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Supporting Information

The crystal and electronic structures of A_2NaIO_6 periodate double perovskites (A= Sr, Ca, Ba): Candidate wasteforms for I-129 immobilisation

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Table S1: Comparison of BVS as calculated in this work against calculations using bond length data from previous work [22].

Compound	Bonds	Expected valence	BVS from previous work	BVS from this work
Ba ₂ NaIO ₆	Ba-O (CN=12)	2	1.980	1.967
	I-O (CN=6)	7	5.840	7.079
	Na-O (CN=6)	1	1.289	1.073
Sr ₂ NaIO ₆	Sr-O (CN=12)	2	1.827	1.892
	I-O (CN=6)	7	5.854	7.077
	Na-O (CN=6)	1	1.341	1.125
Ca ₂ NaIO ₆	Ca-O (CN=12)	2	2.008	1.876
	I-O (CN=6)	7	5.996	7.122
	Na-O (CN=6)	1	1.142	0.982

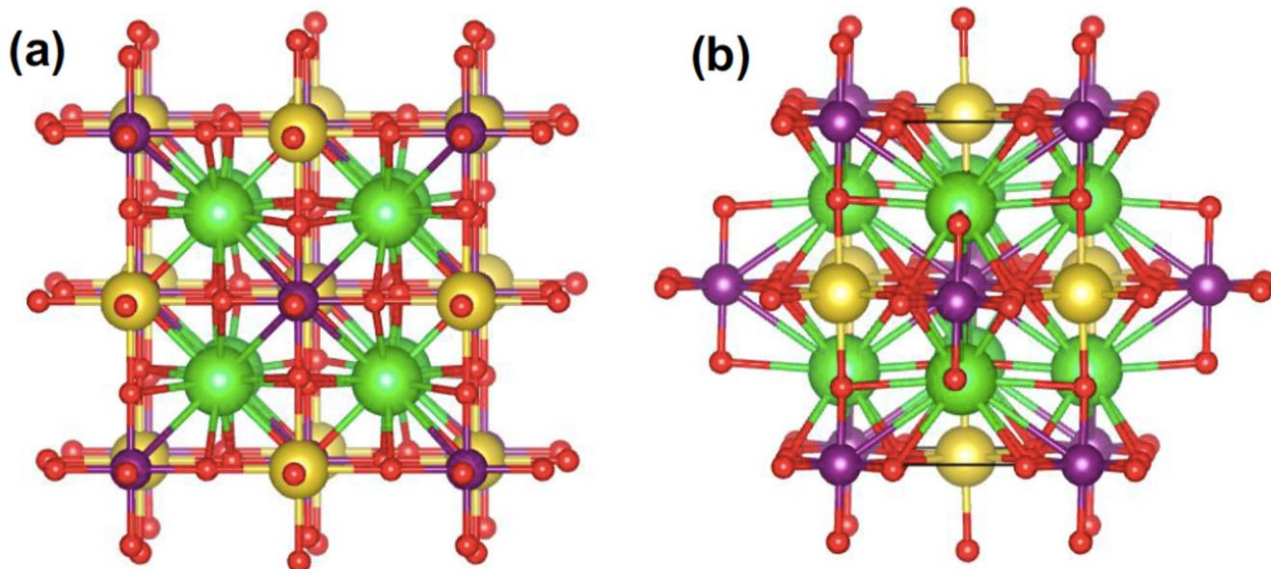


Figure S1: Ball-and-stick representation of the DFT-optimized (a) cubic $Fm-3m$ phase (b) monoclinic $P2_1/n$ phase. Colour legend: green, M = Ca, Sr, or Ba; yellow, Na; purple, I; red, O.

