Supporting Information for
Enhanced Spontaneous Polarization by V^{4+} Substitution in a Lead-Free Perovskite $CaMnTi_2O_6$

Masayuki Fukuda,[†] Takumi Nishikubo,[†] Zhao Pan,[†] Yuki Sakai,[‡,†] Mao-Hua Zhang,[§] Shogo Kawaguchi,[∥] Hongwu Yu,[⊥] Yoichi Okimoto,[⊥] Shin-ya Koshihara,[⊥] Mitsuru Itoh,[†] Jürgen Rödel,[§,#] and Masaki Azuma[*,†,‡]

† Laboratory for Materials and Structures, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

‡ Kanagawa Institute of Industrial Science and Technology, 705-1 Shimoimaizumi, Ebina, Kanagawa 243-0435, Japan

§ Department of Materials and Earth Sciences, Nonmetallic Inorganic Materials, Technical University of Darmstadt, Darmstadt, Germany

∥ Diffraction and Scattering Division, Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

⊥ Department of Chemistry, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan

Tokyo Tech World Research Hub Initiative (WRHI), Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8503, Japan

Email: mazuma@msl.titech.ac.jp

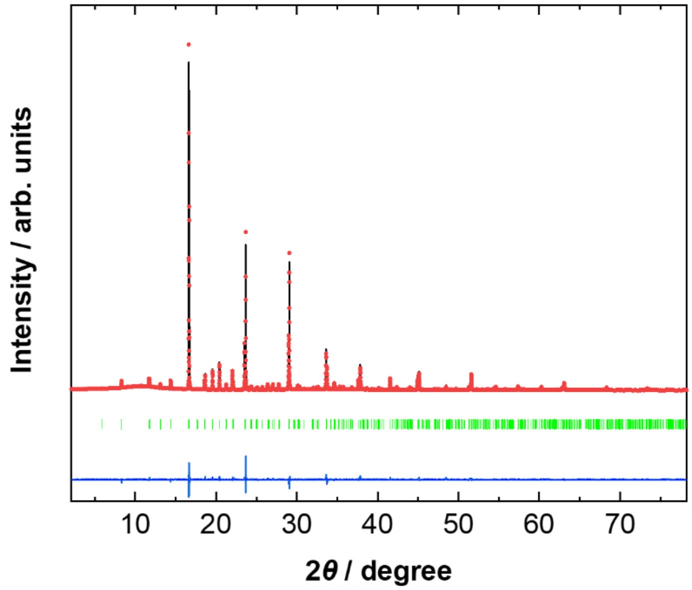

Figure S1. Results of Rietveld refinement against SXRD data (λ = 0.77435 Å) of $CaMnTi_2O_6$ at room temperature. The observed (red circles), calculated (black solid lines), and difference (bottom blue line) profiles are represented. The green ticks correspond to the positions of the allowed Bragg reflections.

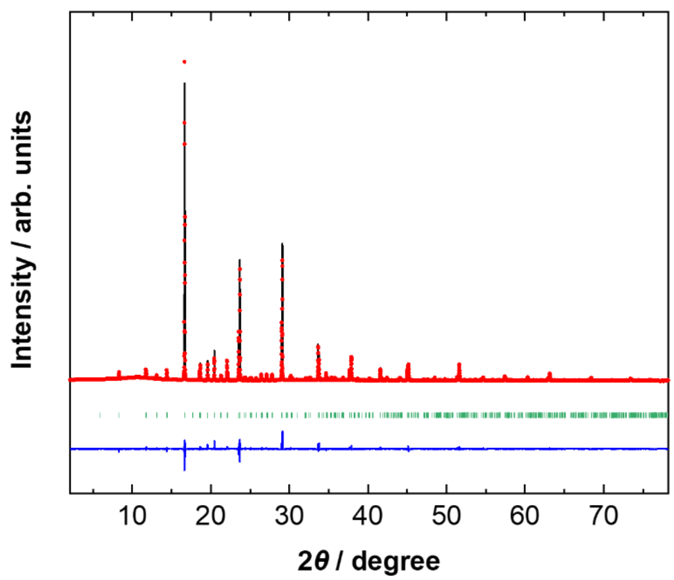

Figure S2. Results of Rietveld refinement against SXRD data (λ = 0.77435 Å) of $CaMnTi_{1.8}V_{0.2}O_6$ at room temperature. The observed (red circles), calculated (black solid lines), and difference (bottom blue line) profiles are represented. The green ticks correspond to the positions of the allowed Bragg reflections.

