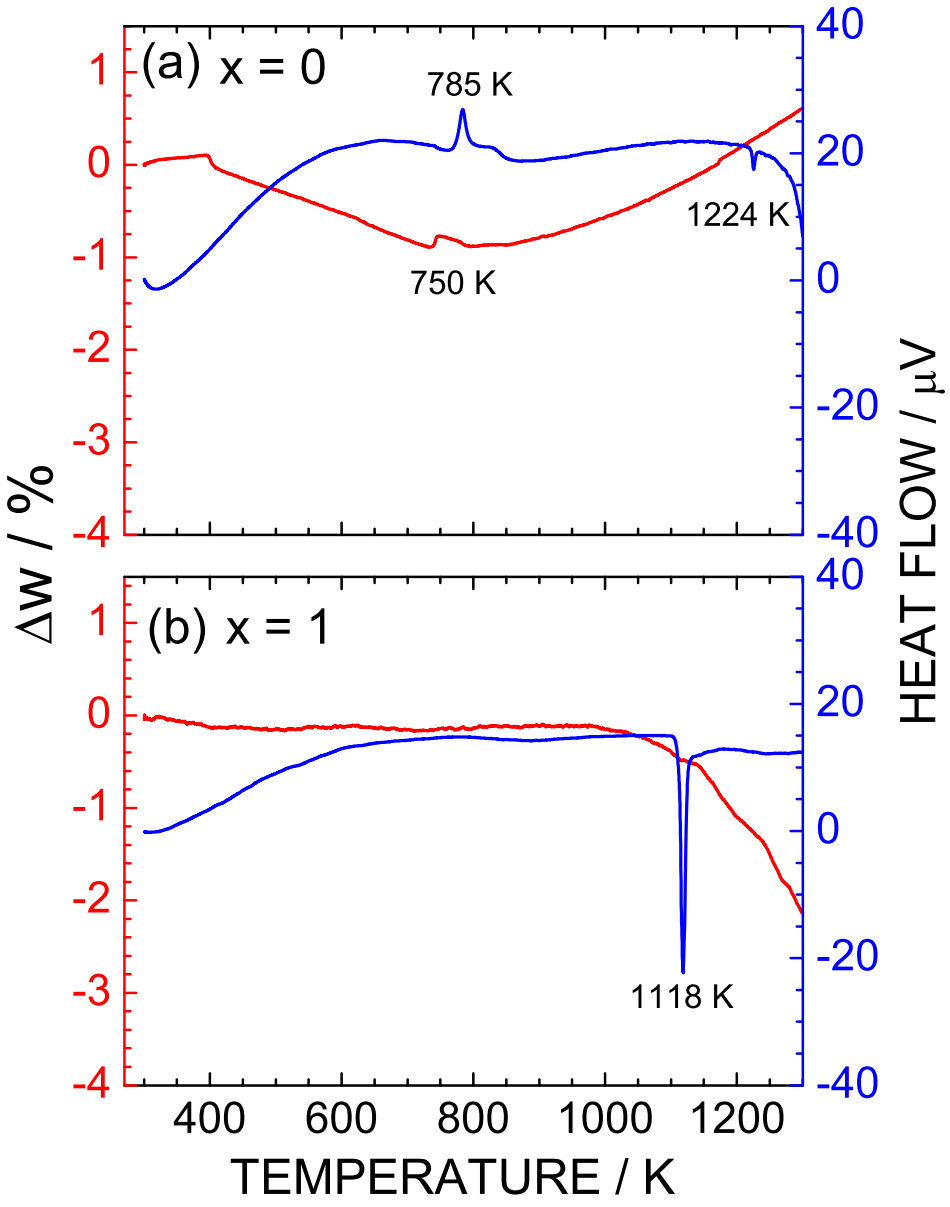

Figure S3: TG/DTA curves of the (a) $x = 0$ and (b) $x = 1$ samples. The right and left axes indicate a weight loss (Δw) and the DTA curve, respectively.

