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«Московский государственный университет имени М.В. Ломоносова»**



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Moscow Autumn Perovskite Photovoltaics  
International Conference

**Сборник тезисов докладов**

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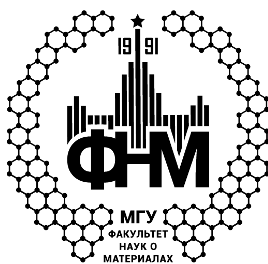
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## Прозрачные проводящие тонкие пленки диоксида титана, допированного ниобием

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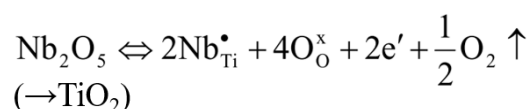
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Проводящие тонкие пленки легированного ниобием диоксида титана интересны с точки зрения их использования в качестве проводящих слоев в фотовольтаике, благодаря своей прозрачности, химической инертности и термической устойчивости.

Целью данной работы является синтез и исследование свойств тонких пленок твердого раствора  $Ti_{1-x}Nb_xO_{2+\delta}$  со структурой рутила на монокристаллических подложках  $\alpha-Al_2O_3$ . Тонкие пленки были получены методом МОСVD по реакции пирогидролиза летучих комплексов  $Ti(i-PrO)_2(thd)_2$  и  $Nb(O-iC_3H_7)_4(thd)$  при 350-500°C в потоке влажного аргона с последующей дополнительной термообработкой при более высокой температуре. Пленки охарактеризованы методами РФА, РЭМ, РСМА и зависимостями сопротивления от температуры.

По данным РСМА состав пленок  $Ti_{1-x}Nb_xO_{2+\delta}$  по всей поверхности образцов одинаков и отвечает исходному соотношению взятых прекурсоров. Сразу после осаждения слои  $TiO_2(Nb)$  обладают неизмеримо высоким электрическим сопротивлением. Это объясняется различием в стехиометрии оксидов  $TiO_2$  и  $Nb_2O_5$ , препятствующим встраиванию ниобия в структуру рутила, и малой диффузионной подвижностью высокочarged катионов. При осаждении оксид ниобия (V) в основном сегрегирует на поверхности зерен  $TiO_2$ , что подтверждается также выявленным с помощью РЭМ фактом сильного уменьшения размера зерен пленок в результате легирования.

Как следует из реакции



растворение оксида ниобия в структуре рутила и появление в их твердом растворе электронной проводимости возможно после высокотемпературной обработки образцов в атмосфере с низким  $pO_2$ . Отжиг при 1150°C (5 ч) с использованием геттера Fe/FeO, обеспечивавшем  $pO_2=10^{-20}$  атм, позволил частично восстановить ниобий до с.о. +4, что привело к растворению оксида ниобия в  $TiO_2$  и повышению проводимости пленок до  $3,7 \cdot 10^{-2}$  Ом\*см. Анализ литературы по данному вопросу показывает, что нами были получены пленки  $Ti_{1-x}Nb_xO_{2+\delta}$  с проводимостью, входящей в число наиболее высоких опубликованных значений, при этом пленки визуально сохраняют высокую прозрачность.

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## Фотовольтаический элемент на основе перовскита $\text{MAPbI}_3$ с наночастицами $\text{FAPbI}_3$ и $\text{PbI}_2$ в приповерхностном слое

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За последнее несколько лет металлоорганические полупроводники со структурой перовскита, из-за их эффективности, привлекают к себе все больше внимания. Наиболее популярным материалом является металлоорганический полупроводник метиламмоний иодида свинца ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ,  $\text{MAPbI}_3$ ) и формамидин иодида свинца ( $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ ;  $\text{FAPbI}_3$ ). Наши исследования показывают, что присутствие в активном слое солнечного элемента на основе  $\text{MAPbI}_3$  наночастиц  $\text{FAPbI}_3$  и  $\text{PbI}_2$  повышают на фотовольтаические характеристики солнечных элементов - ток короткого замыкания и фактор заполнения на 20% и 10%, соответственно.

В работе были исследованы перовскитные фотовольтаические элементы инвертированной архитектуры. Слой перовскита  $\text{MAPbI}_3$  наносили на заранее подготовленную подложку одноступенчатым методом. Исходный раствор, использованный для получения слоя  $\text{MAPbI}_3$ , был приготовлен смешиванием компонентов метиламмония иодида  $\text{CH}_3\text{NH}_3\text{I}$  ( $\text{MAI}$ ) и иодида свинца  $\text{PbI}_2$  в мольном соотношении (1:1) в безводном растворе диметилформамида [1]. Как известно, при данном соотношении  $\text{MAI/PbI}_2$  образуется полупроводник с проводимостью n-типа [2]. При нанесении дисперсии наночастицы  $\text{FAPbI}_3$  и  $\text{PbI}_2$  в толуоле поверх формирующихся микрокристаллов перовскита наночастицы концентрируются преимущественно в приповерхностной области слоя перовскита. Наночастицы создают электронные состояния, которые лежат несколько ниже, чем край зоны проводимости (или LUMO)  $\text{MAPbI}_3$ , и тем самым повышают эффективность переноса электронов на катод. Таким образом, примененный подход позволяет управлять электронными состояниями в перовските у границы с зарядо-транспортным слоем для повышения эффективности устройства.

<sup>1</sup>Работа выполнена при финансовой поддержке РФФИ (грант №19-33-90283).

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## Влияние температуры отжига на электрические и фотоэлектрические свойства тонких пленок перовскита $\text{CH}_3\text{NH}_3\text{PbI}_3$

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Известно, что присутствие фазы  $\text{PbI}_2$  в металлоорганическом перовските  $\text{CH}_3\text{NH}_3\text{PbI}_3$  может влиять на эффективность солнечных элементов, созданных на его основе [1, 2]. В то же время роль  $\text{PbI}_2$  в процессах генерации, переноса и рекомбинации носителей заряда этого двухфазного материала практически не изучена.

Нами исследовано влияние температуры отжига  $T_a$  на проводимость  $\sigma$ , ее температурную зависимость  $\sigma(T)$  и спектральную зависимость фотопроводимости  $\Delta\sigma$  пленок перовскита  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , полученного одностадийным методом из жидкой фазы.

При повышении  $T_a$  от 60 °С до 120 °С наблюдалось уменьшение  $\Delta\sigma$  в 3-4 раза, при этом вид её спектральной зависимости практически не изменялся: фотопроводимость имела плато при энергии фотонов  $h\nu > 1.6$  эВ и экспоненциально уменьшалась с энергией кванта при  $h\nu < 1.6$  эВ. Однако, в случае  $T_a \geq 140$  °С наблюдалось резкое уменьшение на два-четыре порядка величины  $\Delta\sigma$  в области энергий квантов 1.4-2.8 эВ и появление «второго края фотопроводимости» при  $h\nu \approx 2.4$  эВ. Аналогичный характер изменения наблюдался для зависимости  $\sigma(T_a)$ . Увеличение  $T_a$  от 60 °С до 120 °С приводило к монотонному уменьшению в 4 раза величины  $\sigma$  при комнатной температуре и резкому ее спаду на два порядка величины для  $T_a = 140$  °С без дальнейшего изменения при  $T_a = 160$  °С.

Полученные результаты объясняются выделением фазы  $\text{PbI}_2$  в структуре  $\text{CH}_3\text{NH}_3\text{PbI}_3$  при отжиге пленок и изменением при увеличении  $T_a$  роли  $\text{PbI}_2$  в процессах генерации, переноса и рекомбинации носителей заряда в сформированной двухфазной структуре перовскитного слоя. Показана возможность формирования двухслойной планарной структуры, состоящей из материалов с различной шириной запрещенной зоны  $\text{PbI}_2$  и  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .

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**Дырочно-транспортные слои на основе электроосажденных комплексов поли-3,4-этилендиокситиофена с полиэлектролитами различного строения для перовскитных солнечных элементов**

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В перовскитном солнечном элементе (ПСЭ) инвертированной архитектуры важную роль играет дырочный транспортный слой (ДТС), наносимый на прозрачный электрод. Установление связи между структурой полимерного ДТС и фотовольтаическими характеристиками ПСЭ в этой связи является актуальной задачей.

В работе тонкие слои (30-40 нм) поли-3,4-этилендиокситиофена (ПЭДОТ), обладающие дырочной проводимостью, были получены электроосаждением в присутствии сульфокислотных полиэлектролитов различной структуры и формы (кислота или соль). Для электросинтеза слоев ПЭДОТ были использованы гибкоцепные поликислоты: поли-2-акриламидо-2-метил-1-пропансульфоновая кислота (ПАМПСК) и полистиролсульфокислота (ПССК), и жесткоцепные поликислоты: поли-4,4'-(2,2'-дисульфокислота)-дифениленизо-фталамид (изо-ПАСК) и поли-4,4'-(2,2'-дисульфокислота)-дифенилентерефталамид (тере-ПАСК), а также их  $\text{Na}^+$ -соли. Эти полиэлектролиты имеют хорошие пленкообразующие свойства, высокую ионную проводимость и оптически прозрачны.

Полученные слои были исследованы в качестве ДТС в ПСЭ с фотоактивным слоем толщиной 400 нм из металлоорганического соединения  $\text{CH}_3\text{NH}_3\text{PbI}_3$  перовскитной структуры. ДТС наносили на слой ИТО методом электрохимической полимеризации. Метод является перспективным для изготовления устройств ПСЭ, поскольку это одностадийный процесс, обеспечивающий получение тонких слоев с контролируемой толщиной и морфологией. Последнее важно, так как определяет структуру и качество интерфейса с последующими слоями. Кроме того, электросинтез слоев ПЭДОТ в присутствии полиэлектролитов позволяет получать однородные слои с высокой адгезией к подложке. Было обнаружено, что структура полиэлектролита и природа его противоиона влияют на кинетику синтеза и структуру слоев полимерных комплексов ПЭДОТ.

Методами циклической вольтамперометрии и Кельвин-микроскопии были измерены энергетические уровни ВЗМО и работа выхода комплексов ПЭДОТ. Было показано, что уровни ВЗМО всех ДТС лежат на 0.4—0.6 эВ выше, чем край валентной зоны фотоактивного слоя  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (-5,4 эВ), поэтому дырки легко переносятся из слоя перовскита в ДТС и далее на ИТО-электрод в ГСЭ.

Установлено, что структура и форма (кислота или соль) полиэлектролита, на основе которого сформирован ДТС, влияют на вольтамперные характеристики и

эффективность созданных образцов ПСЭ. Наибольшие КПД показали ПСЭ на основе комплексов ПЭДОТ с гибкоцепными полиэлектролитами в кислой форме. При обсуждении фотовольтаических характеристик ПСЭ рассмотрены особенности формирования слоев ПЭДОТ в присутствии полиэлектролитов различной структуры с учетом их степени гидрофобности и конформации макромолекул. Результаты изучения фотовольтаических характеристик ПСЭ показали важную роль полиэлектролита в разработке полимерного ДТС для дальнейшей оптимизации работы ПСЭ.

<sup>1</sup> Работа выполнена при финансовой поддержке РФФИ (Грант №19-29-08048).

## Новые эффективные эмиттеры для органических светодиодов на основе комплексов тербия

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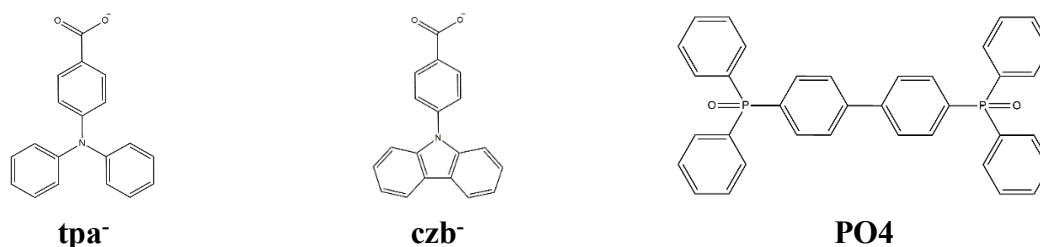
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Координационные соединения (КС) лантанидов являются перспективными материалами для эмиссионных слоёв органических светоизлучающих диодов (OLED), поскольку они обладают узкими эмиссионными полосами (до 10 нм), что позволит достичь необходимую чистоту света. В настоящее время среди различных КС лантанидов, обладающих высокими квантовыми выходами (до 100%), наиболее стабильными являются ароматические карбоксилаты, однако они обладают низкой подвижностью носителей заряда.

В нашей предыдущей работе был предложен способ увеличения электрон-транспортных свойств КС лантанидов за счёт направленного выбора сенсibiliзирующих нейтральных лигандов, обладающих высокой подвижностью электронов [1], [2]. Развитием данного подхода стало увеличение и дырочно-транспортных свойств комплексов за счёт модифицирования анионного лиганда, а именно использования ароматических карбоксилат-анионов ( $\text{tpa}^-$  и  $\text{czb}^-$ , Рис. 1) с высокой дырочной подвижностью. Наконец, объединяя два подхода, мы пришли к дизайну КС лантанидов, где анионные лиганды выбраны в качестве лигандов, повышающих дырочно-транспортные свойства, а нейтральный лиганд – электрон-транспортные.



