A High-Throughput Synthesis Protocol for Accelerated Exploration of Novel Mixed Perovskite Materials

(Accelerated Materials Discovery)

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Abstract.
A high-throughput, partly automated workflow was implemented to rapidly synthesize and electronically characterize many lead-halide and double-metal perovskites via antisolvent crystallization and photoluminescence spectroscopy. More than 500 samples were synthesized and characterized. A large subset of these samples exhibited high stability and bandgap tunability, suggesting a basis for further investigation, and demonstrating the effectiveness of the experimental approach.

1. Introduction

1.1. Accelerated materials discovery

Tremendous leaps of technological progress have been enabled by our discovery of new useful materials, but researching novel materials can be a painstaking, laborious task. From theory to synthesis, the researcher performs many operations which may require great precision and vast informational resources, and many more operations which are difficult to reproduce exactly. Further, the properties of unknown materials are often difficult to predict using current theoretical modeling, especially at the macroscopic scale. [1]

Recent innovations in robotics, data science and artificial intelligence can liberate novel materials research from these constraints, and accelerate materials discovery. Automated laboratory systems are now a burgeoning field of research. [1] Proponents of this field envision a 'self-driving' materials laboratory, which could autonomously generate novel materials based on human-specified criteria. An autonomous lab could predict hypothetical candidate materials by combining computational modeling with experimental databases, produce results using fully robotic synthesis procedures, and close the loop by continuously repeating and improving the experimental process via machine learning. [1]

In the spirit of accelerated materials discovery, this project's objective was to develop and implement a partially-automated high-throughput system for synthesizing and characterizing large numbers of perovskite materials, in the interest of furthering their potential for use as photocatalysts. Although it still requires some human involvement, it's a step towards realizing autonomous laboratories, and has produced contributions to perovskite research.
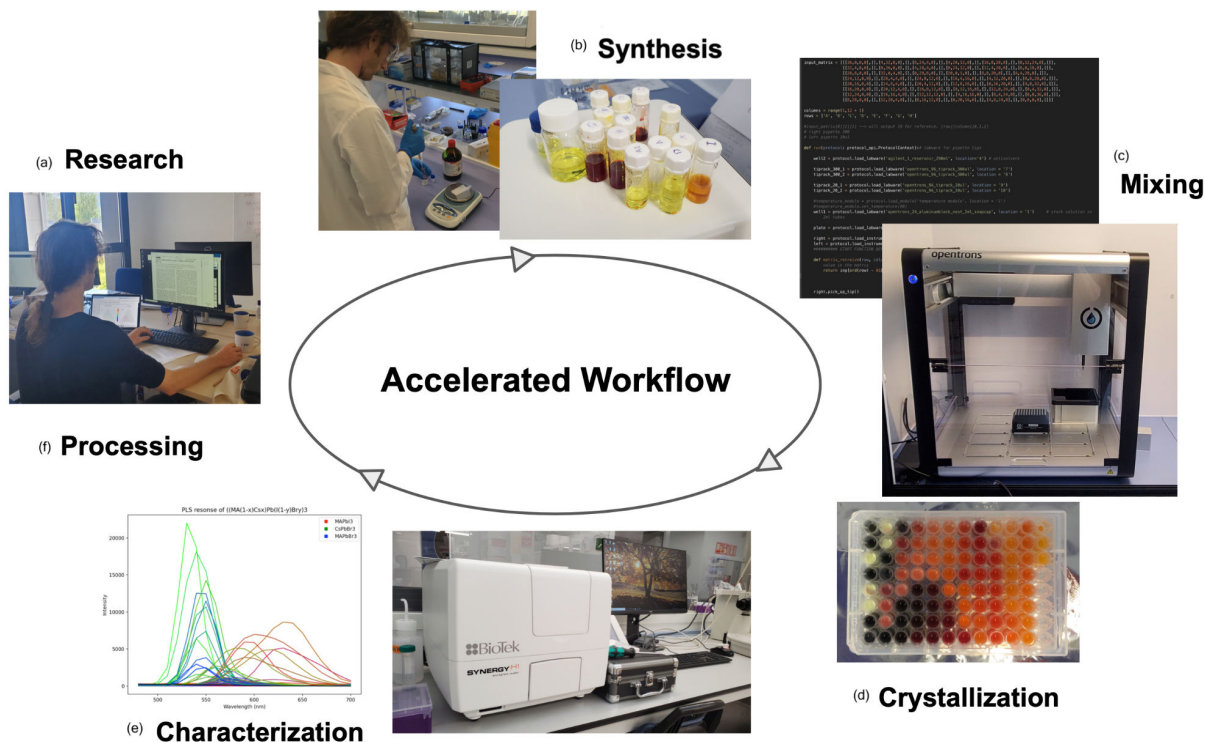
Figure 1. The accelerated workflow. (a) Candidate materials are selected based on criteria for adaptable synthesis. (b) Precursors are synthesized using conventional methods. (c) Precursors are robotically mixed in varying ratios according to a user-defined protocol. (d) Crystallization is accelerated by robotically-applied antisolvent. (e) Samples are rapidly characterized using photoluminescence spectroscopy. (f) Experimental outcomes are processed, and used to inform the next experiment.