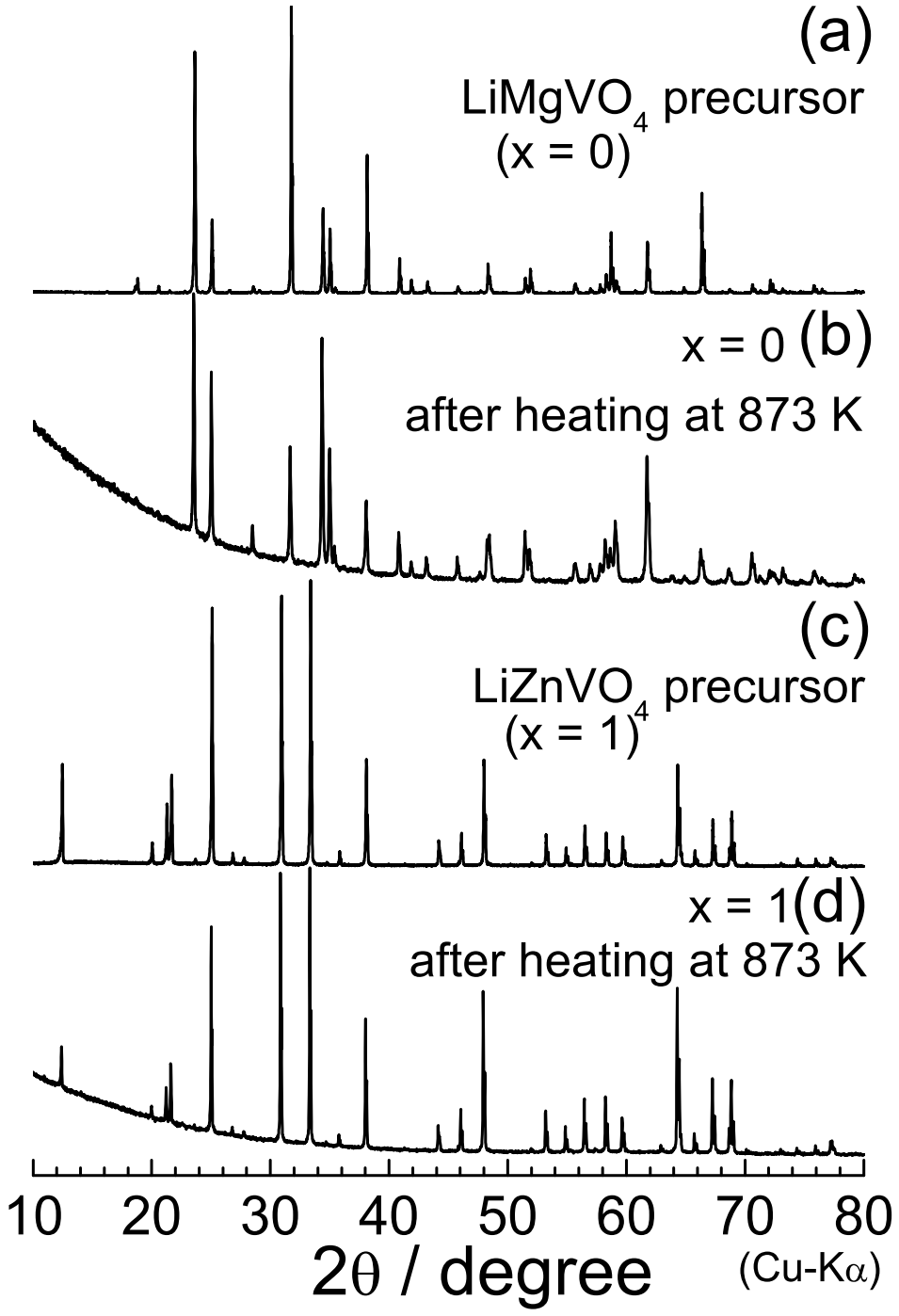

Figure S4: XRD patterns of the before and after heating at 873 K: (a) $LiMgVO_4$ precursor, (b) after heating of the $x = 0$ sample, (c) $LiZnVO_4$ precursor, and (d) after heating of the $x = 1$ sample.

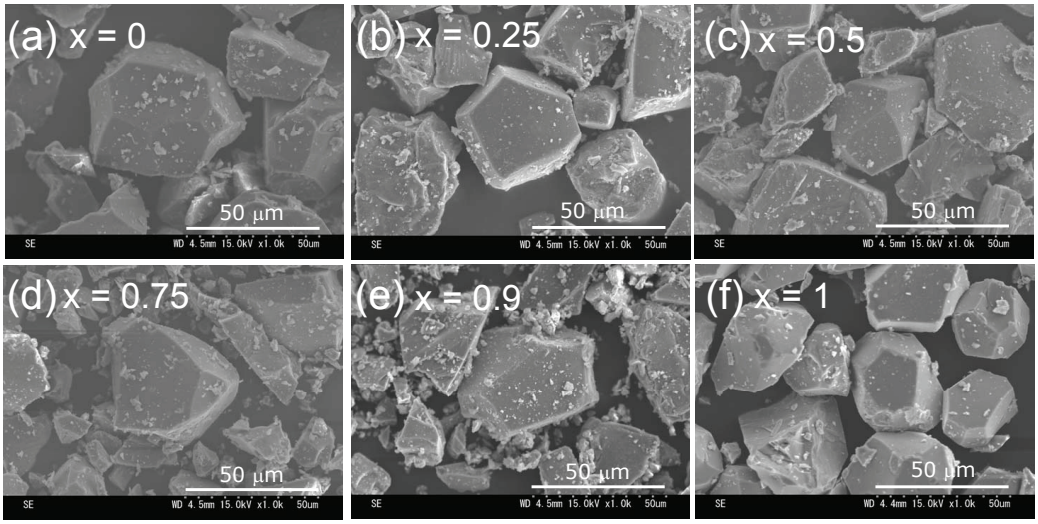

Figure S5: Enlarged SEM images of the (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$, (e) $x = 0.9$, and (f) $x = 1$ samples.

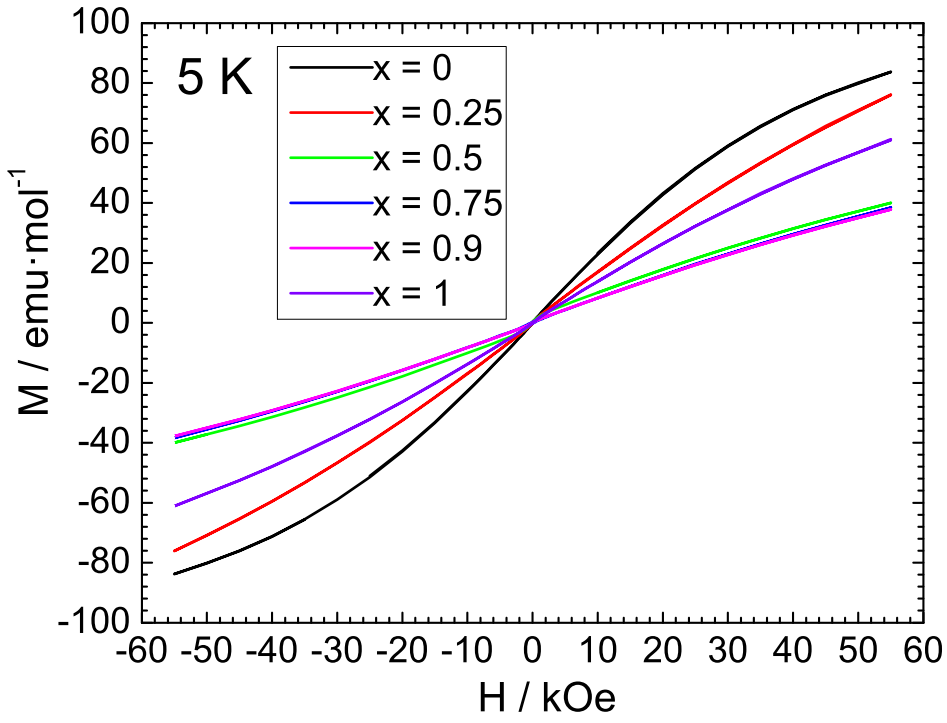

Figure S6: M-H curves at 5 K of the $x = 0$, 0.25, 0.5, 0.75, 0.9, and 1 samples.

