Electronic Supporting Information

Low-Temperature Synthesis of Homogeneous Solid Solutions of Scheelite-

Structured Ca_{1-x}Sr_xWO₄ and Sr_{1-x}Ba_xWO₄ Nanocrystals

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Figures and Tables



Fig. S1 TEM images of (a) $CaWO_4$ and (b) $SrWO_4$ products aged at 22 °C under nitrogen for 24 h and (c) $BaWO_4$ aged at 60 °C under nitrogen for 24 h with associated nanocrystal size distribution histrograms. Diffractograms illustrating the effects of thermal aging are also provided for $CaWO_4$ and $SrWO_4$.



Fig. S2 Rietveld analysis of XRD patterns for $A_{1-x}A'_{x}WO_{4}$ nanocrystal solid solutions. Experimental (O) and calculated (—) patterns are shown for each sample along with the difference curve (—) and tickmarks (|) corresponding to the phase refined. The nominal composition of each phase is indicated in the top right of each pattern. —*Continues on the following page*.



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	Ca _{0.75} Sr _{0.25} WO ₄	$Ca_{0.5}Sr_{0.5}WO_4$	Ca _{0.25} Sr _{0.75} WO ₄
a (Å)	5.2949(10)	5.3368(10)	5.3850(11)
<i>c</i> (Å)	11.5264(22)	11.6616(22)	11.8208(24)
$V(\text{\AA}^3)$	323.16(19)	332.14(19)	342.79(21)
	0.6586(8),	0.6557(6),	0.6542(7),
<i>x</i> , <i>y</i> , <i>z</i> O	0.4942(5),	0.4922(4),	0.4944(5),
	0.2106(3)	0.2096(2)	0.2090(3)
W–O (Å)	1.8742(27)	1.8858(23)	1.8893(27)
$U_{ m A}({ m \AA}^2)^a$	1.35(3)	1.29(2)	1.29(2)
$U_{ m W}({ m \AA}^2)^a$	1.08(2)	2.30(2)	1.03(2)
$U_{ m O}({ m \AA}^2)^a$	2.77(16)	2.64(14)	4.69(18)
$R_{ m wp}$	6.0	5.4	6.0
χ^2	1.80	1.58	1.82
	Sr _{0.75} Ba _{0.25} WO ₄	$Sr_{0.5}Ba_{0.5}O_4$	Sr _{0.25} Ba _{0.75} WO ₄
<i>a</i> (Å)	Sr _{0.75} Ba _{0.25} WO ₄ 5.4500(16)	Sr _{0.5} Ba _{0.5} O ₄ 5.5065(16)	Sr _{0.25} Ba _{0.75} WO ₄ 5.5560(14)
a (Å) c (Å)	Sr _{0.75} Ba _{0.25} WO ₄ 5.4500(16) 12.0684(35)	Sr _{0.5} Ba _{0.5} O ₄ 5.5065(16) 12.3063(37)	Sr _{0.25} Ba _{0.75} WO ₄ 5.5560(14) 12.5046(31)
a (Å) c (Å) V (Å ³)	Sr _{0.75} Ba _{0.25} WO ₄ 5.4500(16) 12.0684(35) 358.47(31)	Sr _{0.5} Ba _{0.5} O ₄ 5.5065(16) 12.3063(37) 373.15(34)	Sr _{0.25} Ba _{0.75} WO ₄ 5.5560(14) 12.5046(31) 386.00(29)
a (Å) c (Å) V (Å ³)	Sr _{0.75} Ba _{0.25} WO ₄ 5.4500(16) 12.0684(35) 358.47(31) 0.6494(11),	$\frac{Sr_{0.5}Ba_{0.5}O_4}{5.5065(16)}$ 12.3063(37) 373.15(34) 0.6459(10),	Sr _{0.25} Ba _{0.75} WO ₄ 5.5560(14) 12.5046(31) 386.00(29) 0.6336(9),
a (Å) c (Å) V (Å ³) x, y, z O	Sr _{0.75} Ba _{0.25} WO ₄ 5.4500(16) 12.0684(35) 358.47(31) 0.6494(11), 0.4929(7),	$\frac{Sr_{0.5}Ba_{0.5}O_4}{5.5065(16)}$ 12.3063(37) 373.15(34) 0.6459(10), 0.4971(8),	Sr _{0.25} Ba _{0.75} WO ₄ 5.5560(14) 12.5046(31) 386.00(29) 0.6336(9), 0.4932(9),