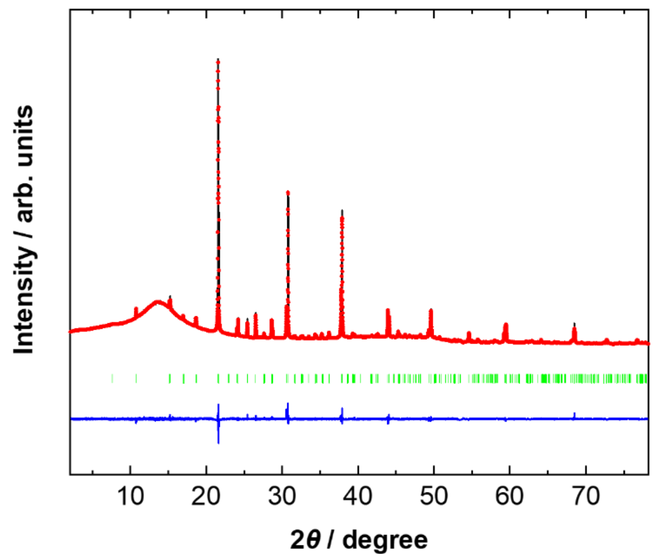

Figure S3. Results of Rietveld refinement against SXRD data (λ = 0.99985 Å) of $CaMnTi_{1.6}V_{0.4}O_6$ at room temperature. The observed (red circles), calculated (black solid lines), and difference (bottom blue line) profiles are represented. The green ticks correspond to the positions of the allowed Bragg reflections.

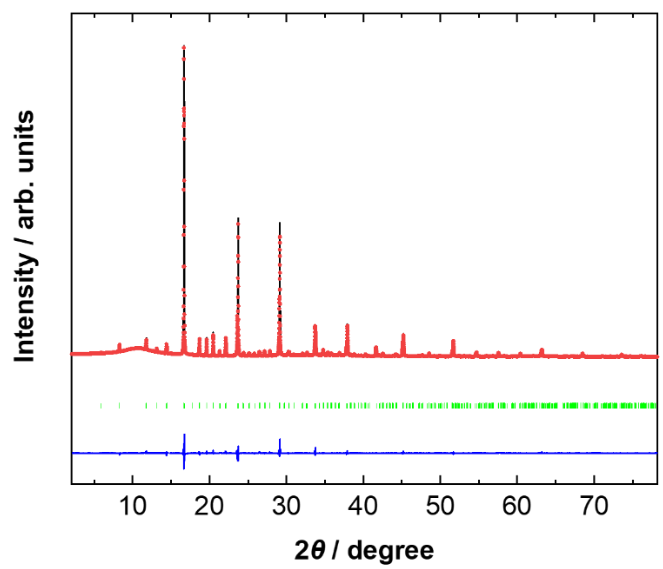

Figure S4. Results of Rietveld refinement against SXRD data (λ = 0.77435 Å) of $CaMnTi_{1.4}V_{0.6}O_6$ at room temperature. The observed (red circles), calculated (black solid lines), and difference (bottom blue line) profiles are represented. The green ticks correspond to the positions of the allowed Bragg reflections.