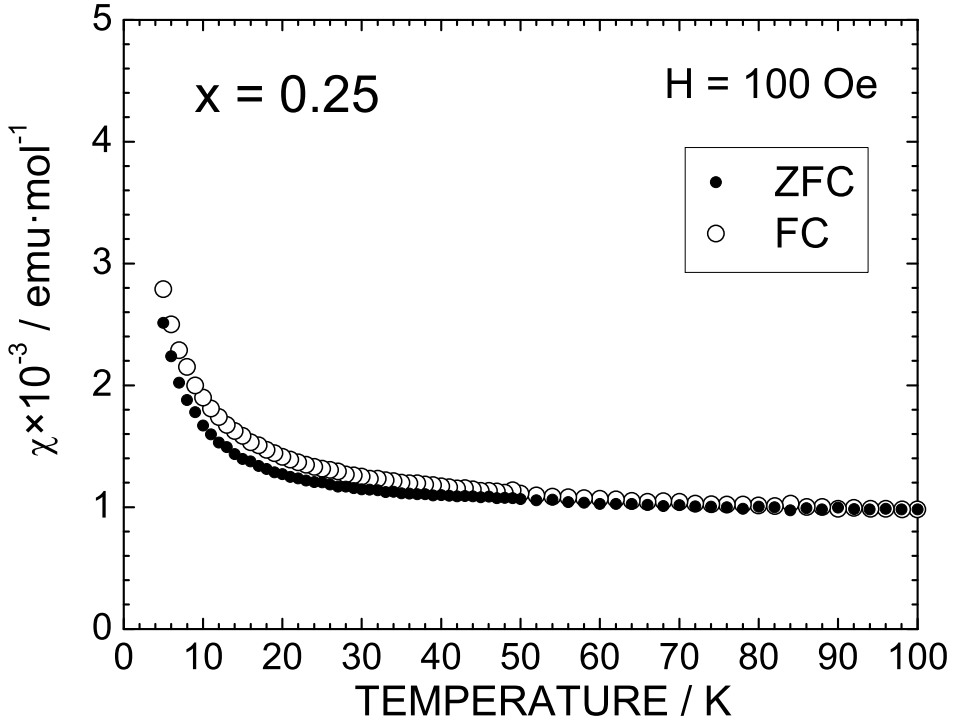

Figure S7: Temperature dependence of χ of the $x = 0.25$ sample measured in the ZFC and FC modes with $H = 100$ Oe.