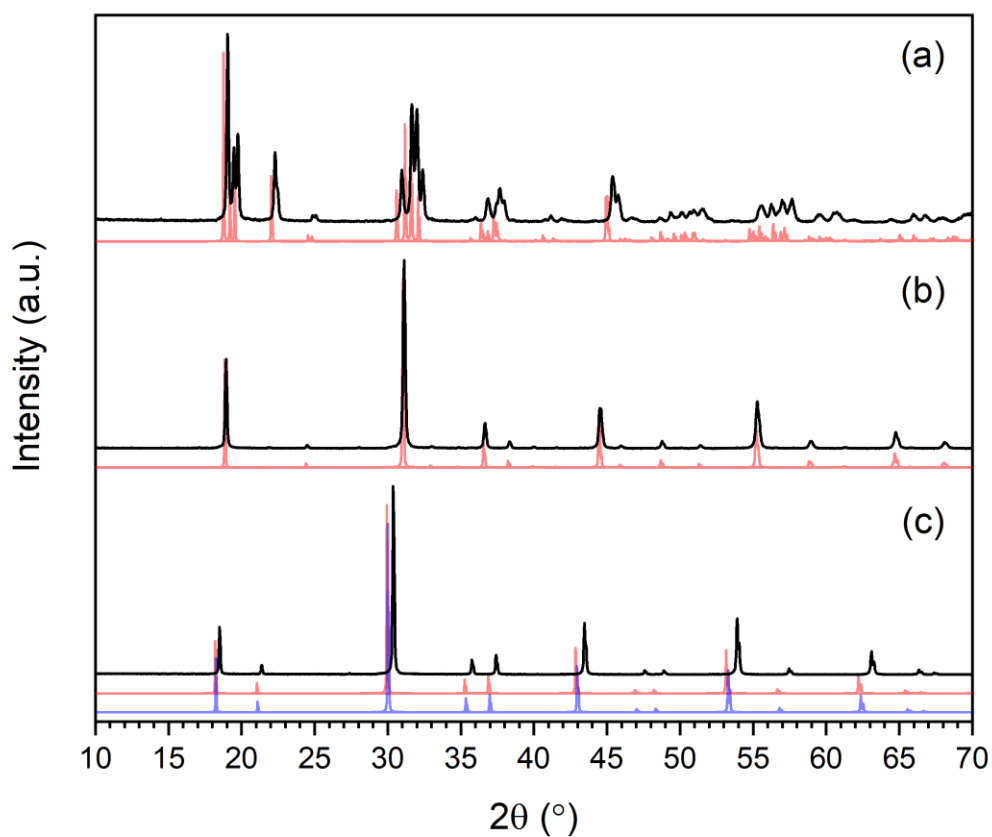


Figure S2: Simulated X-ray diffraction patterns of (a) Ca₂NaIO₆ in the monoclinic *P*2₁/*n* phase, (b) Sr₂NaIO₆ in the monoclinic *P*2₁/*n* phase, and (c) Ba₂NaIO₆ in the cubic *Fm*-3*m* (red) and monoclinic *P*2₁/*n* (blue) phases. Corresponding experimental XRD patterns collected in this study are displayed in black.

Table S2: Comparison of bond lengths obtained via DFT to experimental data acquired in this study (where applicable).

Ba₂NaIO₆ <i>Fm-3m</i>			Ba₂NaIO₆ <i>P2₁/n</i>			Sr₂NaIO₆ <i>P2₁/n</i>			Ca₂NaIO₆ <i>P2₁/n</i>		
Bond	DFT (Å)	Exp (Å)	Bond	DFT (Å)	Exp (Å)	Bond	DFT (Å)	Exp (Å)	Bond	DFT (Å)	Exp (Å)
Ba-O1 (x12)	2.992	2.954	Ba-O1	3.022	-	Sr-O1	3.186	3.186	Ca-O1	3.673	3.617
			Ba-O1	3.021	-	Sr-O1	2.658	2.658	Ca-O1	2.384	2.375
			Ba-O1	2.962	-	Sr-O1	2.553	2.550	Ca-O1	2.352	2.340
			Ba-O1	2.970	-	Sr-O1	3.248	3.248	Ca-O1	3.395	3.364
			Ba-O2	2.945	-	Sr-O2	2.571	2.571	Ca-O2	2.387	2.381
			Ba-O2	3.042	-	Sr-O2	2.790	2.790	Ca-O2	2.697	2.683
			Ba-O2	2.985	-	Sr-O2	2.875	2.875	Ca-O2	2.745	2.725
			Ba-O2	3.001	-	Sr-O2	3.366	3.366	Ca-O2	3.705	3.654
			Ba-O3	3.012	-	Sr-O3	2.820	2.819	Ca-O3	2.562	2.574
			Ba-O3	3.019	-	Sr-O3	2.556	2.556	Ca-O3	2.384	2.366
			Ba-O3	2.976	-	Sr-O3	3.398	3.398	Ca-O3	3.703	3.671
			Ba-O3	2.968	-	Sr-O3	2.846	2.846	Ca-O3	3.020	2.961
I-O1 (x6)	1.908	1.868	I-O1 (x2)	1.909	-	I-O1 (x2)	1.863	1.863	I-O1 (x2)	1.905	1.861
			I-O2 (x2)	1.909	-	I-O2 (x2)	1.869	1.870	I-O2 (x2)	1.900	1.865
			I-O3 (x2)	1.908	-	I-O3 (x2)	1.874	1.874	I-O3 (x2)	1.910	1.874
Na-O1 (x6)	2.314	2.298	Na-O1 (x2)	2.315	-	Na-O1 (x2)	2.281	2.281	Na-O1 (x2)	2.353	2.341
			Na-O2 (x2)	2.318	-	Na-O2 (x2)	2.275	2.275	Na-O2 (x2)	2.287	2.297
			Na-O3 (x2)	2.315	-	Na-O3 (x2)	2.286	2.286	Na-O3 (x2)	2.369	2.368