**Рис. 1.** Лиганды, используемые в работе.

Все комплексы были успешно получены и протестированы в качестве эмиссионных слоёв (EML) в OLED с гетероструктурой ITO/PEDOT:PSS/poly-TPD/EML/TPBi/LiF/Al. Спектры электролюминесценции OLED представляют собой набор узких эмиссионных полос иона тербия. Максимальная яркость электролюминесценции 330 кд/м<sup>2</sup> при напряжении 15В была получена на основе комплекса Tb( $\text{czb}$ )<sub>3</sub>, что является одной из рекордных величин для OLED на основе комплексов лантанидов, нанесенных из раствора.

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## Цвето-температурная зависимость выходной мощности перовскитных фотопреобразователей при работе в условиях рассеянного света

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В настоящее время растет рынок датчиков телекоммуникации, потребляемая мощность которых в основном не превышает 1 мВт. Проблему беспроводного питания IoT-устройств можно решить, используя перовскитные фотопреобразователи в качестве внешнего источника питания [1]. На сегодняшний день именно перовскитные полупроводники являются наиболее перспективными материалами для высокоэффективных солнечных элементов ввиду сочетания таких электрофизических свойств таких как высокая подвижность носителей заряда, высокий коэффициент поглощения и низкие темпы безызлучательной рекомбинации [2-3]. Перовскитные солнечные элементы (ПСЭ) с p-i-n архитектурой показывают высокие значения коэффициента полезного действия (КПД) >20 % и малое значение гистерезиса вольтамперных характеристик (ВАХ) при работе как в условиях прямого солнечного освещения, так и при рассеянном свете при котором беспроводные датчики работают большую часть срока эксплуатации.

Стандартно используемым составом для прототипирования ПСЭ является  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (МАРІ) с шириной запрещенной зоны ( $E_g$ ) ~1.55 эВ [4-6]. Важным аспектом для работы фотопреобразователей при рассеянном свете является сопоставление спектров излучения стандартных осветительных систем со спектром поглощения используемого перовскитного материала.

В данной работе были изготовлены ПСЭ со стандартным составом перовскита МАРІ и мультикатионным составом перовскита  $(\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$  (CsFAMA) с активной областью  $0,14 \text{ см}^2$ . Была исследована зависимость между максимальной выходной мощностью ПСЭ и цветовой температурой светодиодных источников освещения (2700 К, 4000 К, 6500 К); изготовлены перовскитные фотопреобразователи на основе МАРІ с активной областью  $1 \text{ см}^2$ . Значения  $P_{\text{макс}}$  разработанных СЭ на основе МАРІ с активной площадью  $1 \text{ см}^2$  при освещенности 200 и 400 люкс отличаются на 10 % и 5 % от значений референсных образцов, соответственно. Таким образом, разработанный подход позволил масштабировать активную площадь ПСЭ с  $0,14 \text{ см}^2$  до  $1 \text{ см}^2$  с минимальными потерями выходной мощности. Полученные устройства на основе CsFAMA с активной областью  $0,14 \text{ см}^2$  имели значение максимальной мощности -  $15,4 \text{ мВт/см}^2$  и  $31,2 \text{ мВт/см}^2$  при яркости 200 и 400 люкс соответственно. Мониторинг напряжения холостого хода от времени подтвердил повышенную стабильность СЭ на основе CsFAMA по сравнению с СЭ на основе МАРІ. В работе представлены данные световых и темных выходных вольтамперных характеристик.



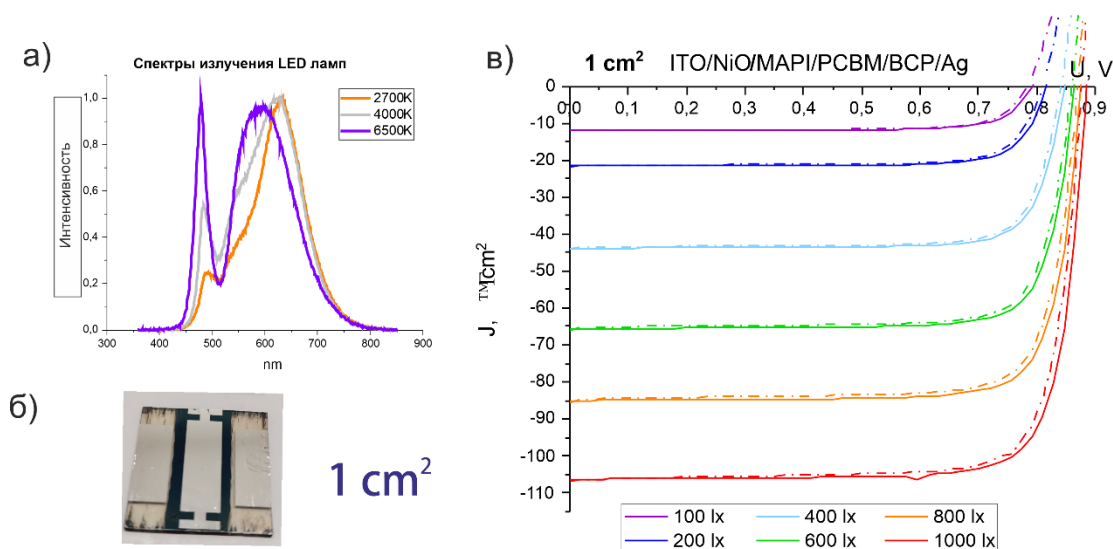


Рисунок 1 – а) Спектр излучения LED лампы с цветовой температурой 4000 К; б) Внешний вид СЭ с площадью активной области 1 см<sup>2</sup>; в) ВАХ СЭ с MAPI с активной площадью 1 см<sup>2</sup> при различных значениях интенсивности света LED лампы

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## Синтез и изучение новых 2-фосфинпиридиновых лигандов и комплексов Cu(I) на их основе для применения в OLED

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На текущий момент разрабатываются различные подходы к увеличению эффективности органических светоизлучающих диодов (OLED) за счет использования энергии триплетных экситонов. Одним из наиболее перспективных подходов является эффект термически активируемой замедленной флуоресценции (TADF). Ключевым фактором для эффективного TADF-процесса является малый энергетический зазор между энергиями HOMO и LUMO эмиттера, который может быть достигнут путем пространственного разделения этих граничных орбиталей. Различные моно- и полиядерные галогениды меди с фосфиновыми лигандами, в которых наблюдается такое разделение, уже рассматриваются в литературе как перспективные TADF люминофоры. Так, в 2014 году опубликован подход к дизайну гетеролептических биядерных иодидов меди, который заключается в замещении мостикового и варьировании вспомогательных лигандов [1], которые определяют растворимость и энергию LUMO, соответственно (Рис. 1).

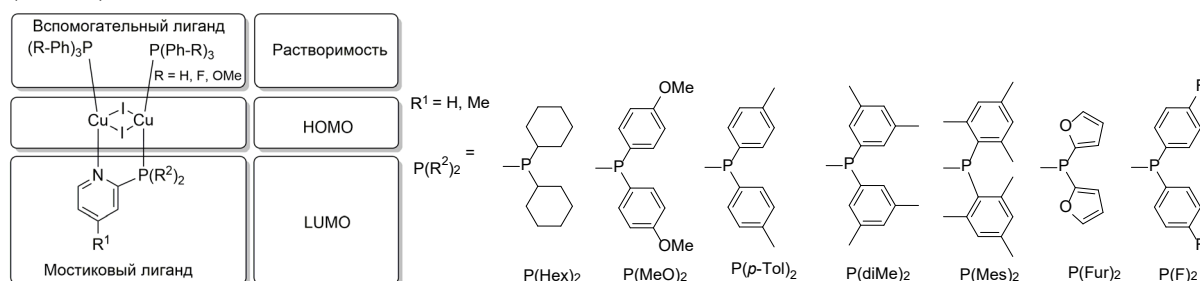


Рис. 1. Схема дизайна комплексов Cu (I) и использованные заместители.

Целью данной работы было изучение влияния замещения фосфиновой части мостикового лиганда на люминесцентные свойства комплексов Cu(I). Методами ароматического нуклеофильного замещения и замещения, катализируемого палладием, в условиях линии Шленка был синтезирован ряд мостиковых 2-фосфинпиридиновых лигандов с различными заместителями. При этом выходы реакции достигали 77%, несмотря на сильную подверженность продукта окислению. Полученные лиганды были использованы в синтезе гетеролептических йодидов Cu(I) с рядом производных трифенилфосфина в качестве вспомогательных лигандов (выход до 99%). Все полученные соединения характеризовали методами ЯМР на ядрах <sup>1</sup>H, <sup>13</sup>C и <sup>31</sup>P, ИК (НПВО) и масс-спектрометрии (FAB и EI), элементного анализа и монокристаллической рентгеновской дифракции.

Все полученные комплексы демонстрируют высокую интенсивность люминесценции в видимом диапазоне от желтого до зеленого в зависимости от

мостикового лиганда с квантовыми выходами фотолюминесценции до 92% и временем жизни до 8 микросекунд. Кроме того, все биядерные комплексы обладают значительной растворимостью в дихлорметане и диэтиловом эфире, что позволяет получать тонкие пленки этих соединений для OLED методом spin-coating.

Квантово-химические расчеты в сочетании с методами абсорбционной спектроскопии и спектроскопии выхода фотоэлектронов позволили определить энергии НОМО и LUMO. Основываясь на полученных значениях энергий граничных орбиталей, были выбраны материалы для гетероструктуры OLED. Дальнейшие эксперименты позволили оптимизировать первоначальную гетероструктуру путем варьирования матрицы матрицы и толщин электрон- и дырочно-транспортных слоёв. В результате лучшим OLED-устройством достигнута яркость электролюминесценции до 5902 Кд/м<sup>2</sup> и эффективность по току до 5 Кд/А.

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## Нелинейное оптическое поглощение тонких пленок галогенидных перовскитов при фемтосекундном возбуждении на длине волны 1064 нм

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Металлоорганические галогенидные перовскиты привлекают пристальное внимание исследователей по причине выдающихся оптических и электронных свойств этих материалов. Помимо хорошо известных свойств, к числу которых относится высокая фотогальваническая эффективность, они также показывают значительный нелинейный оптический отклик при взаимодействии с излучением высокой интенсивности и могут использоваться в качестве перспективной среды для нелинейно-оптических устройств [1,2]. В настоящей работе мы использовали метод Z-сканирования для исследования нелинейного оптического поглощения перовскитных пленок CsPbI<sub>2</sub>Br, MA<sub>0.15</sub>FA<sub>0.75</sub>Cs<sub>0.1</sub>PbI<sub>2.85</sub>Br<sub>0.15</sub> и MA<sub>0.15</sub>FA<sub>0.75</sub>Cs<sub>0.1</sub>PbI<sub>3</sub> (где MA=CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> и FA=CH(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>) при облучении фемтосекундными импульсами длительностью 400 фс на длине волны 1064 нм. Было обнаружено, что тонкие пленки перовскитов (45-65 нм) показывают большие значения коэффициента нелинейного поглощения 261-928 см/ГВт по сравнению с толстыми пленками (250-350 нм) и с меньшими значениями коэффициента нелинейного поглощения 38-55 см/ГВт. Было показано, что интенсивность насыщения нелинейного поглощения для пленок перовскитов зависит от длительности импульса накачки и увеличивается с уменьшением длительности импульса. Также было установлено, что пленки металлоорганических перовскитов демонстрируют большее значение коэффициента нелинейного поглощения по сравнению с пленкой неорганического перовскита CsPbI<sub>2</sub>Br.

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## Комплексы иттербия с 2-(тозиламино)-бензилиден-N-(2-галогенбензоил)-гидразонами для создания ИК-излучающих OLED

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Из-за попадания в окно прозрачности живых тканей и кварцевого оптоволокна, ИК-излучающие органические светодиоды становятся востребованными в медицине, в области телекоммуникаций и в обороне. В то же время в отличие от OLED, излучающих в видимом диапазоне, диоды, излучающие в ближнем инфракрасном диапазоне (700-1000 нм), находятся только на стадии разработок. Материалы на основе соединений лантанидов, в частности иттербия, которые известны своими уникальными оптическими свойствами, являются наиболее перспективными люминесцентными материалами для этих приложений: узкие полосы люминесценции с постоянным положением в спектре идеально подходят для детектирования. В то же время для создания на их основе OLED требуется повысить как квантовый выход комплексов, так и подвижность носителей заряда и растворимость. Комплексы иттербия с основаниями Шиффа на основе 2-(тозиламино)-бензилиден-N-(2-бензоил)-гидразонов уже зарекомендовали себя как эффективные материалы для эмиссионных слоев OLED [1], однако отдельной задачей является повышение растворимости таких комплексов в органических растворителях для применения растворного метода нанесения слоев. Для этого мы предложили галогенировать выбранные основания Шиффа.

Целью данной работы является исследование влияния галогенирования на растворимость комплексов иттербия с этими лигандами, а также на подвижность носителей заряда и квантовый выход люминесценции. В качестве объектов исследования были выбраны комплексы иттербия с 2-(тозиламино)-бензилиден-N-(2-галогенбензоил)-гидразонами ( $L^{Hal}$ , где Hal = F, Cl, Br, I).