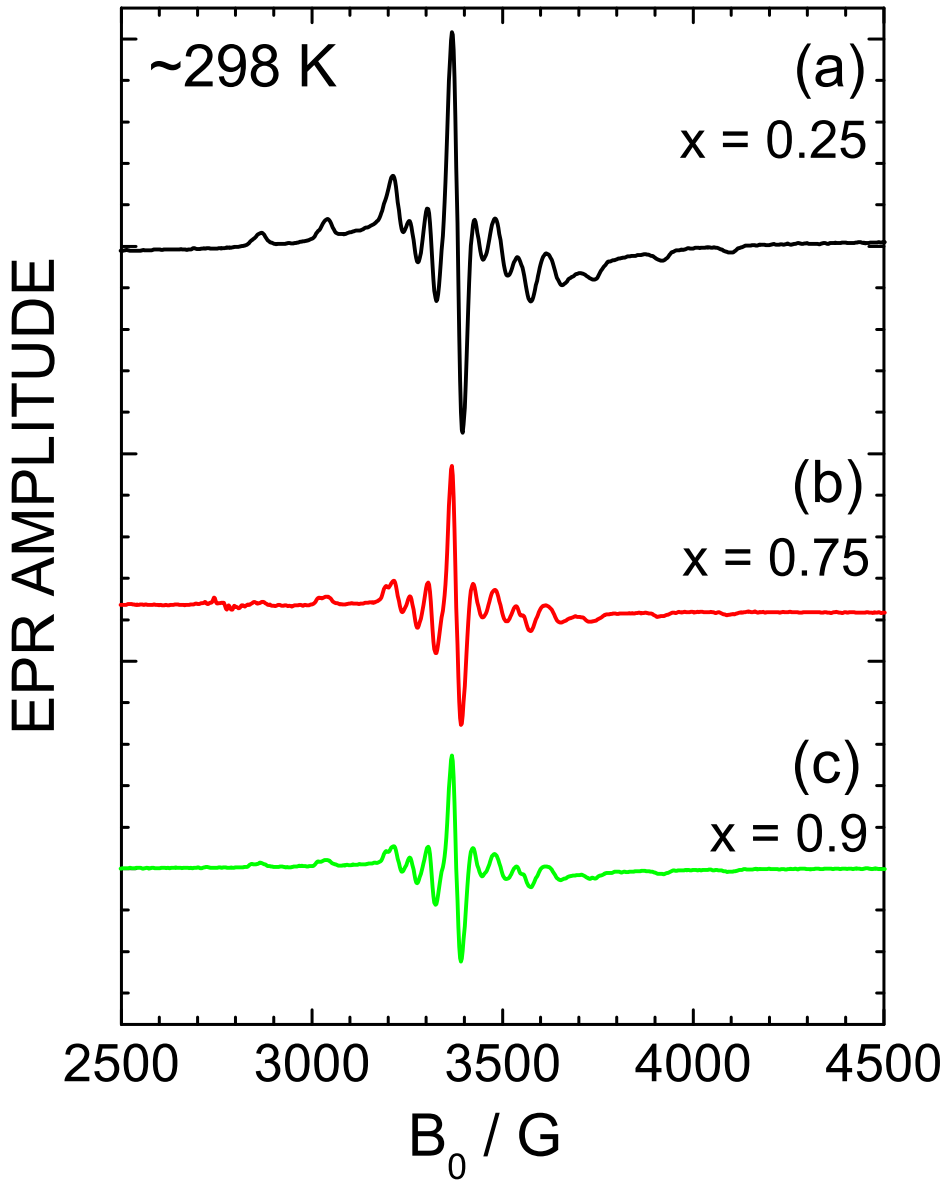

Figure S8: EPR spectra of the (a) $x = 0.25$, (b) $x = 0.75$, and (c) $x = 0.9$ samples at ~298 K.

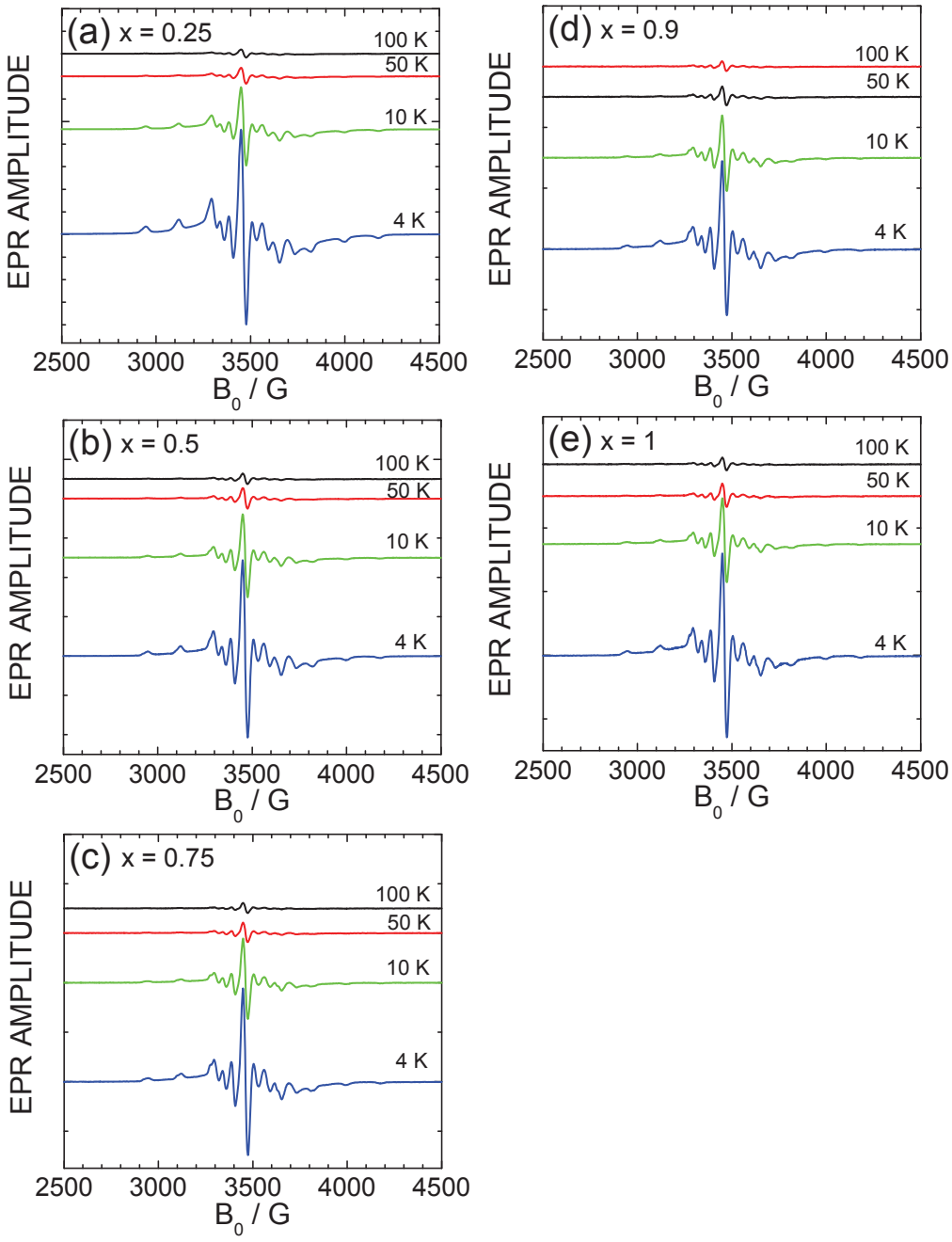

Figure S9: Temperature dependence of the EPR spectra of the (a) $x = 0.25$, (b) $x = 0.5$, (c) $x = 0.75$, (d) $x = 0.9$, and (e) $x = 1$ samples.