1.2. Perovskite

Materials with the perovskite crystal lattice are among the most naturally abundant on Earth, [2] and they have recently emerged as a subject of great research interest, owing to their diversity, tunability, and ease of synthesis. [2] Researchers have found promising applications for perovskites in various devices, including photovoltaics, LEDs, fuel cells, and catalytic cells. [3] Despite the versatility and promise of artificially-synthesized perovskites, many of them suffer from a host of significant drawbacks. For example, lead-halide perovskites have shown great potential for applications in solar cells and other photonic technologies due to their bandgap tunability. However, they are not commercialized because they are highly unstable under ambient conditions, and they contain toxic lead. [2] Due to the limitations of present theoretical models, researchers are still actively involved in the difficult process of physically synthesizing and characterizing new perovskites, [2] but their versatility, and their adaptability to solution-processing techniques, makes them ideal candidates for high-throughput materials research. [4]
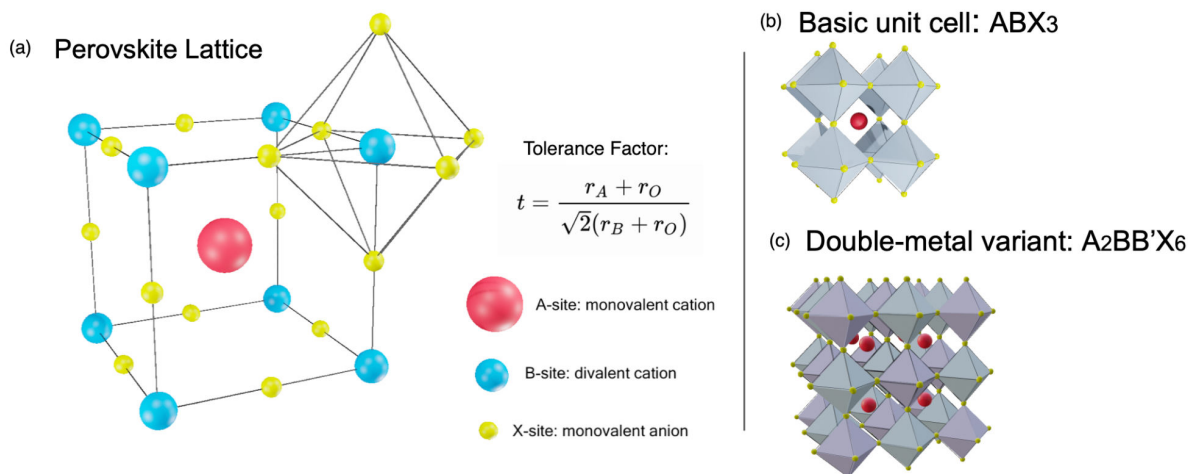
Figure 2. The perovskite lattice. (a) Possibility and ideality of the structure is given by the tolerance factor, t. (b) The basic unit cell is given. (c) In double metal perovskite, B-sites are interchangeably occupied by monovalent and trivalent metals, (B and B',) provided that the tolerance factor is satisfied by their atomic radial average.

In this work, we present a partially-automated workflow for material synthesis and characterization, which may be implemented in most chemical research laboratories without requiring major renovations. This workflow was found to produce 48 unique perovskite samples within 75 minutes. We describe its advantages and limitations, and we present results collected from more than five-hundred perovskite material samples which were created and analyzed this way.

2. Methods

The general workflow is adapted from reference [4], and it is illustrated in figure 1.

Our automated workflow begins with a human-informed decision about which materials to synthesize and test, since not all materials are suitable for this process. Synthesis procedures from literature may be considered for adaptation into the high-throughput workflow if they meet the following criteria:

- Synthesis may be performed under an ambient laboratory atmosphere, at temperatures between 20ºC and 90ºC, without adverse effects from photosensitivity, and with tolerance for kinetic instability.
- Materials can be characterized using Photoluminescence Spectroscopy, (PLS,) or absorbance spectroscopy, (ABS.)
- Different basic liquid precursors might be combined to form new stable materials.
- Precursors are made from solvents which will not produce a strong reaction with the plastic components of the robot, the sample wells, or the other precursors.
- Materials are stable enough to remain intact throughout the synthesis and characterization process.