В ходе работы была получена серия комплексов иттербия ( $Yb(L^{Hal})(HL^{Hal})$  и  $KYb(L^{Hal})_2$ ), которые обладают практически одинаковыми квантовыми выходами (~0.9%), энергиями граничных орбиталей (НОМО ~5,8 эВ) и энергиями триплетных уровней (~18 000  $cm^{-1}$ ). Для всех КС характерна растворимость, достаточная для растворного метода нанесения слоя (> 5 г/л в ТГФ).

Несмотря на равенство физико-химических характеристик, эффективности электролюминесценции OLED существенно зависят от введенного галогена и падают в ряду  $F > Cl > Br > I$ . Максимальную эффективность электролюминесценции в OLED – 113 мкВт/Вт – продемонстрировал  $Yb(L^F)(HL^F)$ ; это является вторым по величине результатом среди КС иттербия и первым – среди КС иттербия, нанесенных из раствора.

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## Нанесение и исследование тонких плёнок сложных фторидов NaREF<sub>4</sub> с ап-конверсионной люминесценцией

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Фториды РЗЭ отличаются высокой прозрачностью в оптическом диапазоне, химической стабильностью, а также низкой энергией фононных колебаний, что вызывает к ним большой интерес в качестве основы для оптических устройств, твердофазных лазеров и люминесцентных материалов [1]. Цель данной работы – разработка методики получения тонких плёнок сложных фторидов натрия-РЗЭ, обладающих эффективной ап-конверсионной люминесценцией (АКЛ) из растворов координационных соединений.

Тонкие плёнки фторидов были получены путём термического разложения гелей перфторированных карбоксилатов (трифторацетатов, пентафторпропионатов и гептафторбутиратов) металлов при 600 °С:



Перфторакарбоксилаты металлов были синтезированы взаимодействием карбонатов металлов с 5%-м избытком соответствующей кислоты (H(tfa), H(pfp), H(hfb)). Исследовано теомическое поведение, гидратный состав, а также продукты разложения прекурсоров по данным ТГ-ДСК-МС анализа в искусственном воздухе (N<sub>2</sub> + O<sub>2</sub>) и инертной атмосфере (Ar).

Нанесение тонких плёнок осуществлялось на подложки из c-Al<sub>2</sub>O<sub>3</sub> из четырёх растворов с различных катионных составов: Na:Y:Yb:Er:Gd = 100:78:20:2:0, 200:78:20:2:0, 100:48:20:2:30 и 200:48:20:2:30. По данным РФА и спектрам ап-конверсионной люминесценции показано, что гексагональная фаза β-NaREF<sub>4</sub> обладает более эффективной АКЛ по сравнению с кубической α-NaREF<sub>4</sub>. Использование различных составов показало, что увеличение концентрации натриевого прекурсора, как и замещение 30% иттрия на гадолиний способствуют увеличению содержания β-фазы в целевом продукте. По данным АСМ тонкие плёнки оказались поликристаллические, однородным интерфейсом, со средней шероховатостью 33 нм и толщиной порядка 100 нм, что согласовывалось с теоретически рассчитанной толщиной по уравнению Ландау-Левича.

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## **Beyond lead: halide complexes of 15 and 16 group elements, their polyhalide derivatives and their use in materials design**

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While Pb(II) halometalates are being very intensively investigated in the course of photovoltaic devices design, related derivatives of neighboring elements – bismuth, antimony and tellurium – remain significantly less considered in this area. Hereby, we present our recent achievements in synthetic chemistry of Bi(III), Sb(III) and Te(IV) halometalates and their polyhalide hybrids, as well as in their utilization in creation of solar cells and photodetectors. This project was performed in close collaboration with Prof. Pavel A. Troshin (Skoltech, Russia).

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## Nuclear Quadrupole Resonance of multinary $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_{3-y}\text{Br}_y$ perovskites

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Formamidinium (FA)-based hybrid lead iodide perovskites ( $\text{FAPbX}_3$ ,  $X = \text{I}$  or  $\text{Br/I}$ ) have recently led to significant improvements in the performance of perovskite photovoltaics. One of the remaining major hurdles is the instability of  $\alpha\text{-FAPbI}_3$ , which undergoes a phase transition from the desired three-dimensional cubic perovskite phase to a non-perovskite one-dimensional hexagonal lattice. Partial substitution of FA with Cs and, concomitantly, iodide with bromide is known to stabilize the material's cubic perovskite structure, as shown by X-ray diffraction. Nuclear quadrupole resonance (NQR) has been reported to resolve structural changes with accuracies commensurate with synchrotron X-ray diffraction and scattering.<sup>[1]</sup> We report the  $^{127}\text{I}$  NQR spectra of  $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_{3-y}\text{Br}_y$  ( $x = 0 - 0.1$ ,  $y = 0 - 3$ ) showing not only the averaged but also the local iodide structures. Upon ion replacement, massive line broadening and new species can be observed, and these new species could be assigned to various coordination environments. These findings showcase the great potential of halide NQR for characterizing perovskite-based materials.

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## Hybrid perovskite single crystals: optical properties and low-temperature features

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Metal-organic halide perovskite  $\text{CH}_3\text{NH}_3\text{PbX}_3$  ( $\text{X}=\text{I}, \text{Br}$ ), *i.e.* methylammonium-lead iodide or bromide, respectively, is currently considered as a promising material for solar cells of new generation [1]. The exceptional functionality of hybrid halide perovskites is due to their physical properties, such as high optical absorption coefficient, long charge-carrier lifetime, high carrier mobility [2]. Many of these properties are closely related to the features of the phonon spectrum and electron-phonon interaction. Conversely, in the current research, the reflection spectra in terahertz region and transmission spectra in the mid- and near-infrared (IR) regions of a  $\text{CH}_3\text{NH}_3\text{PbX}_3$  are studied for the first time for single crystals.

High quality perovskite single crystals  $\text{CH}_3\text{NH}_3\text{PbX}_3$  were grown in the Rzhanov Institute of semiconductor physics SB RAS in Novosibirsk [3]. Using terahertz reflection spectra, the TO-LO splitting was determined for the strongest IR active low-frequency mode. In the IR transmission spectra ( $2500\text{--}12000\text{ cm}^{-1}$ ), the said features were observed at the temperatures of the phase transitions: from the cubic to the tetragonal phase ( $\sim 330\text{ K}$ ) and from the tetragonal to the orthorhombic phase ( $\sim 160\text{ K}$ ) for the iodide sample. For the bromide perovskite, these features were investigated at the transition from the cubic to the tetragonal phase I ( $\sim 236\text{ K}$ ), to the tetragonal phase II ( $\sim 153\text{ K}$ ), and then to the orthorhombic phase ( $\sim 146\text{ K}$ ). Moreover, precisely recorded temperature dependence of the mode frequency during cooling and heating of the samples demonstrates hysteresis, which is also typical for a first-order phase transition. The temperature behavior of the multiphonon spectrum is consistent with the freezing of a free rotation of an organic cation in the orthorhombic phase and the transition to tunnel dynamics with a further decrease in temperature [4].

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## Layered hybrid perovskites and related lead-free single crystals obtained via novel approach and their optical properties

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Despite the significant progress achieved in increasing the stability of hybrid halide perovskite materials, their degradation under the exposure to external factors, such as moisture and oxygen, is still one of the main problems of modern perovskite photovoltaics. The other problem is the toxicity associated with the presence of lead in the vast majority of the studied materials. Both of these problems are the reason for a growing interest in two-dimensional layered perovskite-like materials, which are known for their increased stability compared to 3D perovskites, as well as lead-free perovskite-like materials.

Due to the difficulties in obtaining single crystals of layered perovskites, most studies of their optoelectronic properties have been carried out on polycrystalline thin films, whereas due to the typically lower concentration of defects studying high-quality single crystals is necessary to determine the structure and fundamental properties of the material.

In this work we demonstrate the possibility of obtaining 2D perovskite single crystals of various composition, including compounds with  $n \leq 3$ , such as  $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$  ( $n = 1-4$ ), mixed perovskites  $\text{BA}_2(\text{FA}_{0.75}\text{MA}_{0.25})_{n-1}\text{Pb}_n\text{I}_{3n+1}$  ( $n=2-3$ ), and lead-free perovskite-like iodobismuthates  $\text{A}_3\text{Bi}_2\text{I}_9$  ( $\text{A} = \text{Cs}^+, \text{NH}_4^+, \text{FA}^+$ ) by a new method of a solvent conversion induced rapid crystallization (SCIRC). Single crystals of mixed-cation layered perovskite  $\text{BA}_2(\text{MA}_{0.25}\text{FA}_{0.75})_2\text{Pb}_3\text{I}_{10}$ , as well as formamidinium iodobismuthate  $\text{FA}_3\text{Bi}_2\text{I}_9$  were obtained for the first time.

The grown crystals of layered perovskites show bright photoluminescence with narrow FWHM and sharp absorption edges, which implies a low concentration of intrinsic and surface defects, and therefore a low non-radiative recombination. One of the most intriguing results is achieving unusually high charge carriers lifetimes for the mixed-cation layered perovskite  $\text{BA}_2(\text{MA}_{0.25}\text{FA}_{0.75})_2\text{Pb}_3\text{I}_{10}$  ( $\tau_{\text{average}} = 61 \text{ ns}$ ) in comparison with the similar single-cation perovskite  $\text{BA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$  ( $\tau_{\text{average}} = 28 \text{ ns}$ ).

The high quality of obtained single crystals shows significant prospects for the synthesis of various lead and lead-free perovskite-like compounds by new SCIRC approach.

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**A<sub>2</sub>CuX<sub>3</sub> (A=Rb, K; X= Cl, Br): High stability, nontoxic copper halides with near-unity photoluminescence quantum yield blue emission**

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All-inorganic copper halides have recently gained interest in the optical materials community as viable, relatively non-toxic alternatives to luminescent lead halides. Bulk powder samples and single crystals of A<sub>2</sub>CuX<sub>3</sub> (A=Rb, K; X= Cl, Br) were prepared using high temperature solid-state and solution techniques. The all-inorganic alkali-copper halides have been investigated through an in-depth optical characterization, including diffuse reflectance, photoluminescence, and radioluminescence. A<sub>2</sub>CuX<sub>3</sub> are found to exhibit narrow blue photoluminescence with record high efficiencies as evidenced by the measured photoluminescent quantum yields up to unity (100 %). Through variation in the A<sup>+</sup> cation site, stability of the material can be dramatically increased, while retaining similar optical performance. The bright emission in this family has been attributed to self-trapped excitons localized on [CuX<sub>3</sub>]<sup>2-</sup> anionic substructure based on exhaustive photoluminescence studies supported by the density functional theory (DFT) calculations. Our combined experimental and computational study suggests strong potential of A<sub>2</sub>CuX<sub>3</sub> as phosphors for radiation detection and solid-state lighting applications.

## Alternating Thiophene-Benzothiadiazole Oligomer as Electron Transport Material for Inverted Perovskite Solar Cells

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Perovskite solar cells (PSCs) represent one of the most promising emerging technologies for conversion of solar energy to electricity, which has attracted a massive attention during the last years, in particular due to their high efficiency of >25%.<sup>1</sup> Although PSCs have a good commercial potential i.e. due to low cost of raw materials and ease of the device fabrication, low operational stability is severely impeding their practical application.

Among different device architectures of PSCs, the p-i-n configuration with the fullerene-based top electron transport layer (ETL) is one of the most intensively studied. The fullerene derivative [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) has been widely used as ETL material because of its high electron mobility and good solubility in non-polar solvents. Although PC<sub>61</sub>BM delivers high efficiencies in p-i-n PSCs, this material has such drawbacks as high cost and poor stability under environmental conditions as well as upon exposure to light or heat.<sup>2,3</sup> Therefore, new ETL materials with optimal electronic and physicochemical properties need to be developed for achieving efficient and stable p-i-n PSCs.

In this work, we investigated alternating oligomeric compound TBTBT (“T” - thiophene, “B” - benzothiadiazole) as electron transport material for p-i-n PSCs. The fabricated devices demonstrated good performance delivering the power conversion efficiency (PCE) of 10.5% in preliminary experiments. The device performance was largely improved by inserting a thin PC<sub>61</sub>BM interlayer between the perovskite absorber layer and TBTBT-based ETL. Such modification resulted in spectacular improvement in the device fill factor (FF) from 52% to 82%, which also boosted PCE from 10.5% to 17.8%. Most importantly, using TBTBT as ETL material improved operational stability of perovskite solar cells under continuous light illumination as compared to the reference devices assembled with the conventional PC<sub>61</sub>BM-based ETL.

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## **Robust Encapsulation of Perovskite solar cells to Sustain Ambient Stress**

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Perovskite solar cells (PSCs) have emerged as potential disruptive photovoltaic (PV) technology in recent years. Considering the immense potential and power conversion efficiencies as high as 25.5% make them a favorable candidate for commercialization. However, their limited ambient stability halts their advancement towards operation deployment. Herein, we present an easy and scalable encapsulation method for PSCs using a commercially available epoxy resin OrmoComp. This is an ultraviolet radiation and thermally curable epoxy which gives a glass like finish and is found to be a robust material for solar cell encapsulation. The moisture and oxygen ingress are effectively suppressed via this technique to make PSCs lasting over several hundred hours under 100 mW/cm<sup>2</sup> light intensity. Further area sealing is found to enhance the solar cell lifespan significantly.