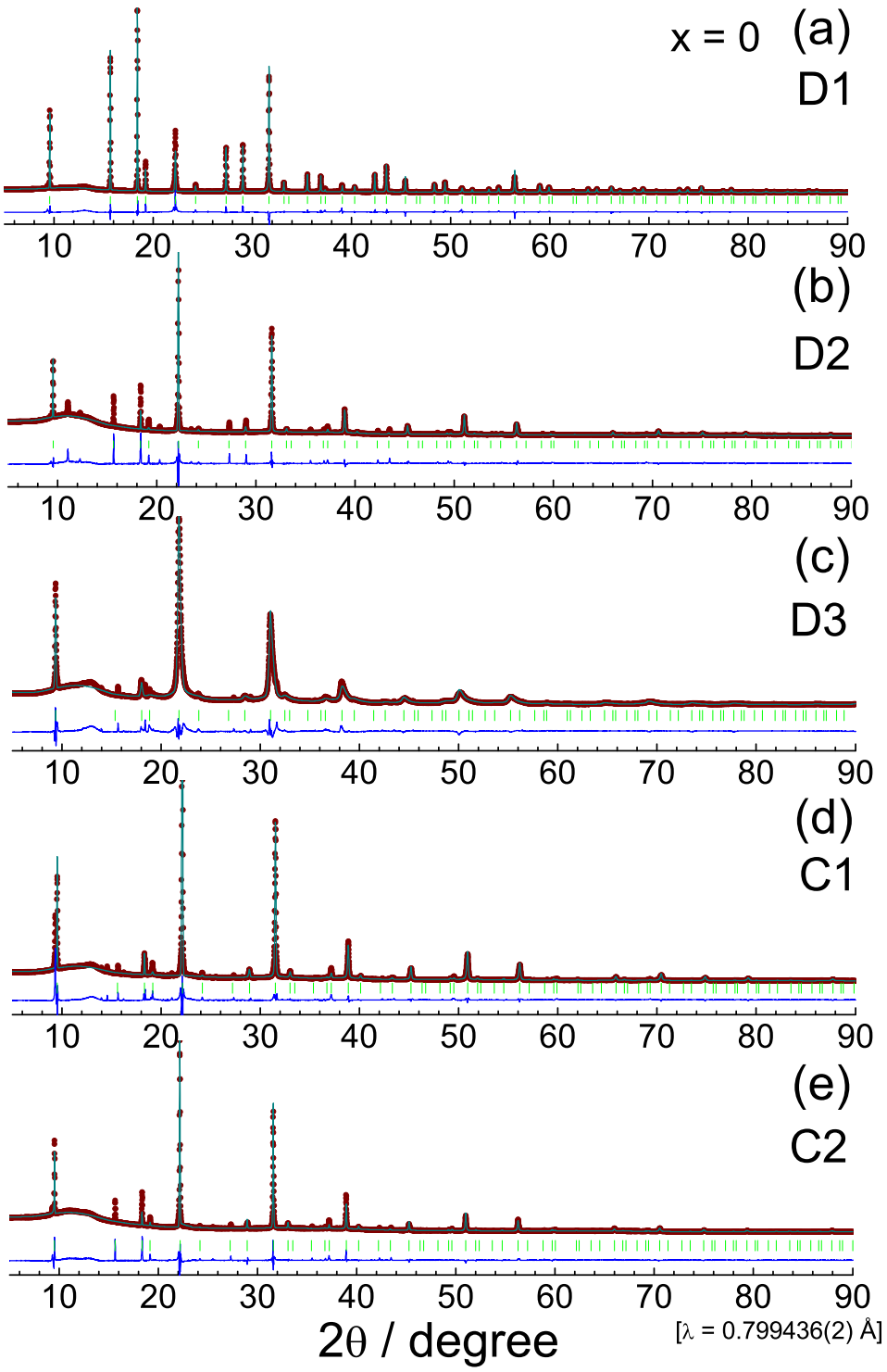

Figure S10: Rietveld refinement results of the $x = 0$ sample at discharged points (a) D1, (b) D2, and (c) D3 and charged points (d) C1 and (e) C2.

Table S2: Structural Parameters of the $x = 0$ Sample at Discharged Points D1, D2, and D3 and Charged Points C1 and C2

State	Atom	Wyckoff position	Occupancy[a] (g)	x	y	z	B_{iso} / Å^2
D1	V1	8a	0.746(1)	0.125	0.125	0.125	0.4
	V2	16d	0.054(1)	0.5	0.5	0.5	0.9
	Mg1	16d	0.5	0.5	0.5	0.5	0.9
	V3	16c	0.073(1)	0	0	0	0.9
	O1	32e	0.997	0.245(1)	0.245(1)	0.245(1)	0.5
$a_{\mathrm{c}} = 8.2797(1)$ Å, $R_{\mathrm{wp}} = 9.64$ %, $R_{\mathrm{p}} = 6.04$ %, and $S = 1.62$							
D2	V1	8a	0	0.125	0.125	0.125	0.4
	V2	16d	0	0.5	0.5	0.5	0.9
	Mg1	16d	0.5	0.5	0.5	0.5	0.9
	V3	16c	0.5	0	0	0	0.9
	O1	32e	0.997	0.245(1)	0.245(1)	0.245(1)	0.5
$a_{\mathrm{c}} = 8.3015(1)$ Å, $R_{\mathrm{wp}} = 8.71$ %, $R_{\mathrm{p}} = 4.95$ %, and $S = 1.17$							
D3	V1	8a	0	0.125	0.125	0.125	0.4
	V2	16d	0	0.5	0.5	0.5	0.9
	Mg1	16d	0.5	0.5	0.5	0.5	0.9
	V3	16c	0.5	0	0	0	0.9
	O1	32e	0.997	0.243(1)	0.243(1)	0.243(1)	0.5
$a_{\mathrm{c}} = 8.4495(1)$ Å, $R_{\mathrm{wp}} = 6.64$ %, $R_{\mathrm{p}} = 4.37$ %, and $S = 1.16$							
C1	V1	8a	0	0.125	0.125	0.125	0.4
	V2	16d	0	0.5	0.5	0.5	0.9
	Mg1	16d	0.5	0.5	0.5	0.5	0.9
	V3	16c	0.5	0	0	0	0.9
	O1	32e	0.997	0.244(1)	0.244(1)	0.244(1)	0.5
$a_{\mathrm{c}} = 8.3184(1)$ Å, $R_{\mathrm{wp}} = 9.65$ %, $R_{\mathrm{p}} = 4.31$ %, and $S = 0.95$							
C2	V1	8a	0	0.125	0.125	0.125	0.4
	V2	16d	0	0.5	0.5	0.5	0.9
	Mg1	16d	0.5	0.5	0.5	0.5	0.9
	V3	16c	0.5	0	0	0	0.9
	O1	32e	0.997	0.241(1)	0.241(1)	0.241(1)	0.5
$a_{\mathrm{c}} = 8.3047(1)$ Å, $R_{\mathrm{wp}} = 7.39$ %, $R_{\mathrm{p}} = 4.31$ %, and $S = 0.95$							