For completely novel materials, the suitability of the workflow cannot be anticipated with certainty. In the present work, we have restricted our candidate materials to novel combinations of known materials, with synthesis procedures known to be implementable.

After candidate materials were selected, precursors were manually synthesized using traditional methods, in desired concentrations, and according to stoichiometric ratios. [4,5]

To synthesize novel materials from combinations of precursors, we used a liquid-handling robot, (OT-2, Opentrons.) [6]
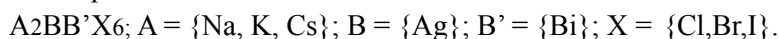
The robots's primary function is to aspirate and dispense μL amounts of liquids between different container wells with precision, cleanliness and efficiency. Within a partially-enclosed operation space, a robotic gantry equipped with automated pipettes moves between container wells mounted on an operation surface, descending and ascending to aspirate or dispense liquids. Pipette tips may be automatically discarded and replaced to prevent cross-contamination of samples. Operating protocols are written using the built-in Python API, in which the user defines the sequence of steps to perform. [6] Our robot is particularly well-suited to work with the standard 96-well sample plates commonly used for research in cellular biology; the photoelectronic properties of samples contained in these plates may be obtained using a separate piece of equipment.

We used a photoluminescent plate reader to characterize our samples, (Synergy H1 Hybrid Multi-Mode Reader, Biotek.) [7] This machine collects information about the photoelectronic properties of materials by stimulating them with monochromatic light, and recording the material's response across a spectrum of longer wavelengths. As the material is electronically excited by absorbed photons, it emits new photons of energies close to the material's bandgap as it relaxes. [7] The photons captured this way reveal information about the material's composition, purity and crystallinity, as well as optoelectronic characteristics essential for technological applications. [7]

We focused our research on lead-halide perovskites of the form:
$$ABX_3; A = \{MA, FA, Cs\}; B = \{Pb\}; X = \{Br, I\}$$
And silver-bismuth double perovskites of the form:
$$A_2BB'X_6; A = \{Na, K, Cs\}; B = \{Ag\}; B' = \{Bi\}; X = \{Cl,Br,I\}.$$

Lead-halide, (PbH,) perovskites are well-known for their bandgap tunability and ease of synthesis, and have been extensively researched for their potential applications to photovoltaic technologies. [2]

Silver-bismuth-type perovskites, (AgBi,) are the archetype for double-metal perovskites, which are gradually emerging as stable, non-toxic, tunable alternatives to lead-halides, and finding potential applications as photocatalysts and fuel cell components. [8]

We created ten different precursors for our experiments. Some of these precursors, such as $Na_2AgBiBr_6$, have not been shown to produce viable perovskites by themselves, but in liquid form, they can be used to perform doping and site-substitution on the standard $Cs_2AgBiBr_6$.

Table 1. Precursors used in the experiment.

Precursor	Reagents	Solvent
MAPbI$_3$ (0.3M)	MAI (0.2861 g)	Gamma Butyrolactone; GBL (6

	Pb(II)I$_2$ (0.8298 g)	mL)
MAPbBr$_3$ (0.3M)	MABr (0.0672 g) Pb(II)Br$_2$ (0.2202 g)	Dimethyl Formamide; DMF (2 mL)
CsPbBr$_3$ (0.3M)	CsBr (0.2554 g) Pb(II)Br$_2$ (0.4404 g)	Dimethyl Sulfoxide; DMSO (4 mL)
FAPbBr$_3$ (0.3M)	FABr (0.2249 g) Pb(II)Br$_2$ (0.6606 g)	Dimethyl Formamide; DMF (6 mL)
Cs$_2$AgBiBr$_6$ (0.5M)	CsBr (0.4256 g) AgBr (0.1878 g) Bi(III)Br$_3$ (0.4487 g)	Dimethyl Sulfoxide; DMSO (9 mL)
Cs$_2$AgBiCl$_6$ (0.5M)	CsCl (0.1684 g) AgCl (0.0717 g) Bi(III)Br$_3$ (0.1577 g)	Dimethyl Sulfoxide; DMSO (3 mL)
Cs$_2$AgBiI$_6$ (0.5M)	CsI (0.2598 g) AgI (0.1174 g) Bi(III)I$_3$ (0.2948 g)	Dimethyl Sulfoxide; DMSO (1.8 mL)
Na$_2$AgBiBr$_6$ (0.5M)	NaBr (0.1029 g) AgBr (0.0939 g) Bi(III)Br$_3$ (0.2243 g)	Dimethyl Sulfoxide; DMSO (2.8 mL)
K$_2$AgBiBr$_6$ (0.5M)	KBr (0.1190 g) AgBr (0.0939 g) Bi(III)Br$_3$ (0.2243 g)	Dimethyl Sulfoxide; DMSO (2.75 mL)

All precursors were stirred gently and heated for at least one hour; (70ºC for PbH precursors and 130ºC for AgBi precursors,) until fully dissolved, then allowed to rest for at least one hour before use. All chemicals were purchased from Merck Sigma-Aldrich, and they were used without further purification.