## New universal approach of 3D and 2D hybrid perovskites single crystals growth via in-situ solvent conversion

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The growth of high-quality single crystal is a key step both for measuring of the physical properties of materials and for fabrication of photovoltaic and optoelectronic single-crystalline devices. Although many different solution approaches of hybrid halide perovskite (HHPs) single crystal growth are known up to date there no universal and facile approach for high-quality single crystals HHPs with different composition and dimensionality.

In this research, we propose for the first time an utterly new effective single crystal growth strategy applicable for 3D and 2D HHPs of different compositions: solvent conversion induced rapid crystallization (SCIRC).

As a proof-of-concept of universality of the proposed strategy we successfully grew high-quality single crystals of both 3D hybrid perovskites  $\text{APbX}_3$  ( $\text{A} = \text{MA}^+$ ,  $\text{FA}^+$ ;  $\text{X} = \text{Br}$ ,  $\text{I}$ ) with pure and mixed  $(\text{FA}_x\text{MA}_{1-x})\text{Pb}(\text{Br}_y\text{I}_{1-y})_3$  compositions, typical layered 2D perovskites  $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$  ( $n = 1, 2, 3, 4$ ) [1], and even Bi-based layered perovskite-like counterparts  $(\text{NH}_4)_3\text{Bi}_2\text{I}_9$ ,  $\text{Cs}_3\text{Bi}_2\text{I}_9$ ,  $\text{MA}_3\text{Bi}_2\text{I}_9$  and  $\text{FA}_3\text{Bi}_2\text{I}_9$ .

The SCIRC process is fundamentally different from all the existing crystallization approaches for its unique chemical nature of saturation generation ensured by gradual chemical conversion of the initial mixture of good solvents into a non-solvent. As a representative example, we propose a simple solvent system based on a pair of two green and widely available solvents: cyclic carbonate ( $\text{S}_1$ ) and water ( $\text{S}_2$ ), irreversibly reacting with each other in the acidic media (for example, with catalytic HI additive). The initial solvent mixture exhibits high solubility of the most hybrid complex metal halides, whereas the final products of the reaction, glycols, poorly dissolve the HHPs [2]. We named such solution systems as “fugitive”, due to their ability “to escape” (from lat. *fugere*) from the initial state, losing their dissolving nature. This allows to grow easily single crystals within a few hours by simply keeping the solution at constant temperature without any heating / cooling or low-pressure evaporation steps or slow diffusion of antisolvent vapors.

All 3D perovskite single crystals grown by SCIRC approach demonstrate excellent optoelectronic properties such as sharp absorption edge, narrow linewidth photoluminescence and long charge carrier lifetimes. The obtained single crystals of the different 2D HHPs are distinguished by narrow FWHM of photoluminescence peaks approaching FWHM for reported “molecularly thin” 2D HHPs single crystals [3].

The object of particular interest is the 2D perovskite  $\text{BA}_2(\text{MA}_{0.25}\text{FA}_{0.75})_2\text{Pb}_3\text{I}_{10}$  synthesized for the first time, which demonstrates a uniquely high charge carrier lifetime (slow component up to 368 ns), which by an order exceeds the typical reported values for related layered 2D perovskite single crystals.

The most important technological advantages of the SCIRC approach is the minimization of time costs and the number of operations. In contract to existing approaches for

single crystal growth, SCIRC has no specific technical requirements other than maintaining the solution at moderate temperature. Moreover, it is free of toxic, highly corrosive solvents and poses the high yield, reaching 90%.

We believe that a conceivable rich variety of fugitive systems for crystallization represents a virginly novel field of chemistry, the study of which is of significant fundamental interest and may conceal unexpected discoveries behind its unusual properties.

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## Investigating a new 0D hybrid organic indium bromide halide with efficient sky - blue emission

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Currently, zero – dimensional (0D) hybrid organic – inorganic metal halides are receiving increasing attention because of their outstanding photophysical properties, customizable light emission properties, and high photoluminescence quantum yields (PLQY). However, despite their excellent photophysical properties, there are concerns over the innate toxicity of constituent metals (e.g., the presence of toxic lead in lead halide perovskites) and poor stability in air under continuous irradiation and heating. Here, we report a new, lead-free hybrid organic inorganic compound (C<sub>18</sub>H<sub>22</sub>N)InBr<sub>4</sub>. Hybrid organic-inorganic indium(III) halides are underexplored in literature with only a few known examples. In this work, a luminescent organic cation C<sub>18</sub>H<sub>22</sub>N<sup>+</sup> was chosen to design a highly luminescent hybrid that demonstrates improved stability as compared to the individual organic component. This novel compound has a sky-blue emission with PLQY value of 16.36%, which is a two-fold increase compared to the precursor organic salt. Further, we find that the hybrid compound demonstrates improved air, moisture, and photostability as compared to the precursor salts. Preparation of nontoxic, rare-earth free luminescent metal halides with improved stability could be key for the practical implementation of this materials class in optical applications.



## New iodine bismuthates of phenylendiammonium and its derivatives: synthesis, structure and properties

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The development of photovoltaics based on perovskite prompted researchers to search for new halide complexes of mainly metals of fourth and fifth groups, including bismuth(III). Such interest is caused by the need to search lead-free perovskite-like materials. One of the most significant problems is to find lead-free halide semiconductors demonstrated high photovoltaic efficiency and also high stability, so it is known that complex halides of bismuth is more sustainable than lead ones. In addition, halide bismuthates are interesting as objects of fundamental research because of their structural diversity.

Our work is based on synthesis of new halide complexes of bismuth(III), formed during to interaction of bismuth(III) iodide with phenylendiammonium derivatives in presence of hydroiodide acid and research of crystal structure and properties of new compounds.  $[\text{C}_6\text{H}_4(\text{NH}_3)_2][\text{BiI}_4]_2(\text{I}_2)$  was formed when we use significant excess of iodine in reaction between phenylendiamine and  $\text{BiI}_3$  in ratio of 1 to 2 in concentrated HI solution. The crystal structure of new complex consist of anionic chains  $[\text{BiI}_4]_\infty^-$ , connected by bridging  $\text{I}_2$  molecules through weak  $\text{I} \dots \text{I}$  interactions.<sup>[1]</sup> The cations and  $\text{I}_2$  molecules alternate along the axis forming a supramolecular arrangement running parallel to the  $[\text{BiI}_4]_\infty^-$  chains. Presence of acetone in the stock solution leads to cation conversion and crystallization of new complex -  $[\text{C}_6\text{H}_4(\text{CNH}(\text{CH}_3)_2)_2][\text{BiI}_4]_2$ , composed of the same anionic chains which are connected to pseudo-three-dimensional structure only by hydrogen bonds.

The new complex with discrete tetra-core anions -  $[\text{C}_6\text{H}_4(\text{NH}_3)_2]_2[\text{Bi}_4\text{I}_{18}]^{4-}$  was obtained in presence of copper(I) iodide. In the course of syntheses, p-phenylenediamine iodides and polyiodides were obtained, isolated and studied as by-products. In addition, we have developed a method for the synthesis of compounds such as  $[\text{C}_6\text{H}_4(\text{NH}_3)_2]\text{I}_2$  and  $[\text{C}_6\text{H}_4(\text{NH}_3)_2](\text{I}_3)_2 \cdot \text{H}_2\text{O}$ . According to our assumptions, that compounds can be used as starting compound in out syntheses.

Complexes with  $[\text{BiI}_4]$  chains were also obtained in the same conditions when we changed cation to N,N-dimethylphenylendiammonium. Chloride was used as a cation  $[\text{C}_6\text{H}_4(\text{NH}_3)(\text{NH}(\text{CH}_3)_2)]^{2+}$  source, so it became possible to substitute some of iodine atoms in structure of formed compounds to chlorine atoms. This led to the production of a new series of compounds -  $[\text{C}_6\text{H}_4(\text{NH}_3)(\text{NH}(\text{CH}_3)_2)]_n[\text{BiI}_{6-n}\text{Cl}_n]\text{Cl}$ . The structure researching of the complexes showed that the substituted iodine atoms occupy the same positions. In addition, due to the use of N, N-dimethyl-p-phenylenediammonium chloride, we were able to investigate a new hybrid complex -  $[\{\text{C}_6\text{H}_4(\text{NH}_3)(\text{NH}(\text{CH}_3)_2)_2\text{Cl}\}][\text{BiI}_6]$ .  $[\text{BiI}_6]$  anions are linked together in a chains by weak  $\text{I} \dots \text{I}$  interactions, in cation part  $\text{Cl}^-$  are connected with  $\{\text{C}_6\text{H}_4(\text{NH}_3)(\text{NH}(\text{CH}_3)_2)\}^{2+}$  by hydrogen bonds to form two-dimensional structure.

A number of compounds with interesting structure such as  $[\text{C}_6\text{H}_4(\text{NH}_3)(\text{NHMe}_2)]_3[\text{BiI}_6](\text{I}_3) \cdot 1.5\text{H}_2\text{O}$ ,  $[\text{C}_6\text{H}_4(\text{NH}_3)(\text{NHMe}_2)](\text{I}_3)\text{I}$  were formed by varying synthesis conditions.

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## Dynamical 2D/3D Interfaces a boost to Perovskite Solar Cell Stability: what's behind?

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Engineering two-/three- dimensional (2D/3D) perovskite solar cells is nowadays a popular strategy for efficient and stable perovskite solar cells<sup>1-3</sup>.

However, the exact function of the 2D/3D interface in controlling the long-term device behavior and the interface physics therein are still obscure.

Here I will discuss the 2D functions which can simultaneously act as surface passivant, electron blocking layer, a sheath to physically protect the 3D underneath, but also impact on the ion movement and charge accumulation. We found a peculiar dynamical structural mutation happening at the 2D/3D interface: the small cations in the 3D cage move towards the 2D layer, which acts as an ion scavenger. If structurally stable, the 2D physically blocks the ion movement at the interface boosting the device stability. Otherwise, the 2D embeds them, dynamically self-transforming into a quasi-2D structure.<sup>2</sup>

In concomitance, we discovered that the stable 2D perovskite can block ion movement, improving the interface stability on a slow time scale.<sup>2,4</sup>

The judicious choice of the 2D constituents is decisive to control the 2D/3D kinetics and improve the device lifetime, but also can impact on the interface energetics, which can vary and influence the interface processes and ultimately device open circuit voltage. This knowledge turns fundamental for device design, opening a new avenue for perovskite interface optimization.

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## Measure is treasure: proper iodine vapor treatment as a new method of morphology improvement of lead-halide perovskite films

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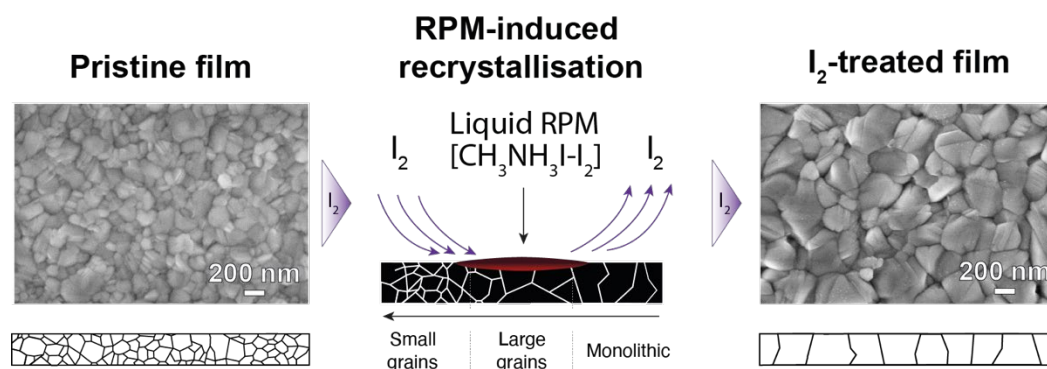
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Halide perovskites  $AMX_3$  ( $A=CH_3NH_3^+$ ,  $(NH_2)_2CH^+$ ,  $Cs^+$ ,  $Rb^+$ ;  $M=Sn, Pb$ ,  $X=Cl, Br, I$ ) emerged as a new class of materials for optoelectronic applications in the last 12 years which triggered extensive investigations on their chemical and physical properties. Considering the pronounced effect that molecular oxygen exerts on physical properties of various oxide materials, it was to be expected that researchers would take an interest in deciphering the effect of molecular halogens ( $Cl_2$ ,  $Br_2$ ,  $I_2$ ) on halide perovskites.

Several reports have shown that exposure of halide perovskites to molecular iodine can induce chemical transformations and tune physical properties of these materials. The experimental data available in the literature may be divided into three categories according to the partial pressure of iodine at a given temperature. At low iodine partial pressures ( $<10^{-2}$  mbar, RT - room temperature) iodine only affects defect concentration thus altering conductivity and luminescent properties. On the other hand, severe decomposition occurs under oversaturated iodine vapor pressure ( $\sim 10$  mbar, RT). However, the effect of exposure to molecular iodine under intermediate iodine pressure ( $\sim 10^{-1}$  mbar at RT) has not been reported so far.

In the present study [3] we show that there exist a range of conditions between these two extremes in which halide perovskites chemically absorb molecular iodine to form RPM. Once being formed, highly reactive RPM acts as a liquid medium, activates mass transport and facilitates the recrystallization of perovskite grains.



