Supporting Information

Rattling behavior in a Simple Perovskite NaWO$_3$

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In this supporting information, we present results of the structure analysis for Na$_x$WO$_3$ (x = 0.5, 0.6, 0.75, 0.8, 1.0) and for Li$_x$WO$_3$ (x = 0.5, 0.8). We also show results of the specific heat analysis for NaWO$_3$, KWO$_3$, Li$_{0.5}$WO$_3$, and CuCu$_3$V$_4$O$_{12}$.

I. Structure analysis and characterization of Na$_x$WO$_3$ (x = 0.5, 0.6, 0.75, 0.8, 1.0)

Synchrotron powder X-ray diffraction (SXRD) data for polycrystalline samples of Na$_x$WO$_3$ (x = 0.5, 0.6, 0.75, 0.8, 1.0) were analyzed by the Rietveld method assuming the *I/4mmm* structure (for x = 0.5, 0.6, 0.75) or the *Im*-3 structure (for x = 0.8, 1.0). We used the program JANA2006 for the refinements. We obtained reasonable fitting results for all samples. Compositions of x were obtained as almost consistent values for nominal ones. The results are summarized in Fig. 1S and refined structure parameters are listed in Tables S1. The results of the sample with x = 1.0 are presented in the main text. The excluded ranges are 2.098º to 5.356º, 6.449º to 8.027º, 10.603º to 10.7º, 15.043º to 15.096º and 19.592º to 19.622º due to the presence of a peaks from small unidentified impurities. Note that refinement of the composition for x = 1 leads to Na$_{0.95(7)}$WO$_3$ with a 7.35% R_{wp}. Fixing the occupancy parameter leads to a 7.37% R_{wp} asgreement parameter implying that the genuine stoichiometry of the material is close to x = 1 but cannot be decisively confirmed using this technique.

According to the Shannon ionic radius[1], the ionic radius of Na$^+$ for 12 coordination is 1.39 Å. However, this value is apparently larger than the free space around Na1 (1.301 Å) and one of the free distances around Na2 (1.152 Å) in NaWO$_3$. We thus think that the actual value of the ionic radius of Na$^+$ of NaWO$_3$ is smaller than the customary value of 1.39 Å. It would be plausible that the value is 1 ∼ 1.2 Å for this compound. The value of 1.2 Å is reasonable for the estimation of the bond valence sum around Na1, which can follow +1 when the bond parameter of R_0 is 1.73. The value of 1 Å is close to the ionic radius of Na$^+$ for 4 coordination[1], which may reflect circumstances that there are three different bond lengths of Na2-O (see Fig. 2d of the main text) consisting of 4 coordination around Na2 each other. Therefore, in the main text of the present paper we tentatively use the value of r(Na$^+$) = 1 Å for the estimation of the guest free space Δ.

II. Structure analysis and characterization of a cubic phase of $Li_{0.5}WO_3$

The obtained polycrystalline sample of $Li_{0.5}WO_3$ was characterized by powder XRD measurements with Cu-$K\alpha$ radiation and neutron diffraction (ND) measurements at room temperature (RT). The structure refinement was performed by the Rietveld method using the program JANA2006. The refinement assuming the cubic perovskite structure with the space group of Im-3 converged and resulted in the lattice parameters of a = 7.4444(1) Å and R factors of R_{wp} = 10.47% and R_p = 7.94%. The goodness-of-fit (GOF) parameter was GOF = 1.12, indicating that the quality of the fitting was good. Obtained results and refined structure parameters are summarized in Fig.S2 and Table S2.

III. Structure analysis and characterization of a rhombohedral phase of $Li_{0.8}WO_3$

The obtained polycrystalline sample of $Li_{0.8}WO_3$ was characterized by powder XRD measurements with Cu-$K\alpha$ radiation and ND measurements at RT. We realized that the ND data contained peaks from small amounts of the cubic Im-3 phase in addition to the main phase. This additional cubic phase is likely due to the unstable nature of $Li_{0.8}WO_3$.

