Supporting Information: On the Existence of $AgM_9(VO_4)_6I$ (M = Ba, Pb)

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Synthesis and Characterization of $AgPb_9(VO_4)_6I$ from PbO, V_2O_5 , and AgI.

Stoichiometric amounts of PbO, V₂O₅, and AgI (9:3:1), respectively, were batched to yield a final reacted composition of AgPb₉(VO₄)₆I and were processed and reacted as reported in the main text. The batched powders were pulverized and mixed as a slurry with isopropanol with an agate mortar and pestle. After drying, the resulting powders were pressed at 2 tonnes into ~ 250 mg, 6mm disk pellets. Pellets were reacted in air in a box furnace or in sealed quartz tubes (10 mm O.D., 8 mm I.D., 180 length) in an alumina tube furnace at 700 °C for 5 hr.

The resulting products were analyzed by PXRD (**Figure S1**), which were comparable to those starting from $Pb_3(VO_4)_2$ and AgI. The SEM/EDX analysis of the sectioned portion of the pellet reacted in a sealed quartz tube is presented in **Figure S2**, once again showing the heterogeneous distribution of Ag-I and Pb-V phases.



Figure S1. Measured PXRD patterns for "AgPb₉(VO₄)₆I" starting from either Pb₃(VO₄)₂ or PbO and V₂O₅ with AgI reacted at 700 °C for 5 hr in sealed quartz tubes or in air. The PXRD pattern of β -Pb₃(VO₄)₂ is given for comparison.



Figure S2. Back-scattering electron (BSE) SEM image at x2000 magnification and EDX map of V (teal), Pb (blue), I (yellow), and Ag (pink) present in $AgPb_9(VO_4)_6I$ produced from PbO, V_2O_5 , and AgI, and reacted at 700 °C for 5 hr in a sealed quartz tube.



Figure S3. EDX spectrum of spot analyses of the β -Pb₃(VO₄)₂ phase in "AgPb₉(VO₄)₆I" reacted at 700 °C for 5 hr in a sealed quartz tube.



Figure S4. EDX map of Ag (pink) and I (yellow) showing the presence of AgI and Ag metal in "AgPb₉(VO₄)₆I" reacted at 700 °C for 5 hr in a sealed quartz tube.



Figure S5. A) BSE image (x2000; scale bar length = $30 \ \mu m$) showing point of measurement on "AgPb₉(VO₄)₆I" reacted at 700 °C for 5 hr in a sealed quartz tube; B) Red-Green-Blue EDX mixed map of Pb (blue), V (red), and I (green) indicating the presence of an overlapping area (white) corresponding to Pb-V-I phase; C) Resulting EDX spectrum of measured point of interest indicating the presence of Pb, V, and I peaks.



Figure S6. TG-DTA analysis of "AgPb₉(VO₄)₆I" reacted at 700 °C for 5 hr in a sealed quartz tube. Temperature listed in red is the reported decomposition temperature for "AgPb₉(VO₄)₆I".



Figure S7. EDX spectra of spot analyses of A) $Ba_3(VO_4)_2$ and B) AgI phases in "AgBa₉(VO₄)₆I" reacted at 700 °C for 5 hr in a sealed quartz tube.



Figure S8. TG-DTA analysis of "AgBa₉(VO₄)₆I" reacted at 700 °C for 5 hr in a sealed quartz tube. Temperature listed in red is the reported decomposition temperature for "AgBa₉(VO₄)₆I".



XRD figure from original publication: M. Uno, A. Kosuga, S. Masuo, M. Imamura, S. Yamanaka, J. Alloy Compd., 384 (2004), pp. 300-302.

Diffraction angle, 2θ (degree)