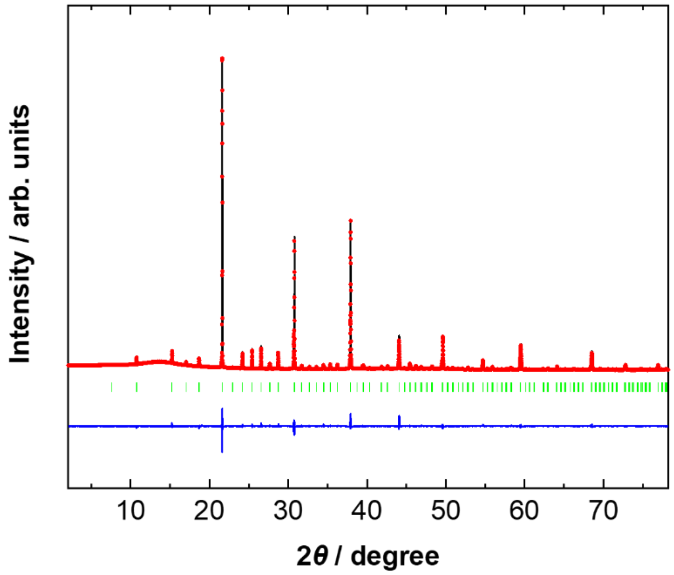

Figure S5. Results of Rietveld refinement against SXRD data (λ = 0.99932 Å) of $CaMnTi_{1.2}V_{0.8}O_6$ at room temperature. The observed (red circles), calculated (black solid lines), and difference (bottom blue line) profiles are represented. The green ticks correspond to the positions of the allowed Bragg reflections.

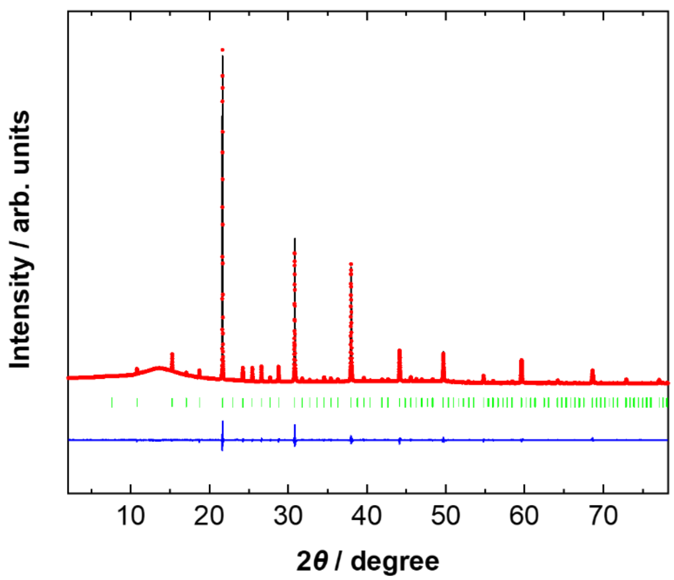

Figure S6. Results of Rietveld refinement against SXRD data (λ = 0.99932 Å) of $CaMnTiVO_6$ at room temperature. The observed (red circles), calculated (black solid lines), and difference (bottom blue line) profiles are represented. The green ticks correspond to the positions of the allowed Bragg reflections.

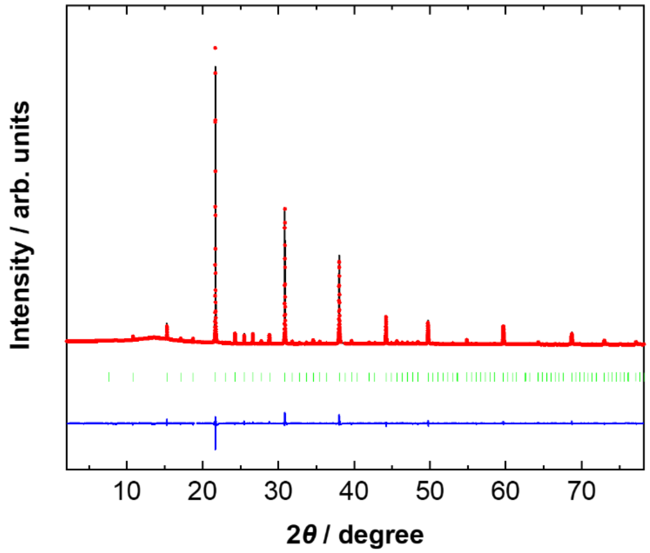

Figure S7. Results of Rietveld refinement against SXRD data (λ = 0.99932 Å) of $CaMnTi_{0.8}V_{1.2}O_6$ at room temperature. The observed (red circles), calculated (black solid lines), and difference (bottom blue line) profiles are represented. The green ticks correspond to the positions of the allowed Bragg reflections.