We performed ten experiments by combining three of these precursors in forty-eight different mixtures using the robot, producing a total of four-hundred and eighty samples.

Table 2: Summary of experiments.

Experiment	Perovskite Formula	Precursors Used
PbH1	(MA$_{1-x-y}$Cs$_x$FA$_y$)Pb(I$_{1-x-y}$Br$_{x+y}$)$_3$	MAPbI$_3$, CsPbBr$_3$, FAPbBr$_3$
PbH2	(MA$_{1-x}$Cs$_x$)Pb(I$_{1-x-y}$Br$_{x+y}$)$_3$	MAPbI$_3$, CsPbBr$_3$, MAPbBr$_3$
PbH3	(MA$_{1-x}$FA$_x$)Pb(I$_{1-y-x}$Br$_{x+y}$)$_3$	MAPbI$_3$, FAPbBr$_3$, MAPbBr$_3$
PbH4	(MA$_{1-x-y}$Cs$_x$FA$_y$)PbBr$_3$	MAPbBr$_3$, CsPbBr$_3$, FAPbBr$_3$
AgBi1	Cs$_2$AgBi(Br$_{1-x-y}$Cl$_x$I$_y$)$_6$	Cs$_2$AgBiBr$_6$, Cs$_2$AgBiCl$_6$, Cs$_2$AgBiI$_6$

AgBi2	$(Cs_{1-x}Na_x)AgBi(Br_{1-y}Cl_y)_6$	$Cs_2AgBiBr_6$, $Cs_2AgBiCl_6$, $Na_2AgBiBr_6$
AgBi3	$(Cs_{1-x}K_x)AgBi(Br_{1-y}Cl_y)_6$	$Cs_2AgBiBr_6$, $Cs_2AgBiCl_6$, $K_2AgBiBr_6$
AgBi4	$(Cs_{1-x}Na_x)AgBi(Br_{1-y}I_y)_6$	$Cs_2AgBiBr_6$, Cs_2AgBiI_6, $Na_2AgBiBr_6$
AgBi5	$(Cs_{1-x}Na_x)AgBi(Br_{1-y}I_y)_6$	$Cs_2AgBiBr_6$, Cs_2AgBiI_6, $K_2AgBiBr_6$
AgBi6	$(Cs_{1-x-y}Na_xK_y)AgBiBr_6$	$Cs_2AgBiBr_6$, $Na_2AgBiBr_6$, $K_2AgBiBr_6$

Perovskites are usually synthesized from precursors through a gradual evaporation process, [5], but we accelerated the crystallization process by robotically applying antisolvent to each precursor mixture, creating liquid microcrystal solutions which are well-suited for rapid PLS. We used chloroform as the antisolvent for all PbH crystals, and isopropyl alcohol as the antisolvent for all AgBi crystals, as in the literature. [4,10] We performed X-ray diffraction (XRD) analysis to verify this synthesis approach for the standard $Cs_2AgBiBr_6$ by comparing conventionally crystallized samples with antisolvent-accelerated crystals. The validity of the antisolvent approach for lead-halide perovskite is already well-documented. [4]

We characterized all of our sample plates using the plate reader, with a single excitation wavelength of 450 nm, and a spectral range from 480 nm to 700 nm.

PLS data was analyzed to determine the wavelengths and amplitudes of maximum responses for individual samples. The data was noisy at wavelengths exceeding 650 nm, especially for samples with weak responses. Extreme irregularities of amplitude above these wavelengths were smoothed by weighted averaging or removed. Datasets from samples which produced no signal were also removed.

3. Results

3.1. The protocol

Our final robotic protocol produced 48 microcrystal solutions from different perovskite precursor mixtures within 55 minutes.

Extra time was allowed for sterile liquid-handling procedures. We found that robotic pipettes often carry unwanted droplets of liquid on their exterior surfaces, so we included extra steps in the process to prevent cross-contamination, programming the robot to touch the tip to the container edges after interacting with liquids, and to constantly replace used pipette tips.

The PLS characterization process took 14 minutes to perform a single spectral sweep for 48 wells. The total protocol run time from precursor synthesis to perovskite characterization was 75 minutes per 48 samples, including time spent transporting sample plates between different laboratories.