Table S3: Atomic positions obtained via DFT and compared to experimental values for Ca_2NaIO_6 ($P2_1/n$), Sr_2NaIO_6 ($P2_1/n$), and Ba_2NaIO_6 ($Fm-3m$ and $P2_1/n$).

Ca_2NaIO_6 $P2_1/n$							
Atom	Wyckoff position	x		y		z	
		DFT	Exp	DFT	Exp	DFT	Exp
Na	2a	0	0	0	0	0	0
I	2b	0	0	0	0	0.5	0.5
Ca	4e	0.018	0.0160	0.558	0.5575	0.243	0.2447
O1	4e	-0.114	-0.1108	-0.057	-0.0537	0.278	0.2809
O2	4e	0.222	0.2243	0.324	0.3266	0.046	0.0453
O3	4e	0.335	0.3381	0.768	0.7666	0.072	0.0705
Sr_2NaIO_6 $P2_1/n$							
Atom	Wyckoff position	x		y		z	
		DFT	Exp	DFT	Exp	DFT	Exp
Na	2a	0	0	0	0	0	0
I	2b	0	0	0	0	0.5	0.5
Sr	4e	0.010	0.0057	0.544	0.5287	0.249	0.2499
O1	4e	-0.080	-0.0665	-0.028	-0.0177	0.278	0.2762
O2	4e	0.238	0.2433	0.315	0.3071	0.038	0.0331
O3	4e	0.320	0.3124	0.761	0.7608	0.047	0.0355
Ba_2NaIO_6 $Fm-3m$							
Atom	Wyckoff position	x		y		z	
		DFT	Exp	DFT	Exp	DFT	Exp
I	4a	0	0	0	0	0	0
Na	4b	0.5	0.5	0.5	0.5	0.5	0.5
Ba	8c	0.25	0.25	0.25	0.25	0.25	0.25
O1	24e	0.226	0.224	0	0	0	0
Ba_2NaIO_6 $P2_1/n$							
Atom	Wyckoff position	x		y		z	
		DFT	Exp	DFT	Exp	DFT	Exp
Na	2d	0.5	-	0.0	-	0.0	-
I	2a	0.0	-	0.0	-	0.0	-
Ba	4e	-0.25	-	0.5	-	0.0	-
O1	4e	-0.005	-	0.775	-	0.226	-
O2	4e	0.226	-	-0.001	-	0.008	-
O3	4e	-0.004	-	0.227	-	0.225	-