We carried out the two phase analysis of Rietveld refinements assuming the $R3c$ (or R-3c) and Im-3 structures. We used the program JANA2006 for the refinements. The refinement assuming the main rhombohedral phase for $R3c$ converged to R_{wp} = 7.62%, R_p = 5.86%, GOF = 2.35 (Fig. 7 in the main text). The refinement assuming the main rhombohedral phase for R-3c also converged R_{wp} = 10.98 % and R_p = 8.36 %, GOF = 1.04 (Fig.S3). These results ensure that the quality of the fittings are good, although the R factors of R-3c are slightly lower quality than those of $R3c$. The volume fractions of $R3c$ (or R-3c) and Im-3 were obtained as 76% and 24%. Refined structure parameters are summarized in Table S3.

IV Specific heat analysis for $NaWO_3$, KWO_3, $Li_{0.5}WO_3$, and $CuCu_3V_4O_{12}$

The specific heat (C_P) of $NaWO_3$, KWO_3, cubic-$Li_{0.5}WO_3$, and an A-site ordered quadruple perovskite $CuCu_3V_4O_{12}$ [Ref. 2] were analyzed by a combined model of Debye and Einstein specific heats, described in the main text. The least squares fittings were carried out using the data in the temperature range of 2 K < T < 200 K for $NaWO_3$, KWO_3 and $Li_{0.5}WO_3$, and 4 K < T < 200 K for $CuCu_3V_4O_{12}$: for $CuCu_3V_4O_{12}$, we used the same data of Fig.3 of Ref. [2], where the contribution of

the electronic specific heat ($C_e = \gamma T$) was subtracted from the total specific heat. So here we didn't consider such contribution for the analysis of $CuCu_3V_4O_{12}$.

The reasonable fittings were obtained for the models with two Debye modes ($i = 2, j = 0$) for KWO_3, and with two Debye and one Einstein modes ($i = 2, j = 1$) for $NaWO_3$ (see also main text) and $Li_{0.5}WO_3$. The data of $CuCu_3V_4O_{12}$ was also analyzed by the same model of two Debye and one Einstein modes, which demonstrated the clear peak structure. These additional terms of the Einstein specific heat represent the main feature of the C_P/T^3 peak, suggesting a rattling-like local vibrational mode for these compounds that host nonequivalent two A sites in the crystal structures. Results of analysis are summarized in Fig.S3 and Table S3.
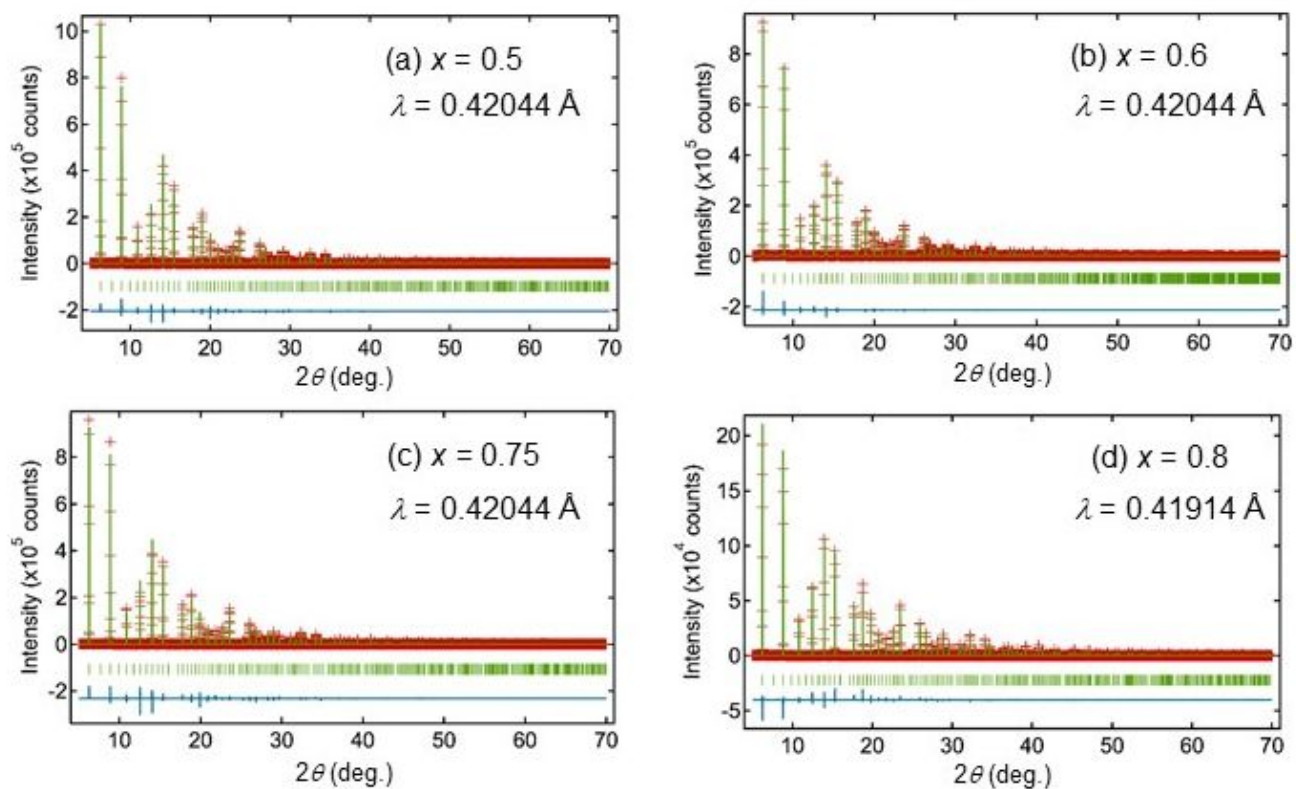
Figure S1. SXRD patterns and Rietveld refinements of Na_xWO_3 for (a) $x = 0.5$, (b) $x = 0.6$, (c) $x = 0.75$, (d) $x = 0.8$. Red crosses, green solid line, and blue solid line represent observed, calculated, and difference intensities, respectively. The green ticks indicate the positions of the Bragg peaks.