Furthermore, under proper conditions chemical sorption appears to be reversible and, once the excess of iodine is liberated from the system, the target perovskite structure is recovered with no signs of  $PbI_2$  or other decomposition products. By means of in-situ Raman spectroscopy we confirmed the formation of RPM during iodine-treatment of halide perovskites. Using scanning electron microscopy, x-ray diffraction, time-resolved photoluminescence spectroscopy we showed that iodine-treatment is beneficial for the overall quality

of perovskite thin films that were fabricated by means of classical solution-based approaches and result in increase of the average grain size, crystallinity, lifetime of charge carriers. A fine control of the iodine partial pressure, temperatures of the substrate and exposure duration allows to apply this method successfully to mixed-cation and mixed-anion perovskites relevant for photovoltaic applications thus proving the versatility of the iodine treatment approach.

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## Optical modelling of non-fullerene organic solar cell with integrated Si nanoparticles

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Continuous efforts in the field of Organic Photovoltaics (OPV) are being made to approach the efficiency minimum at which this technology becomes economically viable [1]. Achieving more than 17% efficiency for single junction organic solar cells (OSC) made it more attractive to the industrial companies [2] offering such advantageous properties as flexibility, lightweight, different colours and semitransparency. Comparing to fullerene-based acceptors, non-fullerene counterparts allowed to overcome such obstacles for OPV as limited absorption performance, nonadjustable molecular energy levels as well as strong aggregation in the photoactive layer under illumination. However, non-fullerene acceptors (NFA) based solar cells can be improved by increasing of short-circuit current density and this is the main goal of this work. It is worth noting, perovskite materials made a photovoltaic revolution in 2009 [3]. As it was shown recently, perovskite solar cells performance can be enhanced by resonance silicon nanoparticles (Si NPs) [4]. In contempt of the perovskite solar cell outstanding properties, their commercialization is complicated regarding to instability and toxicity [5]. In this way, non-fullerene based OSCs are very attractive and their characteristics might be improved by matching an energy band gap to Mie resonances of Si NPs placed in the structure either inside of the photoactive layer or on the interfaces.

The current work focuses on the numerical modeling of the Si NPs optical properties placed inside photoactive layer of OSC. Therefore, a CST Microwave Studio software was used to evaluate transmittance, reflectance, and absorption of OCS sample. The preliminary numerical analysis, which provides Si NPs optimal concentration, size, and space distribution, leads to increasing active layer absorbance of 9.4%. Apparently, the effect of this significant improvement is based on the light trapping and scattering by Si NPs in the organic photoactive layer. Moreover, the thickness of this layer is one of the most important parameters that influences on the total efficiency of the organic solar cell and also requires optimization [6]. It is crucial to find the balance between absorber layer thickness and NPs size, since the short-circuit current density grows with size increasing while after a certain threshold the further thickening of the active layer causes to fill factor reduction.

According to the preliminary computational model results OCS samples were fabricated and showed a growth of the short-circuit current density by 4.4% with simultaneous improvement of the power conversion efficiency by 25% and fill factor up to 10% in comparison with the reference values. Although the present work was devoted to the OSC performance enhancement by Si NPs integration further optimization need to be done.

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# Are Shockley-Read-Hall and ABC models valid for lead halide perovskites?

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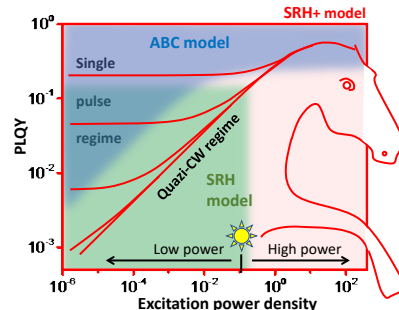
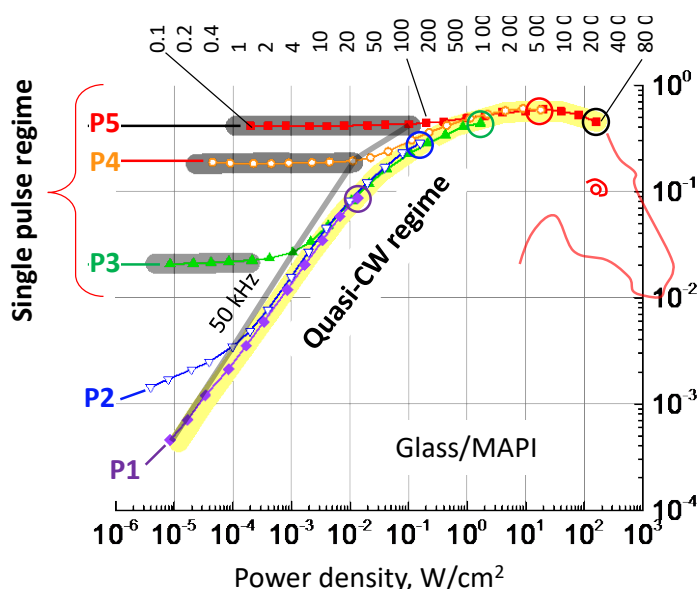
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Metal halide perovskites are an important class of emerging semiconductors. Their charge dynamics is poorly understood due to limited knowledge of defect physics and charge recombination mechanisms. Nevertheless, classical ABC and Shockley-Read-Hall (SRH) models are ubiquitously applied to perovskites without considering their validity. Despite the very large number of published studies describing electronic processes in MHPs using the terminology of classical semiconductor physics to the best of our knowledge, there have been only very few attempts to fit both PL decay and PLQY dependencies of excitation power using ABC/SRH-based models.[1–4] These attempts, however, were of limited success because large discrepancies between the experimental results and the theoretical fits were often permitted.

We decided to examine the validity of the commonly employed ABC and SRH kinetic



PLQY( $f, P$ ) is obtained by scanning rep. rate  $f$  at fixed pulse energy  $P$ .

PLQY( $f, P$ ) map reminds a horse with mane fluttering in the wind.

«Neck» - quasi-CW regime

«Mane» – single pulse regime

models in describing the charge dynamics of metal halide perovskite MAPbI<sub>3</sub> semiconductor. For this purpose, we developed a novel experimental methodology based on PL measurements (PLQY and time resolved decays) performed in the two-dimensional space of the excitation energy and the repetition frequency of the laser pulses (see the figure). The measured PLQY maps allow for an unmistakable distinction between samples and more importantly, between the single-pulse and quasi-continuous excitation regimes.[5]



We found that neither ABC nor SRH model can explain the complete PLQY maps for MAPbI<sub>3</sub> samples and predict the PL decays at the same time. Each model is valid only in a limited range of parameters, which may strongly vary between different samples. On the other hand, we show that the extension of the SRH model by the addition of Auger recombination and Auger trapping (SRH+ model) results in an excellent fit of the complete PLQY maps for all the studied samples. Nevertheless, even this extended model tends to systematically underestimate the PL decay rates at high pulse fluences pointing towards the existence of additional non-linear recombination processes in MAPbI<sub>3</sub>.

Our study[5] clearly shows that neither PL decay nor PLQY data alone are sufficient to elucidate the photophysical processes in perovskite semiconductors. Instead, a combined PLQY mapping and time-resolved PL decays should be used to elucidate the excitation dynamics and energy loss mechanisms in luminescent semiconductors.

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## Light effects on mixed halide perovskite: ion transport and demixing

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Hybrid lead halide perovskites have made great progress in the field of photovoltaics and are attracting attention as fast-advanced optoelectronic materials as well as due to interesting scientific aspects. A massive amount of work has been reported to understand anomalous observations such as low-frequency and long-time behaviors. Among them, one of the critical fundamental questions to be identified is the ionic conduction in lead halide perovskite under equilibrium and light conditions. For this talk, I will describe the light effects on ionic transport in mixed halide perovskite by introducing solid-state ionics techniques and provide an understanding of the fundamental aspects. The state-of-art perovskite solar cells have been achieved significant efficiency and stability improvement based on mixed cations and anions [1,2]. Even though such mixtures are widely used, ionic transport properties in the dark, as well as under light have not been well understood. Previously, we reported the surprising finding that light enhances both electronic and ionic conductivities of MAPbI<sub>3</sub> [3]. The mechanism of this light-enhanced ionic conductivity is based on photo-generated holes self-trapped by the iodide sub-lattice followed by formation of iodine vacancies by pushing neutral iodine into the nearby interstitial site. In this work, the results for the anionic and cationic mixtures are provided and compared with MAPbI<sub>3</sub>. Most interesting in this respect are mixtures of iodides and bromides. Unlike the iodide perovskites, the bromide perovskite does not show a significant light effect as far as the ionic conductivity is concerned. It is also shown that these results give an explanation about the photo-demixing phenomenon [4].

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## Recent Progress in Fully Ambient Air Processed Perovskite Solar Cells for Future Commercialization

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Among all next-generation photovoltaic technology, perovskite solar cells (PSCs) are the most promising modules due to their easy fabrication process and rapid enhancement of power conversion efficiency (PCE). After volatile development within a decade, the PCE of PSCs has been increased from 3.8% to 25.2% with 10000 h stability. Still, this device faces several critical changes like low long-term stability against temperature and water, leadtoxicity, and photocurrent-voltage (J-V) hysteresis. These critical issues should be minimized for commercialization. The preparation of large-area PSCs under full ambient air with high efficiency and superior stability are basic steps for commercialization.

The various defects (surface and grain boundaries defects) identified in PSCs are responsible for low stability towards humidity and temperature. Moreover, grain boundaries in the perovskite film may act as recombination centres that accelerate the degradation of PSCs. Growth of high-quality single crystal (SC) perovskite films are a great strategy for the fabrication of defect-free perovskite solar cells (PSCs). Furthermore, various layered double hydroxides (LDHs) and mixed metal oxides (MMOs) composites are being used for better crystallization and fabrication under ambient condition.

In this mini-review, we summarized the recent progress in full ambient air processed perovskite solar cells and their interface modifications towards commercialization using MMOs, LDHs and SCs. The small quantity of MMO nanoparticles and composites boost the nucleation of homogeneous perovskite and improve the perovskite film quality and orientation of crystallites. Additionally they improve charge separation at electron transport layer (ETL) by drifting the electron and thus reduce carrier recombination. The LDHs improves coalescence and renders reduction in defect sites and as a result improves the smoothness of perovskite film. In case of single crystals of perovskite, unlike the polycrystalline counterpart, the grain boundaries are absent. Therefore, the thermal stability increases. Conclusively these various approaches enable the fabrication of PSCs in ambient conditions and pave a way towards their commercialization.

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## Additive approach to enhance intrinsic photochemical and thermal stability of MAPbI<sub>3</sub> thin films

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The certified efficiencies of perovskite solar cells (PSCs) have reached >25% since the first report on PSCs [1,2]. This improvement in efficiency makes PSCs comparable to the current mainstream photovoltaic technology based on crystalline silicon. Such advantages as simple and low-cost manufacturing technology used to fabricate PSCs makes them highly promising for commercial application. Unfortunately, in presence of moisture, air, elevated temperature and light, perovskite absorber materials tend to degrade. In practical terms, for the operation of solar cells, some of these conditions (e.g. light and heat) are unavoidable [3]. To overcome these stability challenges, different approaches have been suggested. One of them is to perform passivation of defects localized at grain boundaries of perovskite absorber layer. This can be done by using compounds with different chelating functional groups such as carboxyl, amine, thiol or carboxylic, which can further bind with uncoordinated lead or iodine ions [4,5]. To achieve such passivation effect, some additives can be introduced in the absorber material.

Following this concept, herein, we explored the impact of a series of additives [6] on the photochemical and thermal stability of MAPbI<sub>3</sub> thin films. In particular, we utilized natural or nature-inspired biomolecules such as acetylcysteine (**X1**), lactose (**X2**), mercaptosuccinic acid (**X3**) and lipoic acid (**X4**). Our study has revealed that **X1** and **X2** additives enhance the intrinsic photochemical and thermal stability of the absorber layer for over 1000 h under the continuous light soaking (70-80 mW cm<sup>-2</sup>) at 50-60 C. Furthermore, the perovskite solar cells incorporating the stabilizing additives showed decent power conversion efficiencies of 12-13%.

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## Database of 2D hybrid perovskite materials: open-access collection of crystal structures, composition-structure-property relationships and univocal quantitative descriptor for classification of structures

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The family of organic-inorganic layered structures derived from the perovskite structural type, often referred as “2D hybrid perovskites”, exhibits unprecedented structural flexibility which opens prospects for the design of various innovative materials for photovoltaics and optoelectronics.

Prediction of materials properties based on their crystal structure has come to be a useful approach for the directed rational design of the materials. Factual datasets, especially crystallographic databases, are an important tool for structural design since they deliver primary information needed for further analysis.