a (Å) c (Å) V (Å ³) x, y, z O	Sr _{0.75} Ba _{0.25} WO ₄ 5.4500(16) 12.0684(35) 358.47(31) 0.6494(11), 0.4929(7), 0.2046(3)	$\frac{Sr_{0.5}Ba_{0.5}O_4}{5.5065(16)}$ 12.3063(37) 373.15(34) 0.6459(10), 0.4971(8), 0.2090(4)	Sr _{0.25} Ba _{0.75} WO ₄ 5.5560(14) 12.5046(31) 386.00(29) 0.6336(9), 0.4932(9), 0.2092(4)
a (Å) c (Å) V (Å ³) x, y, z O W–O (Å)	$\frac{Sr_{0.75}Ba_{0.25}WO_4}{5.4500(16)}$ $12.0684(35)$ $358.47(31)$ $0.6494(11),$ $0.4929(7),$ $0.2046(3)$ $1.8840(40)$	$\frac{Sr_{0.5}Ba_{0.5}O_4}{5.5065(16)}$ $12.3063(37)$ $373.15(34)$ $0.6459(10),$ $0.4971(8),$ $0.2090(4)$ $1.9110(40)$	Sr _{0.25} Ba _{0.75} WO ₄ 5.5560(14) 12.5046(31) 386.00(29) 0.6336(9), 0.4932(9), 0.2092(4) 1.9220(40)
a (Å) c (Å) V (Å ³) x, y, z O W–O (Å) U _A (Å ²) ^a	Sr _{0.75} Ba _{0.25} WO ₄ 5.4500(16) 12.0684(35) 358.47(31) 0.6494(11), 0.4929(7), 0.2046(3) 1.8840(40) 2.17(3)	$\frac{Sr_{0.5}Ba_{0.5}O_4}{5.5065(16)}$ $12.3063(37)$ $373.15(34)$ $0.6459(10),$ $0.4971(8),$ $0.2090(4)$ $1.9110(40)$ $1.36(3)$	Sr _{0.25} Ba _{0.75} WO ₄ 5.5560(14) 12.5046(31) 386.00(29) 0.6336(9), 0.4932(9), 0.2092(4) 1.9220(40) 0.52(3)
$a (\text{\AA})$ $c (\text{\AA})$ $V (\text{\AA}^3)$ $x, y, z \text{ O}$ $W-O (\text{\AA})$ $U_{\text{A}} (\text{\AA}^2)^a$ $U_{\text{W}} (\text{\AA}^2)^a$	Sr _{0.75} Ba _{0.25} WO ₄ 5.4500(16) 12.0684(35) 358.47(31) 0.6494(11), 0.4929(7), 0.2046(3) 1.8840(40) 2.17(3) 1.73(2)	$\frac{Sr_{0.5}Ba_{0.5}O_4}{5.5065(16)}$ $12.3063(37)$ $373.15(34)$ $0.6459(10),$ $0.4971(8),$ $0.2090(4)$ $1.9110(40)$ $1.36(3)$ $1.09(2)$	$\frac{Sr_{0.25}Ba_{0.75}WO_4}{5.5560(14)}$ $12.5046(31)$ $386.00(29)$ $0.6336(9),$ $0.4932(9),$ $0.2092(4)$ $1.9220(40)$ $0.52(3)$ $0.72(2)$
$a (Å) c (Å) V (Å^3) x, y, z O W-O (Å) UA (Å2)a UW (Å2)a UO (Å2)a$	Sr _{0.75} Ba _{0.25} WO ₄ 5.4500(16) 12.0684(35) 358.47(31) 0.6494(11), 0.4929(7), 0.2046(3) 1.8840(40) 2.17(3) 1.73(2) 7.36(28)	$\frac{Sr_{0.5}Ba_{0.5}O_4}{5.5065(16)}$ $12.3063(37)$ $373.15(34)$ $0.6459(10),$ $0.4971(8),$ $0.2090(4)$ $1.9110(40)$ $1.36(3)$ $1.09(2)$ $6.97(31)$	$\frac{Sr_{0.25}Ba_{0.75}WO_4}{5.5560(14)}$ $12.5046(31)$ $386.00(29)$ $0.6336(9),$ $0.4932(9),$ $0.2092(4)$ $1.9220(40)$ $0.52(3)$ $0.72(2)$ $4.51(28)$
$a (Å) c (Å) V (Å^3) x, y, z O W-O (Å) UA (Å2)a UW (Å2)a UO (Å2)a Rwp$	$\frac{Sr_{0.75}Ba_{0.25}WO_4}{5.4500(16)}$ $12.0684(35)$ $358.47(31)$ $0.6494(11),$ $0.4929(7),$ $0.2046(3)$ $1.8840(40)$ $2.17(3)$ $1.73(2)$ $7.36(28)$ 5.8	$\frac{Sr_{0.5}Ba_{0.5}O_4}{5.5065(16)}$ $12.3063(37)$ $373.15(34)$ $0.6459(10),$ $0.4971(8),$ $0.2090(4)$ $1.9110(40)$ $1.36(3)$ $1.09(2)$ $6.97(31)$ 7.3	$\frac{Sr_{0.25}Ba_{0.75}WO_4}{5.5560(14)}$ $12.5046(31)$ $386.00(29)$ $0.6336(9),$ $0.4932(9),$ $0.2092(4)$ $1.9220(40)$ $0.52(3)$ $0.72(2)$ $4.51(28)$ 8.2