Table S1. Refined structural parameters of Na_xWO_3 for (a) $x = 0.5$, (b) $x = 0.6$, (c) $x = 0.75$, (d) $x = 0.8$.

(a) $x = 0.5$

Atom	Site	g	x	y	z	U_{iso} (10^{-2} Å^2)
Na1	2a	0.29(5)	0	0	0	1.0(3)
Na2	2b	0.48(7)	0	0	0.5	0.47(3)
Na3	4c	0.53(2)	0.5	0	0	0.22(10)
W	8f	1	0.25	0.25	0.25	0.385(2)
O1	8h	1	0.2332(7)	0.2332(7)	0	0.9(9)
O2	16n	1	0	0.252(4)	0.2543(15)	1.4(9)

$I4/mmm$, $a = 7.6480(5)$ Å, $c = 7.6573(6)$, $R_{wp} = 7.06\%$, $R_p = 4.87\%$, GOF = 4.15

(b) $x = 0.6$

Atom	Site	g	x	y	z	U_{iso} (10^{-2} Å^2)
Na1	2a	0.53(6)	0	0	0	0.51(2)
Na2	2b	0.76(6)	0	0	0.5	0.84(2)
Na3	4c	0.51(3)	0.5	0	0	1.0(1)
W	8f	1	0.25	0.25	0.25	0.329(2)
O1	8h	1	0.2310(7)	0.2310(7)	0	0.12(8)
O2	16n	1	0	0.243(3)	0.2538(14)	1.15(8)

$I4/mmm$, $a = 7.6665(5)$ Å, $c = 7.6776(2)$, $R_{wp} = 6.63\%$, $R_p = 4.99\%$, GOF = 4.11

(c) *x* = 0.75

Atom	Site	g	x	y	z	U_{iso} (10^{-2} Å^2)
Na1	2a	0.79(5)	0	0	0	0.42(1)
Na2	2b	0.74(4)	0	0	0.5	0.45(4)
Na3	4c	0.68(2)	0.5	0	0	0.12(10)
W	8f	1	0.25	0.25	0.25	0.285(2)
O1	8h	1	0.2348(7)	0.2332(7)	0	0.66(12)
O2	16n	1	0	0.2485(16)	0.2650(6)	0.82(10)

$I4/mmm$, a = 7.6967(1) Å, c = 7.6872(2), R_{wp} = 6.98%, R_p = 4.76%, GOF = 3.97