We describe the first open-access database of experimentally investigated hybrid organic-inorganic materials with two-dimensional (2D) perovskite-like crystal structure (<http://pdb.nmse-lab.ru>). The database contains a geometrical and crystal chemical analysis of more than 500 structures, which are useful to reveal quantitative structure-property relationships for this class of compounds. We show that the penetration depth of a spacer organic cation into the inorganic layer and M-X-M bond angles increase with the number of inorganic layers (n). The machine learning model is developed and trained on the database, for the prediction of a band gap with accuracy within 0.1 eV. Another machine learning model is trained for the prediction of atomic partial charges with accuracy within 0.01 e. We show that the predicted values of band gaps decrease with an increase of n and with an increase of M-X-M angles for single-layered perovskites. [1]

Despite the unique structural diversity of LHHPs, traditional approaches of describing their structures, such as dividing into Dion-Jacobson (DJ) or Ruddlesden–Popper (RP) phases for most structures are ambiguous and unquantifiable. We proposed a new, universal and quantitative layer shift factor (LSF) for a quantitative comparison and univocal classification of LHHPs and developed a simple Python algorithm for its calculation. We show that the LSF parameter correlates well with the penetration depth of organic cations into inorganic layers, affecting therefore the distortion of inorganic framework and the band gap values. Thus, the calculated band gap of the model A<sub>2</sub>PbBr<sub>4</sub> single-layered perovskites increased by ~1 eV with an increase of the LSF from (0, 0) to (½, ½) (Fig. 1). Therefore, the suggested Layer Shift Factor can be considered as a key parameter for rational crystal chemical analysis revealing composition-structure-property correlations for these materials. [2]

In general, the proposed database, machine learning models and Layer Shift Factor are shown to be useful tools for the rational design of new 2D hybrid perovskite materials.

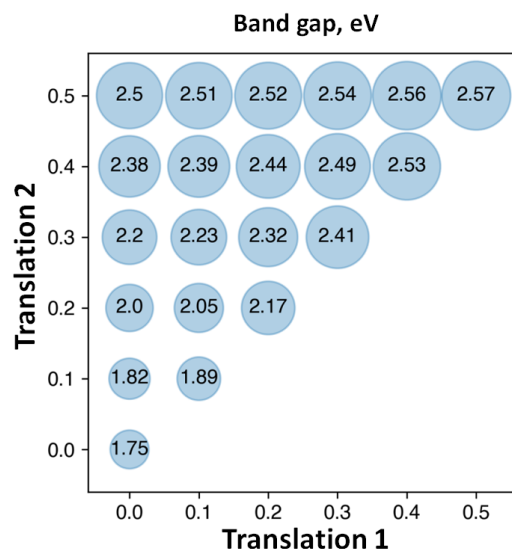


Figure 1. Calculated band gaps for the series of hypothetical  $A_2PbBr_4$  single-layered perovskites with the interlayer distance of 3.5 Å as a function of the LSF ( $T_1$ ,  $T_2$ ).

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## Voronoi-Dirichlet cation polyhedra analysis for doping of hybrid perovskites: effective charges and radii

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Organic-inorganic hybrid perovskite of the composition  $ABX_3$  has recently attracted strong research interest because of its photovoltaic properties. The different components of the perovskite solar cells and using mixtures of ions in the A, B, and X positions affect their optoelectronic properties and conversion efficiency. However, today there is no clear generalized understanding of the crystal chemistry of substitutional defects in hybrid perovskites. Here we use a crystal chemical approach based on the analysis of Voronoi-Dirichlet polyhedra (VDP) of ions to identify the most preferable positions of impurity ions in the structure of a tetragonal  $MAPbI_3$ .

Atomic Voronoi-Dirichlet polyhedron (VDP) is a convex polyhedron whose faces are perpendicular to segments connecting the central atom of VDP and other (surrounding) atoms (Fig. 1) and a dual to coordination polyhedron in the general case. VDP of all atoms form normal (face-to-face) Voronoi-Dirichlet partition of crystal space and can often characterize not only relative, but also absolute atomic size in the crystal structure. [1]

In this work, based on Voronoi-Dirichlet approach we compared the effective radii of the most common impurity cations in  $MAPbI_3$  such as  $K^+$ ,  $Na^+$ ,  $Ag^+$ ,  $Au^+$ ,  $Rb^+$ ,  $Hg^{2+}$ ,  $Ge^{2+}$  etc. with their iodine-formed coordination polyhedra in different crystal structures and crystallographic positions of ions in  $MAPbI_3$ . We also calculated the effective radii of iodine in the structures of methylammonium polyiodides [2].

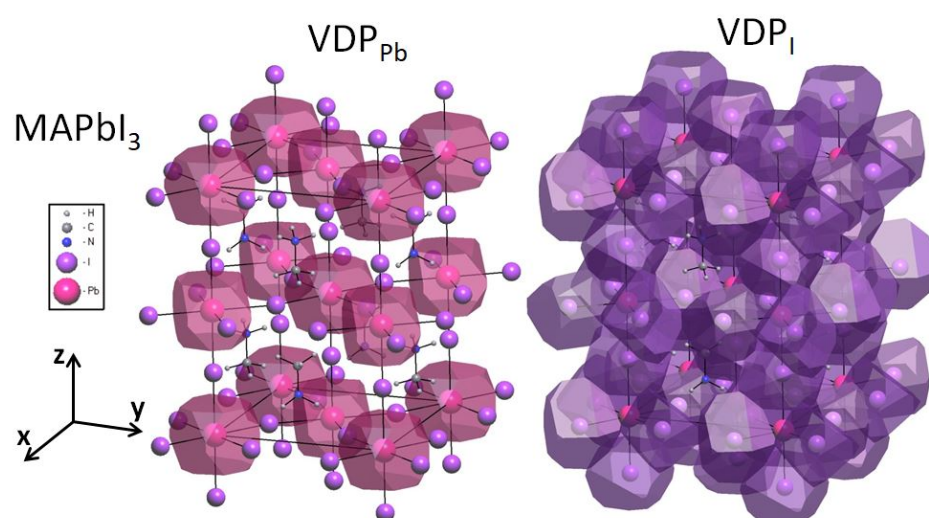


Figure 1. Voronoi-Dirichlet polyhedra of lead and iodine ions in tetragonal  $MAPbI_3$  structure.

Thus, the crystal chemical study of the substitutional doping positions with the estimation of the effective charges and radii in the methylammonium lead iodide structure is reported herein. Our results provide a theoretical guidance for improving current multication engineering strategies.

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## A Step to Optimal Perovskite Solar Cell with back reflector

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By now it has been shown analytically and numerically [1,2] that the open circuit voltage ( $V_{oc}$ ) of solar cell (SC) increases with the decrease of its thickness. Unfortunately thinner SC absorbs less photons and hence has smaller short circuit current ( $I_{sc}$ ) and power conversion efficiency (PCE). It is straightforward to increase absorption in thin SC with some light trapping technique. Recently the optimal thickness of perovskite in  $\text{TiO}_2\text{-CH}_3\text{NH}_3\text{PbI}_3$ -Spiro-OMeTAD SC with Lambertian back surface reflector (LBSR) was found numerically [2]. In the present work, using the same technique we try to estimate the influence of hole transport material (HTM) type on optimal absorber thickness.

The simulation is done in three steps. At first, to analyze the Lambertian reflection on BSR and multiple reflections inside the SC, we use ray tracing simulations with the aid of the ray trace OTSun python package [3]. The OTSun considers Fresnel equations and light polarization to determine the trajectory and the energy of each ray in a solar optical system. Then we use else-where measured local light absorption coefficient to calculate electron-hole generation rate inside all SC layers. Finally, electron and hole transport equations are numerically solved [2] to find solar cell's  $V_{oc}$ ,  $I_{sc}$ ,  $FF$  and PCE.

Simulations show heavy influence of HTM semiconductor type on the value of the optimal absorber thickness. Maximum PCE and optimal  $V_{oc}$ ,  $I_{sc}$ ,  $FF$  are also affected but to a smaller extent. The reasons of this behavior and possible ways of further SC optimization are also discussed.

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## Optimization of active layer thickness in wide-bandgap perovskite optoelectronic devices via drift-diffusion modeling with indirectly validated material characteristics

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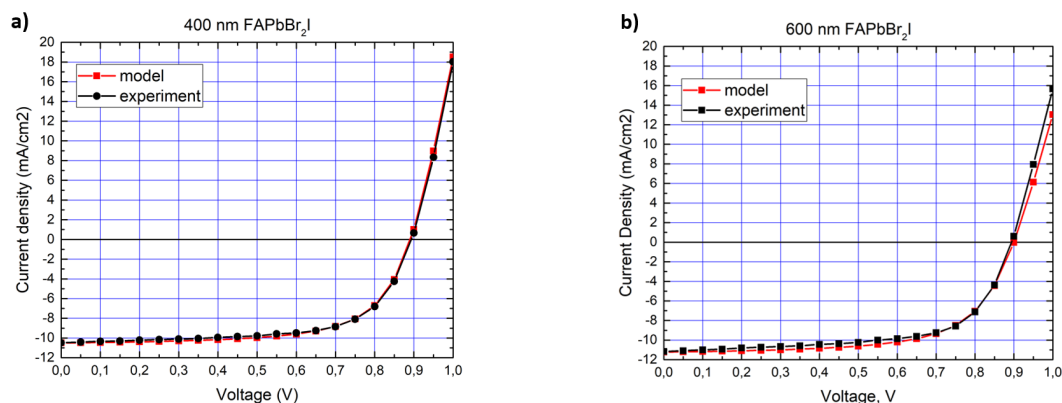
Organo-halide perovskites are one of the most promising solar materials nowadays. The record power conversion efficiency (PCE) of perovskite solar cells (PSCs) has risen to 25.5% since the first work of Tsutomu Miyasaka in 2009 [1] due to their unique physical properties. Moreover, perovskites can be used in tandem solar cells in combination with other photovoltaic materials resulting in 29.1% efficiencies. Thanks to the simplicity of bandgap tunability, wide-bandgap active layers for tandem solar cells can be obtained with mixed-anion perovskites ( $\text{APb}(\text{Br}_x\text{I}_{1-x})_3$ ,  $1 > x > 0$ , A = MA or FA).

Despite recent significant progress in perovskite photovoltaics, their device physics is still not well understood. One of the most efficient ways to get closer to a complete understanding of PSCs operation is theoretical modeling at a microscopic level. Correct multiphysics simulation of the perovskite devices is a challenging task since modeling results are strongly dependent on the accuracy of specified material parameters (band levels, mobility of charge carriers, recombination constants, etc.) which can be uncertain to some extent.

In this work, we show that a good consistency of experimental I-V characteristics in a mixed-anion perovskite solar cell with numerically obtained results for a certain set of material parameters is not sufficient for a PSC model validation. To address this issue, we propose an approach based on thorough fitting the I-V characteristics simultaneously for two working regimes (LED and solar cell) and for two different values of some confident parameters such as a thickness of the perovskite layer.

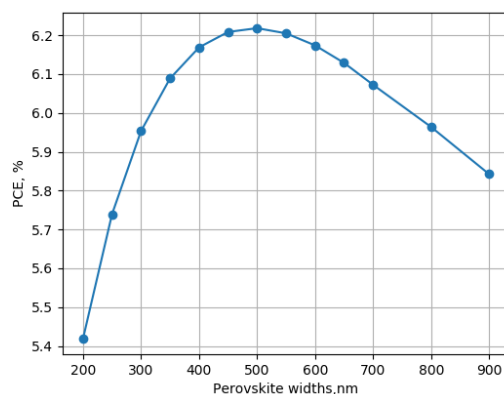
In our experiments, solar cells devices had the following structure: ITO / PEDOT: PSS /  $\text{FAPb}(\text{Br}_{0.66}\text{I}_{0.33})_3$  / C60 / LiF / Ag. J-V characteristics of the devices were measured under the AM1.5G irradiation ( $100 \text{ mW/cm}^2$ ). Drift-diffusion modeling was performed with commercial package TiberCAD while the optical generation rate was separately calculated with Python code based on experimental data from the literature. [2] We used initial material parameters provided by the manufacturer and from the literature.

We prepared two separate series of solar cells with different thicknesses of perovskite layers  $\text{FAPb}(\text{Br}_{0.66}\text{I}_{0.33})_3$ : 400 and 600 nm. After complex parameter fitting, our numerical model well described I-V characteristics of both devices in two regimes – under the sunlight and in the dark condition. Comparison of numerical and experimental I-V characteristics for two different thicknesses in solar cell regime is shown in Fig.1 a,b



**Figure 1.** Experimental and numerical (fitted) I-V characteristics of a solar cell with 400 nm (a) and 600 nm (b) thick perovskite layer.

Using this model, we obtained the dependence of PCE on the perovskite thickness for our PSC. With increasing the perovskite width, we get more generated carriers and thus higher short-circuit current values, but at the same time, we get more defects and resistivity that decrease the Fill factor of solar cell. Based on this, we found the optimal thickness of perovskite for maximizing solar cell PCE – 500 nm (Fig. 2).



**Figure 2.** Modeled dependence of the perovskite solar cell PCE on the perovskite layer thickness.

This work is very important for the further development of perovskite photovoltaics, as it creates a new possibility for optimizing perovskite solar cell, LED, and dual-functional device architecture through numerical modeling. Also, the suggested method can be used to indirectly verify unknown characteristics of materials in photovoltaic devices.

This work was supported by Russian Science Foundation (Project 19-19-00683).

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## Cage-like cations in perovskite-like compounds

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In the last decade, perovskite compounds have attracted increasing interest that is motivated by their physical properties and enormous potential for use in various materials, and that are not only in solar cells.