[a]Constraint: $g(\mathrm{V3}) = 0.5 - 0.5 \times g(\mathrm{V1}) - 1.0 \times g(\mathrm{V2})$.

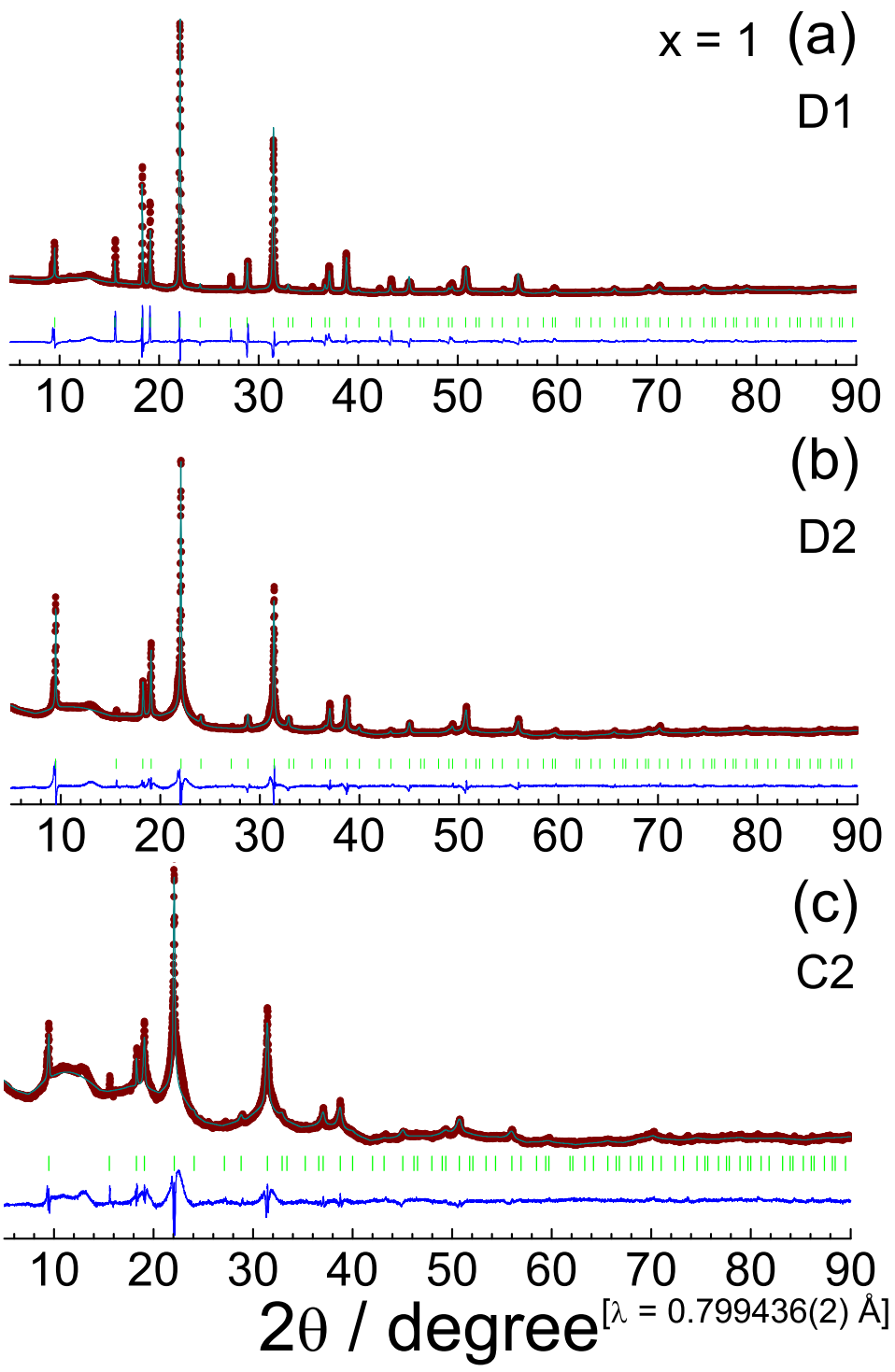

Figure S11: Rietveld refinement results of the $x = 0$ sample at discharged points (a) D1 and (b) D2 and charged point (c) C2.