(d) *x* = 0.8

Atom	Site	g	x	y	z	U_{iso} (10^{-2} Å^2)
Na1	2a	0.66(5)	0	0	0	0.9(2)
Na2	6b	0.73(2)	0	0.5	0.5	2.1(19)
W	8c	1	0.25	0.25	0.25	0.227(3)
O1	24g	1	0	0.2583(12)	0.2294(8)	0.4(7)

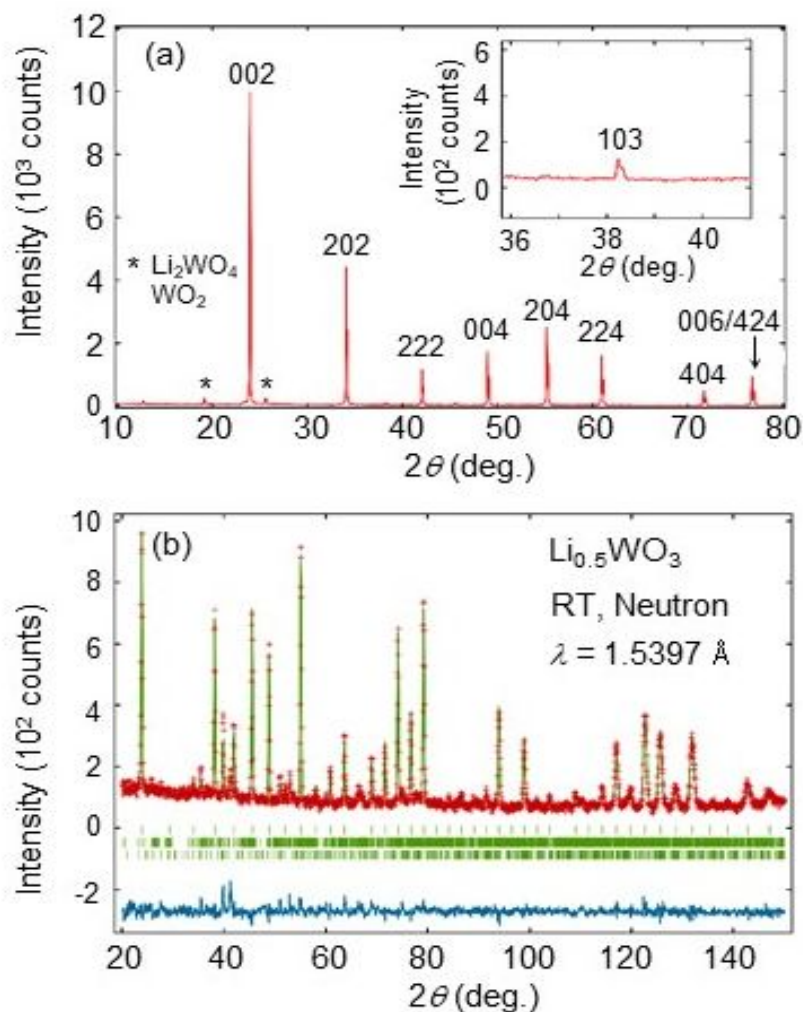$Im-3$ a = 7.7041(4) Å, R_{wp} = 11.24%, R_p = 8.00%, GOF = 2.85