The intention of our work is to study the principles of halometallates's formation depending on the number and type of functional nitrogen atoms, for the case of adamantane like cations. In this work, we used 1,5-dimethyl-3,7-diazadamantane (KMA22), 2-amino-1,5-dimethyl-3,7-diazadamantane (KMA30) and 1,3,5,7-tetraazotricyclo[3,3,1,1]-hexane (HMT).

It was found that in similar conditions compounds  $[\text{HMT}]\text{[Bi}_2\text{I}_9]\cdot 4\text{H}_2\text{O}$ ,  $[\text{KMA30H}_3]\text{[BiI}_6]\cdot 3\text{H}_2\text{O}$  and  $[\text{KMA22H}_2]\text{[H}_3\text{O}]\text{[BiI}_6]\cdot 4\text{H}_2\text{O}$  are formed. A common feature these compounds crystal structures is the combining the anionic and cationic substructures only by water molecules. In the case of  $[\text{KMA22H}_2]\text{[H}_3\text{O}]\text{[BiI}_6]\cdot 4\text{H}_2\text{O}$ , the water molecules "cluster"  $[\text{H}_{21}\text{O}_{10}]^+$  are formed. It connects 4  $\{\text{BiI}_6\}$  octahedra via O-H $\cdots$ I bonds. We will describe in more detail the features of crystal structures and some physical properties of these compounds in our report.

Changing the synthesis conditions we have obtained iodobismuthates from a mixture of solvents with the composition  $[\text{KMA22H}_2]\text{[Bi}_4\text{I}_{16}]\cdot 2\text{ac}\cdot 2\text{H}_2\text{O}$  and  $[\text{KMA30H}_2]\text{[Bi}_4\text{I}_{16}]\cdot 4\text{H}_2\text{O}\cdot 2\text{EtOH}$  containing tetranuclear anions. The cations functional groups difference leads to the weak interactions network changing, and as a result, in  $[\text{KMA22H}_2]\text{[Bi}_4\text{I}_{16}]\cdot 2\text{ac}\cdot 2\text{H}_2\text{O}$  tetranuclear anions are combined into corrugated tapes by short interactions I $\cdots$ I. While in the second compound's  $[\text{KMA30H}_2]\text{[Bi}_4\text{I}_{16}]\cdot 2\text{H}_2\text{O}$  structure tetranuclear anions are isolated from each other.

$[\text{KMA22H}_2]\text{[BiI}_5]$  and  $[\text{HMT}]\text{[BiI}_5]\cdot \text{ac}$  were obtained from acetone in the same conditions. The crystal structures of these compounds are very similar. Each  $\{\text{BiI}_6\}$  octahedron in the  $[\text{BiI}_5]^{2-}$  anionic chains is bound to an organic cation by an N-H $\cdots$ I contact. The orientation of the resulting chains is the same, but in the case of HMT, the void between them is occupied by acetone molecules. [1]

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## Gadolinium Doped Two-Dimensional Phenylethylamine Based Series of Halide Perovskites as Promising Materials for Spintronics

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The immensely growing era of quantum computing has empowered the field of spin-based devices for computation. The perovskites are already being studied for their spin-dependent properties. Among others, the two-dimensional (2D) halide perovskites are in forefront for their promising application in spintronics. Their use in spintronics become apparent due to their intrinsic property of strong spin-orbit coupling owing to their natural “multiple quantum wells” arising from their 2D structure. In light of this, further introduction of a paramagnetic ion in the 2D perovskite lattice with highest number of unpaired spin possible for an atom, may drastically influence the spin-properties of these materials. Herein, we thus introduce the doping of Gadolinium (Gd) in two dimensional phenylethylamine (PEA) based two-dimensional perovskites. Depending on the number of  $\text{PbI}_6$  octahedra layers ( $n$ ) the doping has been achieved for  $n=1,2,3$ . The basic characterization confirming the successful incorporation of the  $\text{Gd}^{+3}$  in the perovskite lattice is reported. The incorporation of the  $\text{Gd}^{+3}$  endowed the  $n=2, 3$  with improved stability. The introduction of the  $+3$  impurity in the  $+2$  cationic lattice can instigate defects, anisotropy, and electric field polarization effects which may amplify the spin properties. Further, the inclusion of  $\text{Gd}^{+3}$  conferred super-paramagnetic properties to the undoped diamagnetic 2D perovskites, observed at 2K temperature using SQUID technique. In addition, the basic optical properties of these Gd doped 2D materials were studied. The results indicated the importance of Gd doping in perovskites for their exploration of magneto-optical properties and prospective applications.



## The study of photostability of layered $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ hybrid perovskite thin films with various composition ( $n = 1-3$ )

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At the moment, stability of hybrid perovskites (HPs) used as light-absorbing materials in perovskite solar cells (PSCs) is the most vital problem in this field. A huge amount of research is dedicated to the study of HPs degradation mechanisms from various factors – humidity, oxygen, elevated temperatures, light irradiation. According to literature data 3D lead halide perovskites show poor stability to atmospheric moisture, which would extensively hinder their applications. As a contrast, two-dimensional (2D) layered perovskites exhibit much better environmental stability due to the presence of a long-chain aliphatic or aromatic cation in the interlayer space with barrier properties (e.g. hydrophobicity). However, scarce information about photostability of 2D HPs **thin films** with a various cation composition and a number of perovskite layers (denoted as  $n$  in chemical formula) is published to date.

In the current study we try to fill this gap and investigate light-induced changes in crystal structure, morphology, and optical properties of layered perovskite thin films  $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$  (where  $\text{MA} = \text{CH}_3\text{NH}_3$ ,  $\text{BA} = \text{C}_4\text{H}_9\text{NH}_3$ ) with different layer thicknesses ( $n = 1, 2, 3$ ) under visible light irradiation ( $\lambda = 465$  nm, power density  $400$  mW/cm<sup>2</sup>) in inert atmosphere. Additionally, we studied the role of layer alignment (in-plane or out-of-plane with respect to a substrate) in  $\text{BA}_2\text{MAPb}_2\text{I}_7$  perovskite on its photostability. Thin films of  $\text{MAPbI}_3$  3D perovskite, irradiated in the same conditions, were used as a reference material for evaluation of 2D  $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$  stability to visible light. Along with inert argon atmosphere, thin films were also exposed to light in a heptane environment to analyze soluble products of perovskite degradation by using optical absorption spectroscopy.

Upon blue light irradiation of 2D perovskite thin films in an argon atmosphere, it was found that the morphology of the films undergo heavy destruction with the formation of a large number of pores and cracks. Comparing films stability in a row of  $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$  with  $n = 1, 2, 3$  and “ $\infty$ ” (which corresponds to  $\text{MAPbI}_3$ ) we revealed the increase in a material stability with increasing  $n$ , where  $\text{MAPbI}_3$  perovskite films retain their initial structure and morphology for the longest time of irradiation. During light-induced perovskite degradation, the color of all films changes from the original to light yellow or even transparent.

Irradiation of thin film samples in a heptane environment leads to the coloration of the non-polar solvent due to the release of molecular iodine and polyiodides during photodegradation of layered perovskites. The presence of  $\text{I}_2$  and  $\text{I}_3^-$  in heptane was detected by optical absorption method (peaks at 520 and 360 nm respectively). It's worth noting that solubility of polyiodides was greatly increased due to the chemical bonding with butylammonium cation with a long non-polar aliphatic chain. In the case of  $\text{MAPbI}_3$  perovskite, no polyiodide absorption was detected. From this point of view, an increase in the number of



layers and, accordingly, a decrease in the buthylammonium content in the perovskite composition leads to a decrease in the intensity of the triiodide absorption peak and a simultaneous increase in the  $I_2$  absorption peak.

Analysis of the samples before and after irradiation in argon and heptane environment by the XRD method showed a reproducible decrease in the intensity of all reflections in the diffraction patterns which indicates a loose of material crystallinity. According to XRD data, it was not possible to reveal the influence of crystallographic orientation of  $BA_2MAPb_2I_7$  material on its stability. A stronger destruction of layered materials in a heptane environment was also found, which is probably associated with the increased solubility of non-polar buthylammonium cations in the composition of 2D perovskite degradation products.

Summing up, in spite of the high stability of layered perovskite films to moisture, widely reported in the literature, this class of materials undergoes a more intense photochemical degradation compared to 3D counterparts (e.g.  $MAPbI_3$ ), which is experimentally confirmed for a row of  $BA_2MA_{n-1}Pb_nI_{3n+1}$  2D perovskites by a number of methods. These results are consistent with the reported results on the photostability of single-crystal  $(PEA)_2PbI_4$  plates, in which a much higher photostability of  $MAPbI_3$  was also shown.[1]

The reported study was financially supported by Russian Science Foundation (research project №19-73-30022).

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## Diversity of hybrid halide single crystals obtained by solvent conversion induced crystallization

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Single crystals of organic-inorganic complex halides form a new class of semiconductor materials for the fabrication of a new generation of optoelectronic devices, including high-efficiency photodetectors, as well as gamma and X-ray radiation detectors [1].

Currently, different solution techniques are used for producing single crystal of hybrid perovskites, in which oversaturation is achieved by slow cooling, slow temperature decrease (in case of retrograde solubility), addition of antisolvents [2,3]. However, the existing approaches suffer from a number of drawbacks, including the use of toxic solvents, difficulty to control solution oversaturation level.

The purpose of this work is to develop a new approach for obtaining single crystals of organic-inorganic complex halides in a wide compositional range using chemical conversion of a solvent.

We have proposed a fundamentally new strategy to achieve a solution oversaturation point based on in-situ conversion of a solution, which has a high solvent capacity, to a solvent, which is not able or poorly able to dissolve organic-inorganic complex halides. A mixture of an organic carbonate (ethylene carbonate or propylene carbonate) with water acid solutions (HI, HBr, CH<sub>3</sub>COOH) was used as a solvent. It was found, that in this solution composition the following reaction with a notable rate is taking place even at slightly elevated temperature (Fig.1):

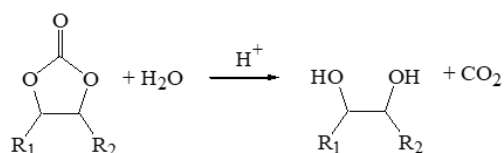


Fig.1 Hydrolysis of cyclic carbonates, where R<sub>1</sub>= CH<sub>3</sub>, R<sub>2</sub>=H or R<sub>1</sub>=R<sub>2</sub>=H.

Single crystals of various hybrid perovskites were obtained by dissolving initial components (a mixture of organic salts and lead or bismuth halides) with a subsequent holding of the solution at elevated temperature (40 – 80 °C). The obtained crystals were separated from the mother-liquor and characterized by XRD, SEM, photoluminescent spectroscopy and diffuse reflectance spectroscopy methods.

Using the developed approach, single crystals of APbX<sub>3</sub> (where A = MA<sup>+</sup>, FA<sup>+</sup>, X = Br<sup>-</sup>, I<sup>-</sup>), FA<sub>x</sub>MA<sub>(1-x)</sub>Pb(Br<sub>y</sub>I<sub>(1-y)</sub>)<sub>3</sub>, as well as MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> and (NH<sub>4</sub>)<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, were obtained and characterized. It is shown, that the proposed approach provides several advantages over the traditional techniques: simple implementation, the use of harmless solvents, high experimental yields (up to 90.5%) and applicability to synthesize hybrid perovskites and perovskite-like compounds of a wide range of compositions.

The research was financially supported by the Russian Science Foundation (Project No. 18-73-10224).

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## A Review on Multidentate ligands for the effective surface passivation of halide perovskites

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Owing to the amazing properties, Organic-Inorganic Metal Halide Perovskites (OIHPs) have attained a certified power conversion efficiency of 25.2%. Specifically, the ternary structure,  $AMX_3$ , allows to obtain different desired functionality by varying A, M, and X (where  $A = MA^+$ ,  $FA^+$ ,  $Cs^+$ ;  $M = Pb^{+2}$ ,  $Sn^{+2}$ ;  $X = Cl^-$ ,  $Br^-$ ,  $I^-$ ). However, these features impose greater defects as compared to the other material like single component Si. Furthermore, the defects act as the source of nonradiative recombination in OIHP photovoltaics which limits the power conversion efficiency. The various imperfections identified in OIHPs responsible for unproductive recombination are intrinsic point defects, extended defects (grain boundaries and surface defects) and impurities. Like for the other materials, passivation of surface defects is critical to their functionalities. Therefore, passivation of these defects has proven to be effective way for obtaining high efficiency solar cells.

The main idea of passivation is to reduce the trap states or push them out of the band gap to protect and/or stabilize the surface. However, the passivation in OIHPs differs from that of its covalently bonded congeners as they possess ionic character. There are many approaches for passivation in OIHPs like passivation by co-ordinate bonding (using Lewis acid/base), through ionic bond formation (using cations/ anions/ zwitterions).

These kind of varied defects need combination of ligands for effective passivation. In this review, various multidentate ligands with emphasis on zwitter ionic passivating agents will be discussed. Zwitterions possess unique properties having both cations and anions which can improve the power conversion efficiency by effectively passivating multiple kinds of defects. The examples reported so far includes L- $\alpha$ -phosphatidylcholine, 3-(Decyldimethylammonio)-propane-sulfonate inner salt, D-4-tert-butyl-phenylalanine etc.