3.2 Lead-Halide (PbH) perovskites

Many PbH samples containing mostly $MAPbI_3$ degraded to non-perovskite phases within minutes, before they could be characterized. Bromine-based PbH perovskites were far more robust, lasting for many days under ambient conditions. Bromine-substitution into $MAPbI_3$ perovskites substantially improved their longevity; bromine-iodine hybrid PbH perovskites containing at least 40% bromine were found to last for several days under ambient conditions.

The most successful PbH experiment was PbH2; results are shown in figure 3. These perovskites showed a bandgap tuning range of 130 nm, from 520 nm to 650 nm. Samples containing Br showed higher energies, narrower bandgaps, and stronger PL responses. Samples containing Cs showed more bandgap narrowing and stronger PLS responses. These results are comparable to those found in literature. [4] PbH4 yielded the most stable results due to its exclusively bromide-type precursor mixtures, but we found no evidence of bandgap tuning. It is already well-documented that pure A-site substitution in PbH perovskite does not produce substantial tunability. [4]
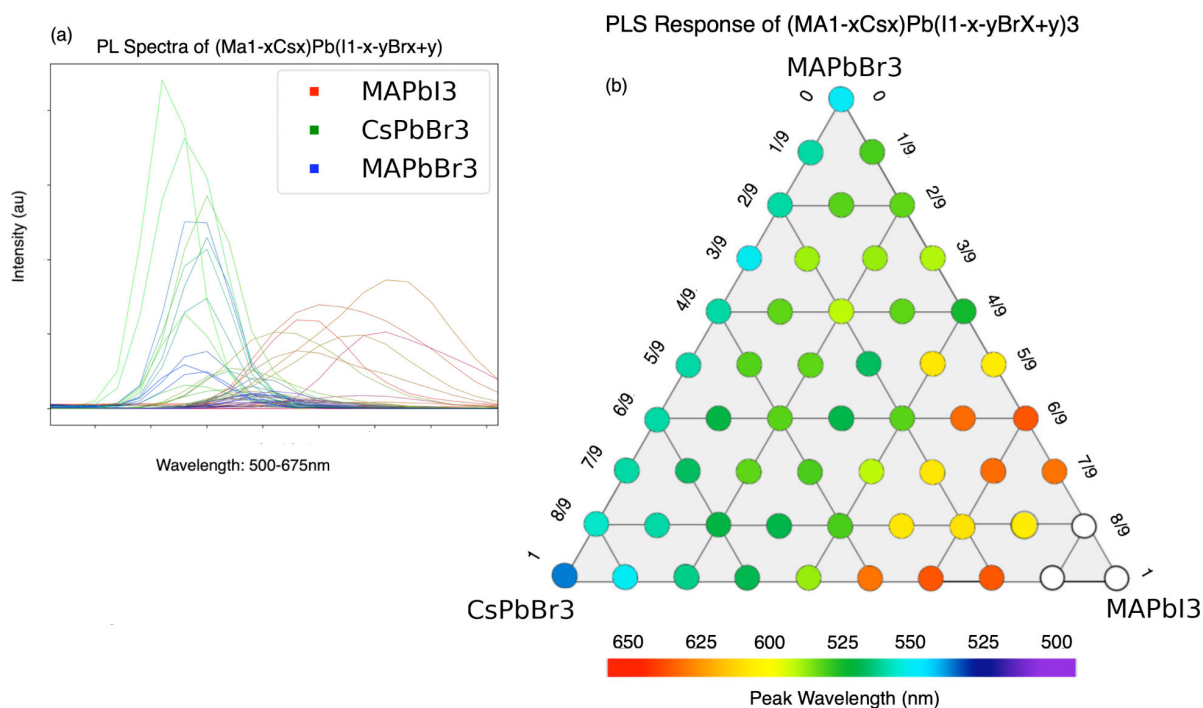
Figure 3. PLS response of PbH2, (A-site substitution by Cs, X-site substitution by I.) (a) PL spectra for thirty different samples are shown; composition ratio is given by the line color. (b) Peak wavelengths are given for a spectrum of perovskites by their composition ratios.
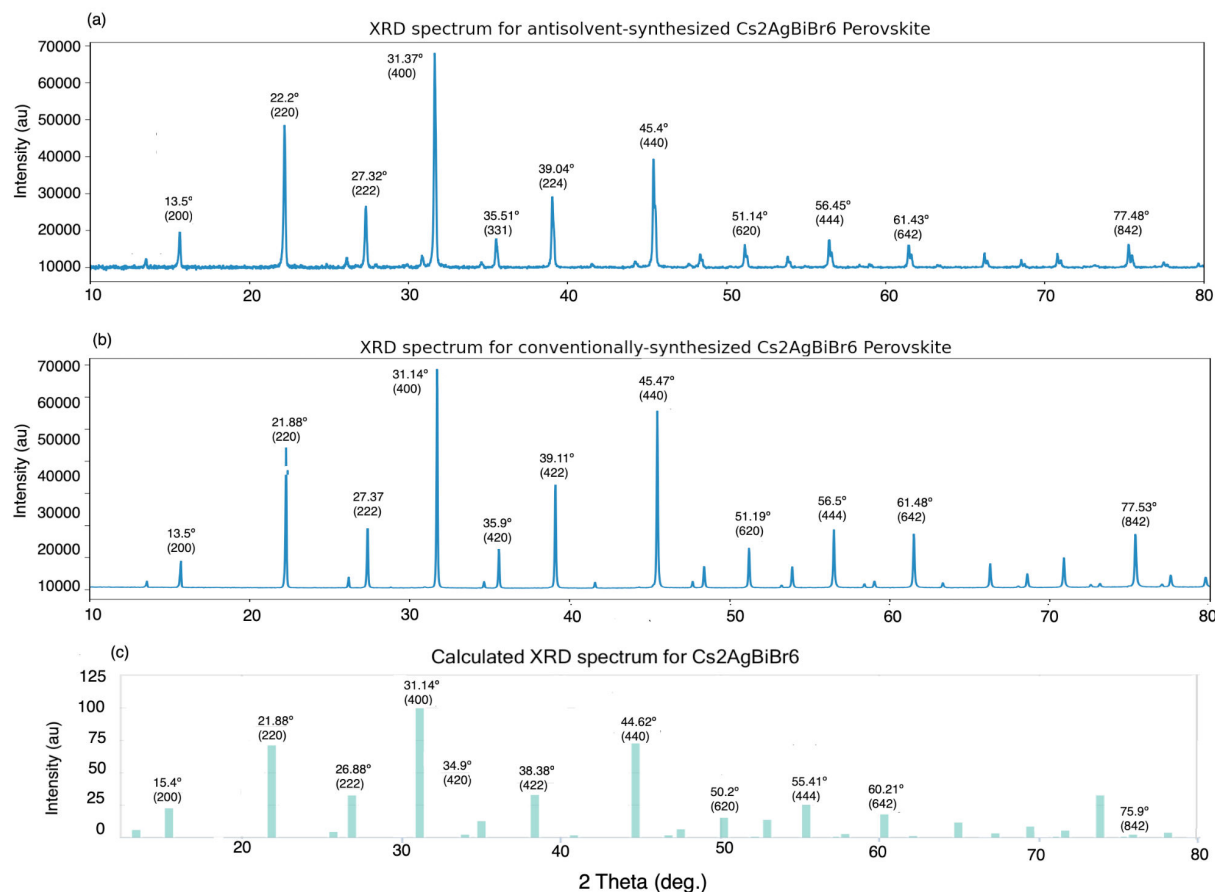
Figure 4. Comparison of Cs₂AgBiBr₆ XRD spectra. (a) XRD peaks from antisolvent-accelerated Cs₂AgBiBr₆ crystals, show very small angular divergence from (b) conventional crystals, The peak at 45.5º is noticeably diminished, which may indicate distortion of the lattice plane. Both samples show slight divergence from (c), the calculated spectrum. [11]