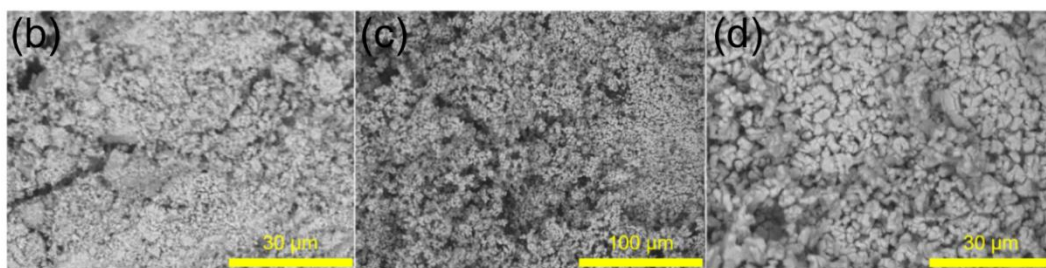
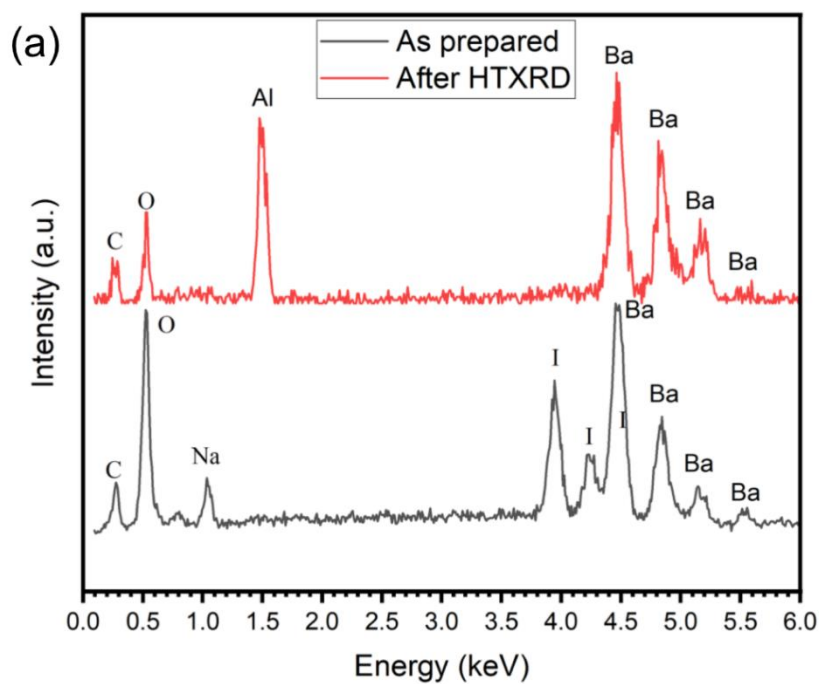


Figure S3: a) EDS analysis of Ba₂NaIO₆ powder pre- (black) and post- HT-XRD (red) showing the loss of Na and I after the heat treatment. The inclusion of Al is attributed to contamination arising from the Al₂O₃ crucible reacting under a combined heat treatment with a mild iodine flux. SEM images show as prepared Ba₂NaIO₆ (b) and after decomposition at 1030 °C to BaO ((c) and (d)).

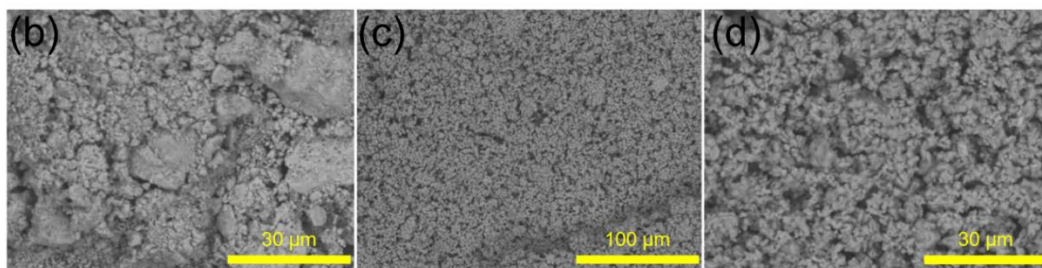
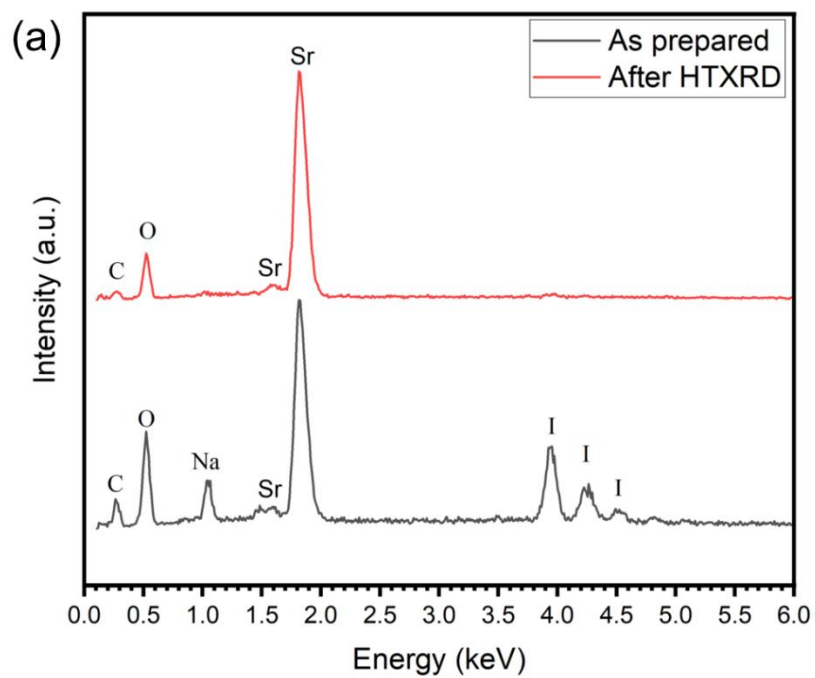