Figure S2. (a) XRD pattern of $Li_{0.5}WO_3$. The main peaks were identified by components of a cubic perovskite with the space group of *Im*-3 (Glaser's notation $a^+a^+a^+$). The inset shows the elongation around the super lattice reflection of the (103) Bragg position, which ensures the cubic *Im*-3 structure. Small amounts of Li_2WO_4 and WO_2 remains unreacted. **(b)** Rietveld refinement using ND data at RT. Here the structure of the cubic *Im*-3 perovskite was assumed. Red crosses, green solid line, and blue solid line represent observed, calculated, and difference intensities, respectively. The top, middle, and bottom green ticks indicate the positions of the Bragg peaks of Li_xWO_3, Li_2WO_4, and WO_2, respectively.
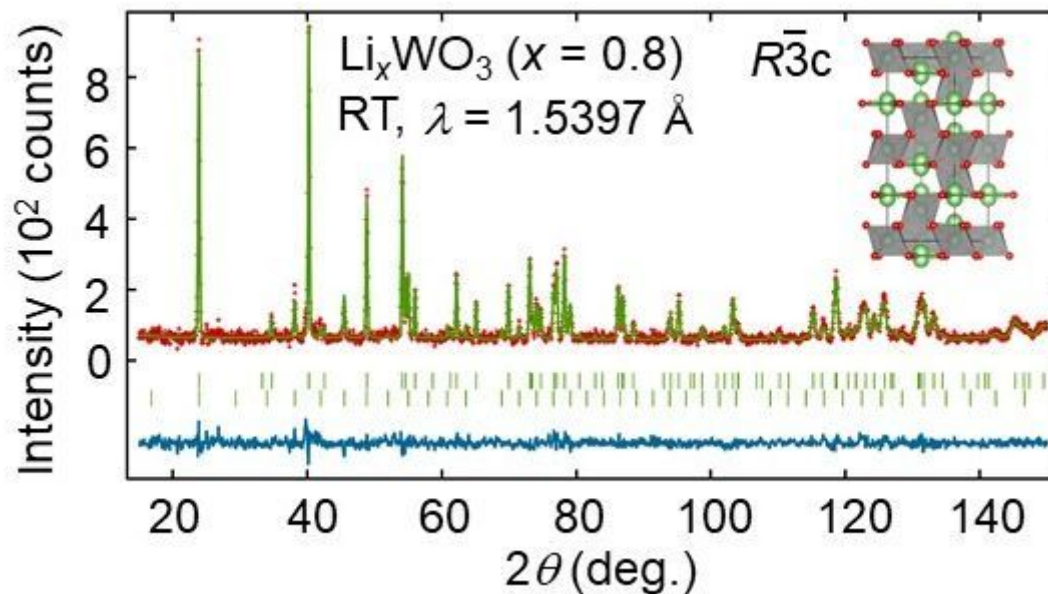
Figure S3 Rietveld refinement of neutron data of Li_xWO3 (x = 0.8) assuming the R-3c structure. Red crosses, green solid line, and blue solid line represent observed, calculated, and difference intensities, respectively. The top and bottom green ticks indicate the positions of the Bragg peaks of the R-3c structure and the cubic Im-3 structure ($x \sim 0.5$).

Table S2. Refined structural parameters of $Li_{0.5}WO_3$ for the cubic perovskite structure with the space group of $Im–3$ (No.204). The Lattice parameter are obtained as a = 7.4444(1) Å. R_{wp} = 10.47%, R_p = 7.94%, GOF = 1.12.

Atom	Site	g	x	y	z	U_{iso} (10^{-2} Å^2)
Li1	2a	0	0	0	0	1
Li2	6b	0.69(5)	0	0.5	0.5	1.6(5)
W	8c	1	0.25	0.25	0.25	0.257(3)
O1	24g	1	0	0.2025(3)	0.2948(2)	0.62(4)

Table S3. Refined structural parameters for Li_xWO_3 (x = 0.8), assuming the $LiNbO_3$-type structure with $R3c$ (No. 161) and its high-temperature polymorph with $R–3c$ (No. 167). a = 5.1664(1) Å and c = 13.443(1) Å. The Li site occupancy of g = 0.70(6) for $R3c$ and g = 0.69(6) for $R–3c$.

R3c

Atom	Site	x	y	z	U_{iso} (10^{-2}Å^2)
Li	6a	0	0	0.2696(9)	1.0(7)
W	6a	0	0	0	0.31(9)
O	18b	0.0664(16)	0.332(3)	0.0797(9)	0.70(7)