Table S3: Structural Parameters of the $x = 1$ Sample at Discharged Points D1 and D2 and Charged Point C2

State	Atom	Wyckoff position	Occupancy (g)	x	y	z	B_{iso} / Å^2
D1	V1	8a	0.222(3)	0.125	0.125	0.125	0.3
	V2	16d	0.064(3)	0.5	0.5	0.5	0.8
	Zn1	16d	0.5	0.5	0.5	0.5	0.8
	V3	16c	0.325(3)	0	0	0	0.8
	O1	32e	0.995	0.245(1)	0.245(1)	0.245(1)	0.5
$a_{\mathrm{c}} = 8.3316(1)$ Å, $R_{\mathrm{wp}} = 4.88$ %, $R_{\mathrm{p}} = 2.39$ %, and $S = 1.24$							
D2	V1	8a	0	0.125	0.125	0.125	0.3
	V2	16d	0.125(1)	0.5	0.5	0.5	0.8
	Zn1	16d	0.5	0.5	0.5	0.5	0.8
	V3	16c	0.375(1)	0	0	0	0.8
	O1	32e	0.995	0.245(1)	0.245(1)	0.245(1)	0.5
$a_{\mathrm{c}} = 8.3464(1)$ Å, $R_{\mathrm{wp}} = 2.58$ %, $R_{\mathrm{p}} = 1.49$ %, and $S = 0.67$							
C2	V1	8a	0	0.125	0.125	0.125	0.3
	V2	16d	0.077(3)	0.5	0.5	0.5	0.8
	Zn1	16d	0.5	0.5	0.5	0.5	0.8
	V3	16c	0.423(3)	0	0	0	0.8
	O1	32e	0.995	0.241(1)	0.241(1)	0.241(1)	0.5
$a_{\mathrm{c}} = 8.3444(1)$ Å, $R_{\mathrm{wp}} = 2.14$ %, $R_{\mathrm{p}} = 1.37$ %, and $S = 0.61$							

[a]Constraint: $g(\mathrm{V3}) = 0.5 - 0.5 \times g(\mathrm{V1}) - 1.0 \times g(\mathrm{V2})$.

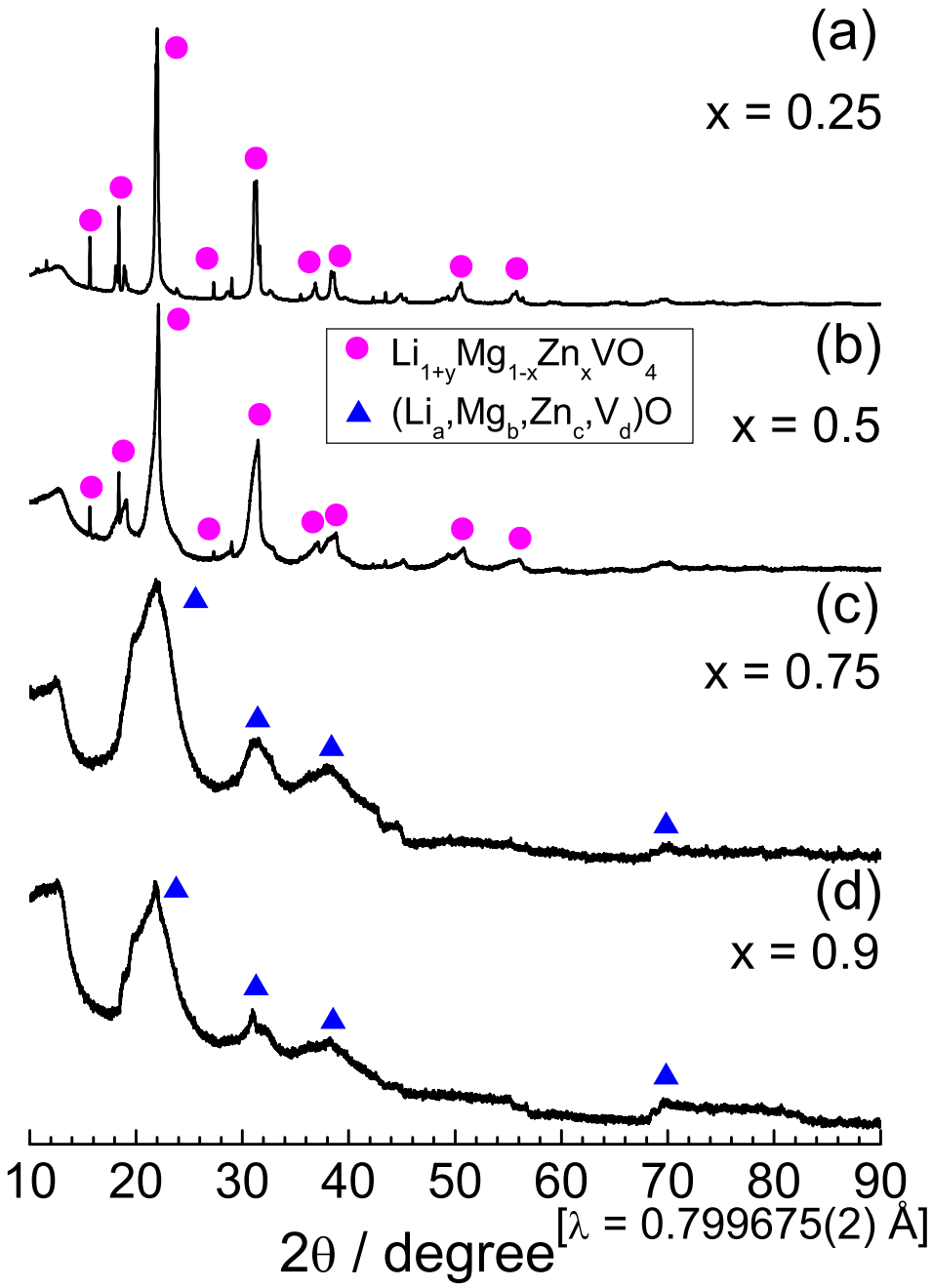

Figure S12: Ex situ XRD patterns at the fully discharged state: (a) $x = 0.25$, (b) $x = 0.5$, (c) $x = 0.75$, and (d) $x = 0.9$.