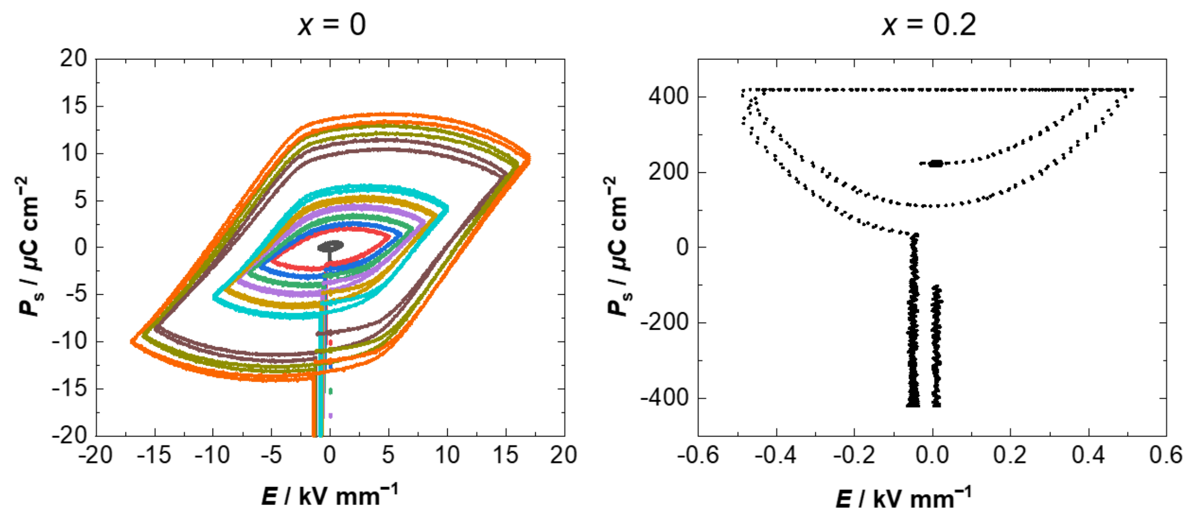

Figure S8. *P*-*E* curves measured on $x = 0$ and 0.2 samples at room temperature. The measurement frequency is 10 Hz.

Table S1. Refined parameters and reliability factors for $CaMn(Ti_{1-x}V_x)_2O_6$

x	0	0.1	0.2	0.3	0.4	0.5	0.6
Source				Synchrotron X-ray			
Temperature				Room temperature			
Wavelength	0.77435	0.77435	0.99985	0.77435	0.99932	0.99932	0.99932
Chemical formula	$CaMnTi_2O_6$	$CaMnTi_{1.8}V_{0.2}O_6$	$CaMnTi_{1.6}V_{0.4}O_6$	$CaMnTi_{1.4}V_{0.6}O_6$	$CaMnTi_{1.2}V_{0.8}O_6$	$CaMnTi_{1.8}V_{0.2}O_6$	$CaMnTi_{1.8}V_{0.2}O_6$
Formula weight	286.75	287.36	287.98	288.59	289.21	289.82	290.44
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_2mc$ (No. 195)	$P4_2mc$ (No. 195)	$P4_2mc$ (No. 195)	$P4_2mc$ (No. 195)	$P4_2mc$ (No. 195)	$P4_2mc$ (No. 195)	$P4_2mc$ (No. 195)
a / Å	7.54607(1)	7.54017(1)	7.53576(1)	7.53288(1)	7.52846(1)	7.51899(1)	7.51271(2)
c / Å	7.59866(1)	7.58728(2)	7.58452(4)	7.56382(3)	7.54713(2)	7.53160(3)	7.51513(3)
V / Å^3	432.692(1)	431.369(1)	430.707(2)	429.204(2)	427.753(1)	425.801(2)	424.160(3)
Z	4	4	4	4	4	4	4
d_{min} / Å	0.39551	0.39551	0.51069	0.39551	0.51042	0.51042	0.51042
d_{max} / Å	10.566	10.566	13.643	10.566	13.636	13.636	13.636
χ^2	8.1058	12.8907	4.2121	6.0142	12.4658	6.7441	3.1966
R_p	4.164	5.291	1.892	3.275	2.848	2.198	3.725
R_{wp}	6.215	8.281	2.762	4.572	4.726	3.214	5.243

Rp = $\Sigma y_{io} - y_{ic}$ / Σy_{io} and $R_{wp} = [\Sigma w_i(y_{io} - y_{ic})^2 / \Sigma w_i y_{io}^2]^{1/2}$, where y_{io} and y_{ic} are the observed and calculated intensities, respectively, and w_i is the weighting factor for point i.