Table S1. Rietveld Analysis of X-ray Diffraction Data for $A_{1-x}A'_xWO_4$ Nanocrystal Solid Solutions

^{*a*}Given as $100 \times U$



Fig. S3 XPS spectra illustrating relevant states for the A-site atoms in the $A_{1-x}A'_{x}WO_{4}$ nanocrystal solid solutions. All doublets can be assigned to divalent alkaline earth atoms.



Fig. S4 XPS survey spectra for the $A_{1-x}A'_{x}WO_{4}$ nanocrystal solid solutions.



Fig. S5 SEM–EDX spectra for the $Ca_{0.5}Sr_{0.5}WO_4$ and $Sr_{0.5}Ba_{0.5}WO_4$ nanocrystals.



Fig. S6 TEM images of (a) $Ca_{0.75}Sr_{0.25}WO_4$, (b) $Ca_{0.5}Sr_{0.5}WO_4$, (c) $Ca_{0.25}Sr_{0.75}WO_4$, (d) $Sr_{0.25}Ba_{0.75}WO_4$, (e) $Sr_{0.5}Ba_{0.5}WO_4$, and (f) $Sr_{0.25}Ba_{0.75}WO_4$ nanocrystals. High-resolution TEM images for single AWO₄ nanocrystals are provided in the insets.



Fig. S7 Nanocrystal size distribution histograms for $A_{1-x}A'_{x}WO_{4}$ nanocrystal solid solutions. The total number of nanocrystals counted (N), mean diameter (μ), and standard deviation (σ) are indicated.



Fig. S8 Representative TEM image of $Sr_{0.75}Ba_{0.25}WO_4$ nanocrystals thermally aged at 100 °C under flowing nitrogen for 24 h.