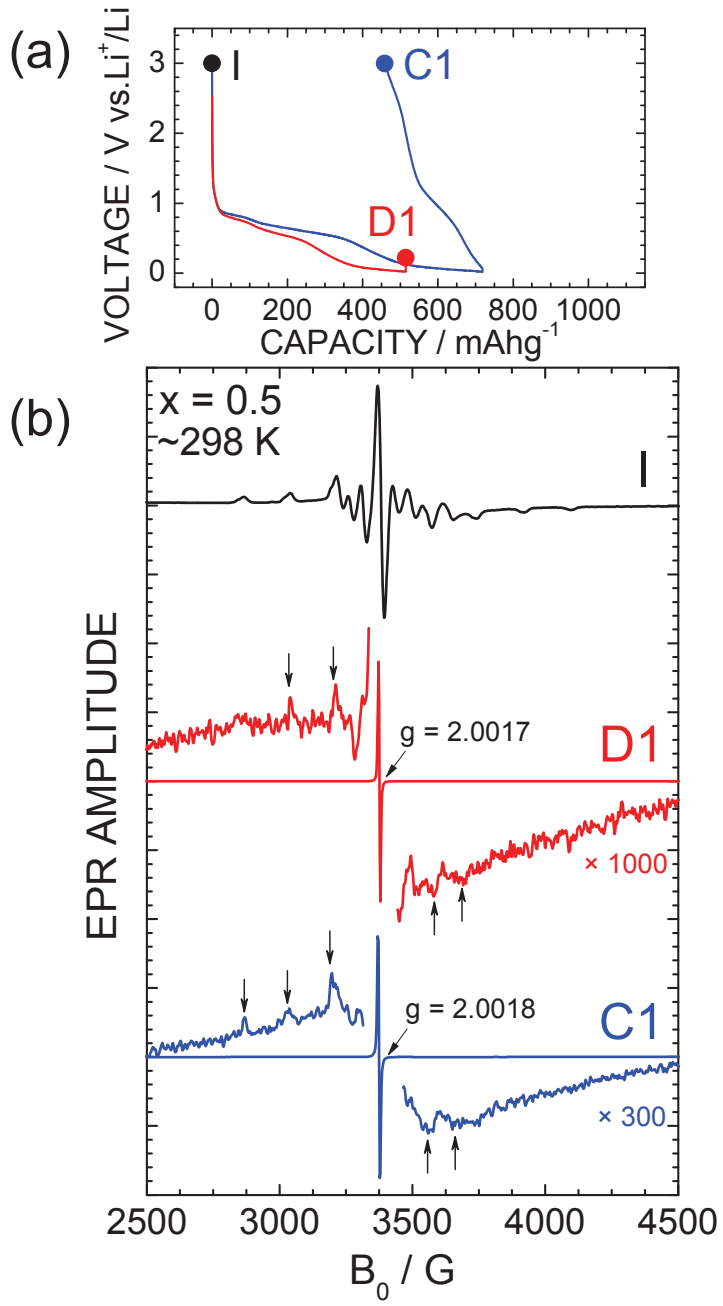

Figure S13: (a) Discharge and charge curves of $x = 0$ for the ex situ EPR measurements and (b) EPR spectra at I (initial), D1 (fully discharged state), and C1 (fully charged state). EPR measurements were performed at ∼298 K.

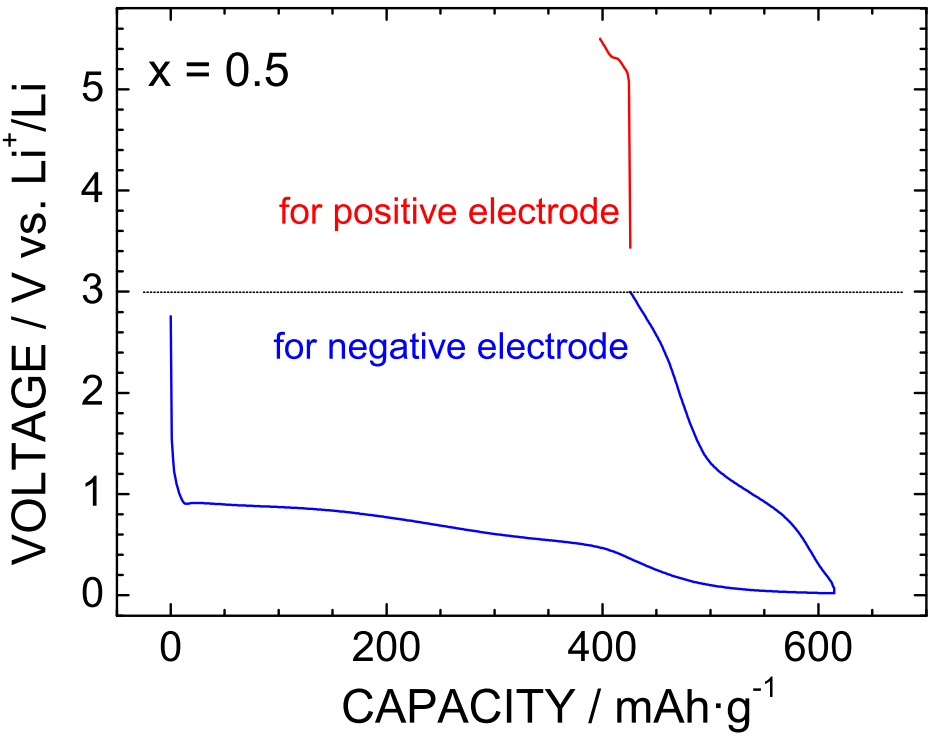

Figure S14: Charge curve of the lithium cell with $x = 0.5$ up to 5.5 V. The lithium cell was re-assembled with an aluminum current collector after the discharge and charge test at voltage range 0.02–3.0 V.