3.3. Silver-Bismuth (AgBi) perovskites

XRD analysis, (figure 4,) showed that the antisolvent-crystallized standard Cs₂AgBiBr₆ perovskite has crystalline quality which is comparable to that of conventional Cs₂AgBiBr₆. Both types of crystal had a similar medium-orange color.

Many AgBi double-metal perovskites proved to be very adaptable to the high-throughput procedure; these samples strongly responded to PLS, and remained stable for weeks after initial characterization was performed.

As with the PbH perovskites, pure A-site substitution of cesium by sodium or potassium in AgBi-type perovskite produced no bandgap tuning, with all samples retaining the same max wavelength as pure Cs₂AgBiBr₆, (640 nm.) Perovskite blends incorporating these elements showed stronger responses to PL excitation, (figure 5.) Some trace amounts of cesium were required to stabilize the materials under these synthesis conditions; it was found that fully A-site substituted materials produced no response.
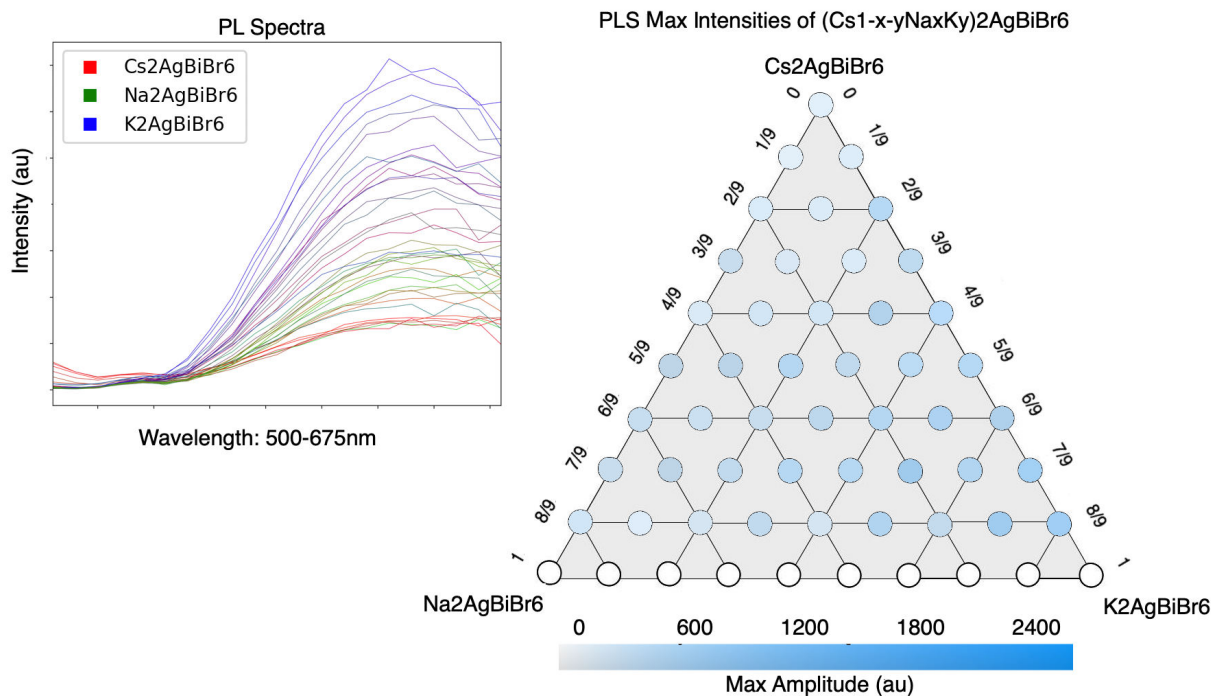
Figure 5. PLS results given by AgBi6, (A-site substitution by Na and K.) (a) PL spectra, with colors indicating material composition. (b) Max intensities are given for a spectrum of perovskites by their composition ratios.

X-site substitution by chlorine proved to be favorable for our experiments. Chlorine-doped samples showed a bandgap tunability of 60 nm, from 620 nm to 680 nm. These samples were bright yellow, visibly indicating a bandgap shift into shorter wavelengths, (figures 6b and 7b.) They also showed a much stronger PLS response, (figures 6a and 7a.)

Samples containing iodine produced inconclusive results. These samples were dark-red, (possibly indicating a bandgap shift into longer wavelengths,) and apparently stable, but they produced no appreciable PLS response. This may be because the bandgap of Cs_2AgBiI_6 is outside of the range of our spectrometer, or it may be due to the instability of these perovskites, which has been reported elsewhere. [10]

Incorporating sodium into these perovskites diminished the response quality, (figure 6.) while incorporating potassium improved the response, and slightly narrowed the bandgap (figure 7.)

If we make the partially-informed assumption that some unmeasured iodine substitution took place, we may propose that these results suggest that incorporating X-site components of increasing atomic radii shifts the bandgap of these materials to larger wavelengths by tightening the octahedral formations of the perovskite lattice, thus allowing electronic excitation to occur at lower photonic energies. Further, incorporating A-site components of diminishing atomic radii increases excitability at the expense of stability by loosening the cubic formations of the lattice. Additional experiments incorporating Rb or organic molecules, (MA, FA,) at the A-sites of AgBi-type perovskites should be performed.