Figure S4 a) EDS analysis of Sr_2NaIO_6 powder pre- (black) and post- HT-XRD (red). SEM images show prepared Sr_2NaIO_6 (b) and after decomposition at 950 $^\circ\text{C}$ to SrO ((c) and (d)).

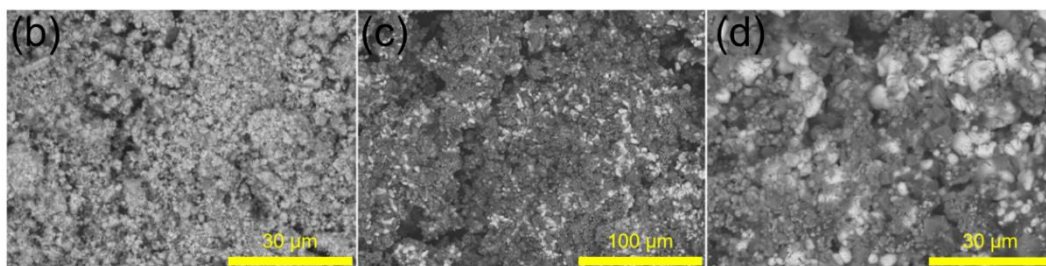
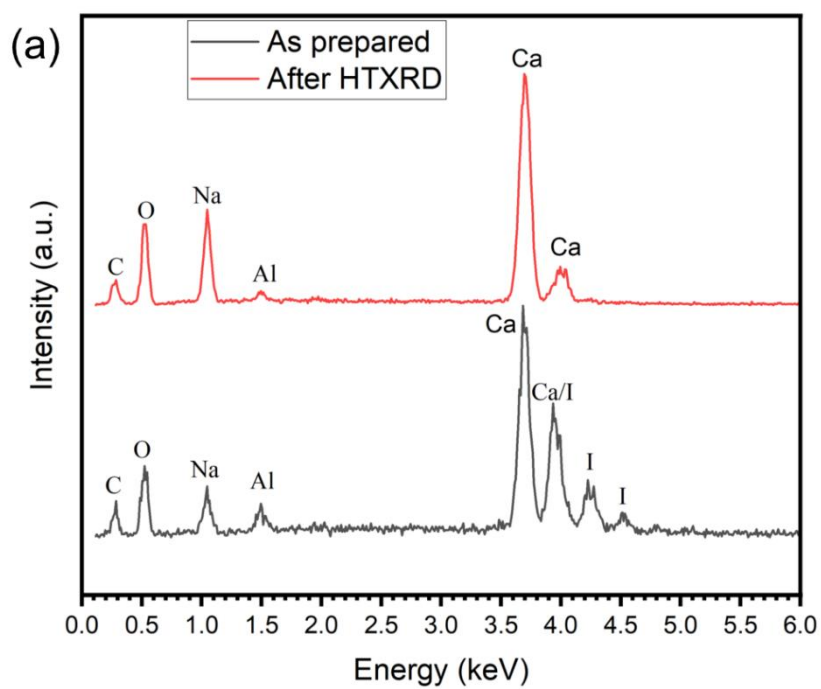


Figure S5: a) EDS analysis of Ca_2NaIO_6 powder pre- (black) and post- HT-XRD (red). A small amount of Sr contamination is visible both before and after HT-XRD. SEM images show as prepared Ca_2NaIO_6 (b) and after decomposition at 750 $^\circ\text{C}$ to CaO ((c) and (d)).