R-3c

Atom	Site	x	y	z	U_{iso} (10^{-2}Å^2)
Li	6a	0	0	0.2719(17)	1.0(7)
W	6b	0	0	0	0.35(9)
O	18e	0.0660(4)	0.3333	0.0833	0.69(6)
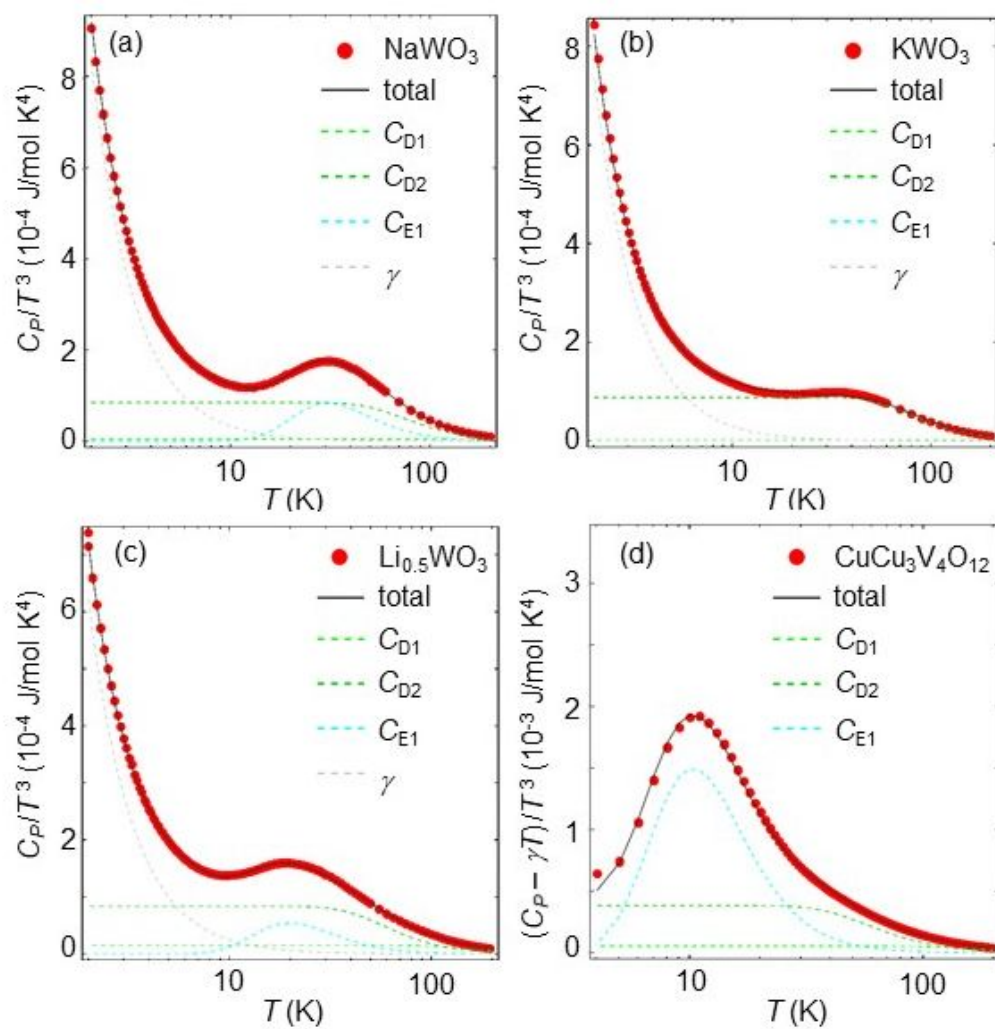
Figure. S4 Results of fitting of C_P data for (a) $NaWO_3$, (b) KWO_3, (c) $Li_{0.5}WO_3$, and (d) $CuCu_3V_4O_{12}$.

Table S4. Parameters obtained by the fitting of C_P data for $NaWO_3$, KWO_3, $Li_{0.5}WO_3$, and $CuCu_3V_4O_{12}$.

	$NaWO_3$	KWO_3	$Li_{0.5}WO_3$	$CuCu_3V_4O_{12}$
θ_{D1} (K)	962	1099	756	717
θ_{D2} (K)	371	409	289	257
f_{D1}	6.62	5.85	10.08	48.93
f_{D2}	6.74	9.15	3.13	9.99
θ_{E1} (K)	151	-	98.4	51.1
f_{E1}	1.64	-	0.29	1.08
γ (mJ/K^2)	3.34	2.99	2.50	-

References of the supporting information

(1) Shannon, R. D., Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst. A* **1976**, *32*, 751–767.

(2) Akizuki, Y.; Yamada, I.; Fujita, K.; Taga, K.; Kawakami, T.; Mizumaki, M.; Tanaka, K. Rattling in the Quadruple Perovskite $CuCu_3V_4O_{12}$. *Angew. Chemie Int. Ed.* **2015**, *54*, 10870–10874.