In light of these favorable experimental results, we also propose that deeper investigation of the $(Cs_{1-x}K_x)AgBi(Br_{1-y}Cl_y)_6$ perovskites, (experiment AbgBi3) could yield robust, tunable, non-toxic and easily-synthesized new materials with potential optoelectronic or photocatalytic applications.
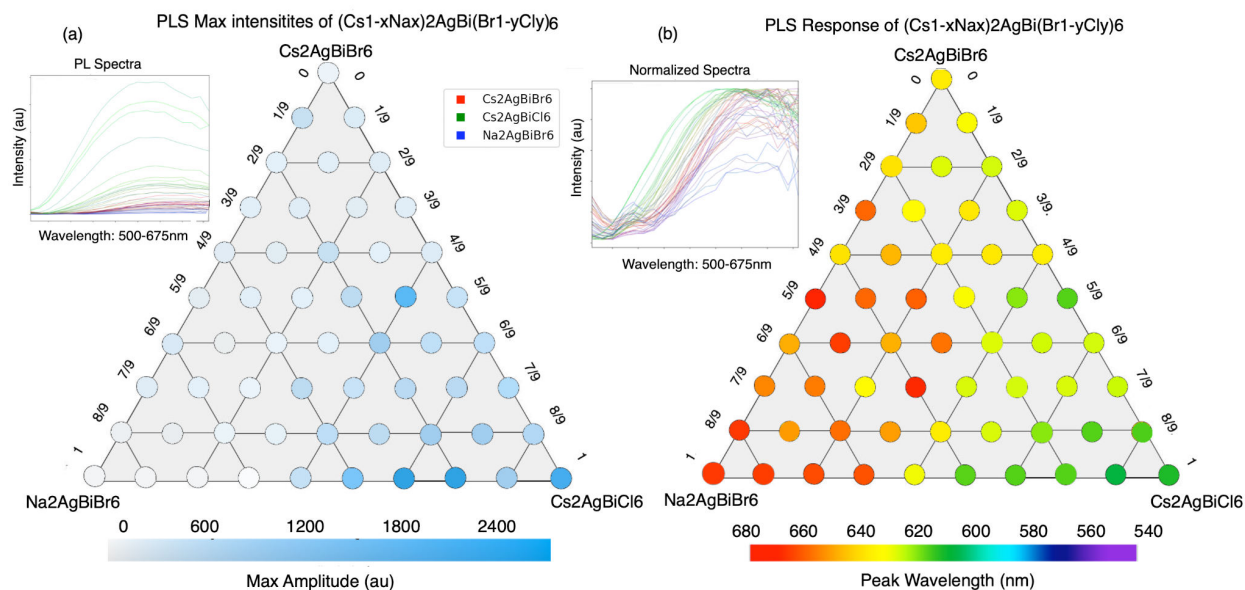
Figure 6. PLS results given by AgBi2, (A-site substitution by Na; X-site substitution by Cl.)
(a) PL spectra and max intensities; (b) Normalized PL spectra and peak wavelengths.
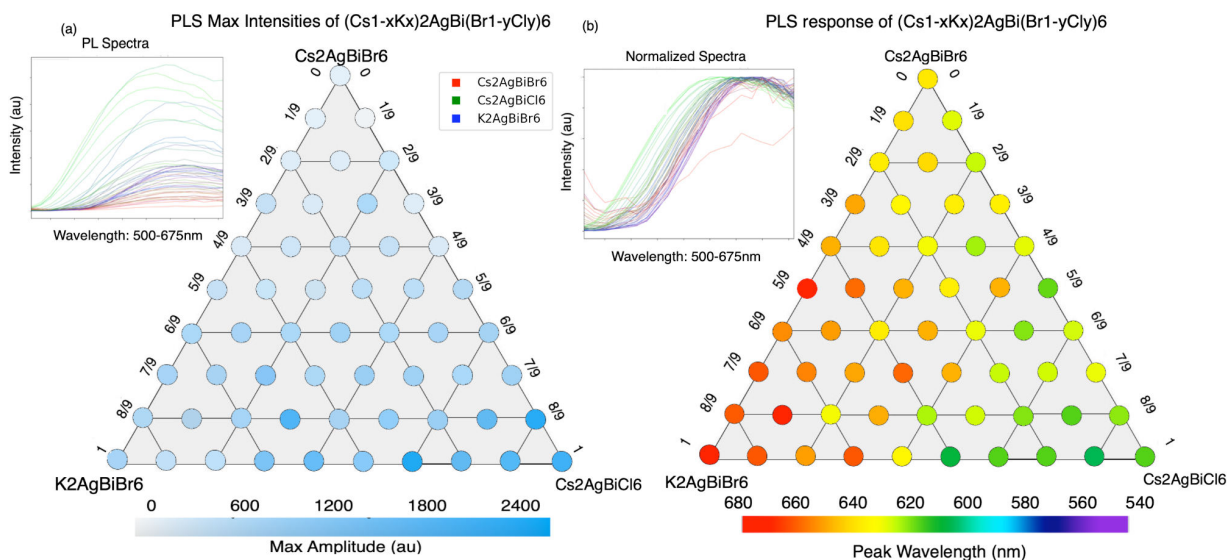

Figure 7. PLS results given by AgBi3, (A-site substitution by K; X-site substitution by Cl.) (a) PL spectra and max intensities; (b) Normalized PL spectra and peak wavelengths.

Conclusion:

This work presents an innovative, practical method for high-throughput perovskite synthesis and characterization, and it may be applied to other material types which satisfy the selection criteria. The method generates large amounts of data, which may be refined using machine-learning algorithms. It is a step towards a closed-loop experimental process, which could develop novel materials with minimal human intervention.

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