Conclusively, to reach optimal passivation an in depth understanding of structure-function relationship of the passivating agents and their interaction with perovskite surface needs to be developed in taking account all the aspects like size, charge, orientation, shape etc.

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## Compositional Study of Mixed Halide Perovskite Films $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ and $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ Prepared by Close Space Sublimation

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The preparation and characterization of homogeneous and crystalline films of perovskites  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$  and  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$  by the close space sublimation method are reported. Perovskite with a mixture of halide was prepared by the sublimation of methylamine halide  $\text{CH}_3\text{NH}_3\text{Br}$  or  $\text{CH}_3\text{NH}_3\text{Cl}$  over pre-deposited lead iodide films at different sublimation-times to modify the I:Br or I:Cl ratio. The perovskite films  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$  showed a bandgap shifting. For  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$  films with sublimation times 2.5-40 minutes no changes were observed; however, for longer times the absorption spectrum was similar to  $\text{CH}_3\text{NH}_3\text{PbCl}_3$  material. In this study, the mixed halide perovskites  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$  and  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$  were prepared just with two precursors instead of the common approaches that use  $\text{PbI}_2$ ,  $\text{PbBr}_2$ , MAI and MABr or  $\text{PbI}_2$ ,  $\text{PbCl}_2$ , MAI and MACl, respectively. Perovskite layers were applied for the fabrication of solar cell devices, efficiencies of 9.9 % and 10.2 % were achieved for  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$  and  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ , respectively. In addition, perovskite LEDs were also prepared. While the well-known green emission at 533 nm was observed for  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ , for the  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$  based-devices a broad emission spectrum like a warm white emission was obtained. Therefore, it is reported a new approach through the sublimation method to fabricate solar cells and LEDs where the main parameter to care is the sublimation time.

## New DMSO and DMF solvate phases in the systems FAI-PbI<sub>2</sub> and FABr-PbBr<sub>2</sub>

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Hybrid organic-inorganic halide perovskites have become one of the most intensively investigated compounds owing to their outstanding physical properties and advanced photovoltaic applications. Formamidinium-based perovskites and perovskites with mixed compositions are of special interest and considered nowadays as the most promising materials due to their enhanced stability and higher efficiency. [1]

Solution processing from dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) solutions remains the most common route to produce high-quality films and devices with record efficiencies. It is well-known that perovskite crystallization process goes through formation of a number of intermediate phases which strongly affect the morphology and properties of the final devices [2]. Still, there is a large gap in understanding the pathways of crystallization of perovskite from the solutions with different compositions. In particular, no intermediates with formamidinium cations have been reported so far.

We for the first time conducted a comprehensive study on crystallization of hybrid perovskites for the systems with different cations (FA<sup>+</sup>/MA<sup>+</sup>), anions (I<sup>-</sup>/Br<sup>-</sup>), solvents (DMSO/DMF) and precursors ratio (3:2/1:1/1:3) [3]. We screened the whole compositional space for all 24 cases and found for the first time 4 new solvates with formamidinium cations: (FA)<sub>2</sub>Pb<sub>3</sub>I<sub>8</sub>·4DMF, FAPbI<sub>3</sub>·DMF, (FA)<sub>5</sub>Pb<sub>2</sub>I<sub>9</sub>·0.5DMSO, and even the bromide solvate (FA)<sub>2</sub>PbBr<sub>4</sub>·DMSO. A deep analysis of the structural peculiarities of all the solvate phases is performed and discussed in the view of the role of solution composition on the early stages of crystallization of target perovskite films.

We also analyzed crystallization in the 26 cases of multi-compositional perovskite films and identified phases that crystallize from mixed cation and mixed anion solutions. In particular, we found that the crystallization of the mixed anion I/Br compounds evidences the competition between formation of cubic crystals of bromide-rich perovskite phase and needle-like crystals of iodide-rich adduct, which should be taken into account in the film processing of hybrid perovskites with mixed compositions.

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## Effect of organic halides excess on the structure and optoelectronic properties of the hybrid perovskites

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In recent years, the excellent optoelectronic properties and facile solution processing of hybrid halide perovskite-based materials have called great attention of the researchers due to high perspectives for applications in thin film solar cells and LED devices. A widespread strategy to improve the luminescence properties of hybrid perovskites such as MAPbI<sub>3</sub>, FAPbI<sub>3</sub> (where MA<sup>+</sup> = methylammonium, FA<sup>+</sup> = formamidinium) is addition of excess organic halides<sup>1,2</sup>. It is believed that such excess reduces the non-radiative recombination, and therefore improves the PL quantum yield<sup>2,3</sup>. However, there is a lack of understanding of the key dependences between the non-stoichiometry, structure and optical properties of the hybrid perovskites.

Here we present the first comprehensive research of the full compositional space of (FA<sub>y</sub>MA<sub>1-y</sub>)<sub>x</sub>PbI<sub>2+x</sub> with y = 0–1 and x = 1–2. The phase composition and optical properties of the thin films with a given stoichiometry were investigated by means of XRD, absorption spectroscopy and photoluminescence (PL) steady-state and time-resolved spectroscopy (TRPL).

In particular, it was found that in the case of y = 0 and x from 1 to 2 (MAI excessive MAPbI<sub>3</sub>), defect phases are formed, the optical properties of which differ little from stoichiometric 3D perovskite. In contrast, in the case of FAPbI<sub>3</sub> with FAI excess, the formation of low-dimensional ordered phases is observed. Interestingly, the moderate FAI excess leads firstly to stabilization of cubic FAPbI<sub>3</sub> and then to formation of a "hollow" perovskite (FA<sub>1.5</sub>PbI<sub>3.5</sub>), which demonstrates a small PL blue shift (~ 1.6 eV) as compared to the 3D phase (~ 1.5 eV). When FAI content is increased up to 2, a layered (110)-oriented perovskite phase FA<sub>2</sub>PbI<sub>4</sub> is stabilized, exhibiting a larger blue absorption shift (2.3–2.4 eV). Moreover, thin films of this phase exhibit bright PL at ~ 1.95 eV. The low-dimensional phases are also formed for the mixed-cation compositions. Surprisingly, according the PL and absorption spectroscopy the most pure 2D phase of A<sub>2</sub>PbI<sub>4</sub> is formed for thin films with y = 0.75. However, the further increasing of MA/FA ratio leads to destabilization of low-dimensional phases.

Moreover, according to TRPL data thin films with moderate AX excess demonstrate longer charge carrier lifetimes comparing with stoichiometric ones. However, relatively low charge carrier lifetimes are observed in the case of A<sub>2</sub>PbI<sub>4</sub> composition. The former can be explained by defect healing on the boundaries of 3D phase grains through the hollow perovskite capping layer formation. The second fact is consistent with formation of layered perovskite phase with high quantum confinement and fast radiative recombination rate.

Therefore, our research opens a simple way for precise tuning of the optoelectronic properties of formamidinium and methylammonium perovskites through the directed phase engineering via organic halide excess manipulation.

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## From Metallic Lead Films to Perovskite Solar Cells through Lead Conversion with Polyhalide Solutions

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Solutions of methylammonium and formamidinium polyhalides ( $AX_{1+n}$ ,  $A = \text{MA, FA}$ ,  $X = \text{I, Br}$ ) in isopropanol are introduced as novel versatile precursors for the fabrication of  $\text{APbX}_3$  hybrid perovskite thin films via oxidation of metallic Pb. In the present work, we propose a simple and fast laboratory solution-based protocol for perovskite solar cell fabrication by means of metallic lead thin-film deposition with a subsequent spin-coating of polyhalide isopropanol solution followed by a post-treatment in iodine vapor.

In contrast to the existing methods for hybrid perovskite synthesis by using the direct oxidation of metallic lead with polyhalides, the proposed method utilizes only the standard equipment used for the lab-scale fabrication of perovskite solar cells: a vacuum thermal evaporation system for metal electrode deposition and a spin-coater. The use of polyhalide solutions can significantly improve the controllability and reproducibility of the conversion process by adjusting the reactivity of the precursors and the dynamics of Pb conversion with polyhalides, which enables fine-tuned morphology and composition of perovskite films. Only compounds naturally present in the perovskite structure are involved in the process after isopropanol evaporation, and no intermediate phases are formed, thus warranting the final film purity. In contrast to the weak chemical driving force for the classical interdiffusion reaction of two halides, that is,  $\text{PbI}_2 + \text{MAI} \rightarrow \text{MAPbI}_3$ , that frequently leads to diffusion-limited and incomplete conversion of  $\text{PbI}_2$ , the redox reaction of metallic Pb with liquid  $\text{MAI}_3$  changes the oxidation states of  $\text{Pb}^0$  to  $\text{Pb}^{2+}$  and  $\text{I}^{3-}$  to  $3\text{I}^-$ , which in turn creates a strong driving force for the conversion process and facilitates complete conversion with a perfect resultant film morphology. Furthermore, the high volume expansion upon the conversion of Pb to perovskite is beneficial to the morphology of the perovskite layer in terms of elimination of pinholes and improved coverage.

We introduced a simple and versatile method for the fabrication of perovskite thin films and solar cells from metallic lead through the spin-coating of the polyhalide solution, followed by the iodine vapor treatment. The iodine addition to the organic halide precursor solutions contributes to a uniform distribution of precursors over the metallic lead surface because of the instant highly reactive polyhalide melt formation upon solvent evaporation. The use of  $\text{MAI}_{2-4}$  precursor solutions within a proper concentration range results in a uniform morphology of the final perovskite films. We showed that this approach can be implemented for promising  $\text{FAPbI}_3$ -based multication and multianion film syntheses, achieving PCEs of 16.2 and 17.2% for champion solar cells within the  $\text{FTO}/\text{SnO}_2/\text{TiO}_2/\text{perovskite}/\text{Spiro-OMeTAD}/\text{Au}$  (perovskite =  $\text{MAPbI}_3$  or  $\text{MA}_{0.25}\text{FA}_{0.75}\text{PbI}_{2.75}\text{Br}_{0.25}$ , respectively) planar architecture.

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## Assessment of the intrinsic stability of all-inorganic halide perovskite through a DFT analysis

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Despite their vertiginous growth in power conversion efficiency (PCE) terms and their ultra-competitive cost, perovskite solar cells (PSC) carry stability as their main warhorse towards commercialization. Pursuing solutions to a key problem of instability in most commonly used MAPbI<sub>3</sub> caused by the rotation of the complex organic molecules located in the A position (chemical formulae ABX<sub>3</sub>), all-inorganic perovskites like CsPbI<sub>3</sub> and relatives are attracting considerable attention, although in comparison they present only promising results yet, being necessary a profound study of their properties to overcome new problems.

The scope of this work is focused on the effects of the modification of the chemical composition on structural, thermodynamical and mechanical stability of all-inorganic cesium perovskites with general formula CsPb<sub>1-b</sub>Sn<sub>b</sub>(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>. Through a Density Functional Theory study, a wide range of chemical compositions have been covered knowing in detail how the composition changes affect the different properties of these perovskites. Firstly, stability has been assessed through a series of structural tolerance parameters, like the Goldschmidt factor, the Sun's parameter and the intrinsic hardness. Also, thermodynamical stability has been evaluated by means of formation enthalpies according to standard procedures, taking into account two different synthetization/degradation pathways. Furthermore, bulk modulus, as an important characteristic for their integration in complex multilayer devices or flexible and wearable applications, which also have a big impact on their absorptivity that relies on their crystallinity and stress state, has been obtained by fitting the Birch-Murnaghan equation of state, using for that a series of volume deformations applied to all the crystal structures. All those properties will define a complete set that properly describes the different stabilities of these halide perovskites and their correlation, providing a guide of how to impact on them through composition engineering.

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## Mxenes doped inverted perovskite solar cells

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Halide perovskite solar cells (PSC) are one of the most promising directions in modern optoelectronics due to outstanding semiconductor properties and low-cost solution processing methods for the fabrication. However, the use of crystallization processes from the liquid phase tends to form defects in the bulk and surfaces that could negatively affect the charge collection. Moreover, the heterostructure's energy level alignment cannot be controlled by chemical doping as for Si and III-V semiconductors. The interface engineering for microcrystalline perovskite absorbers and charge transporting layer of the PSC was demonstrated as an effective approach for the passivation of traps and reduction of the offsets between energy levels at junctions. A new class of low dimensional materials – Mxenes (typically  $\text{Ti}_3\text{C}_2\text{T}_x$ , where  $\text{T}_x$  shows functional termination (OH, O or F, etc.)) showed unique properties for tuning the optoelectronic properties in PSC due to control of work function values (from of 1.6 to 6.5 eV concerning termination group); high electronic conductivity and charge carrier mobility. Recent works showed impressive results for the gain in PCE(20+ %)[1,2] and the shifting of the work function in perovskite absorber and ETL for n-i-p structures of PCSs[2].

In this work, we demonstrate the first results for the use of  $\text{Ti}_3\text{C}_2\text{T}_x$  (MX) in the structure of an inverted planar perovskite solar cell. The output characteristics of the fabricated devices (ITO/NiO/perovskite/PCBM/BCP/Ag) were significantly improved with direct correlation to incorporation of MXenes in perovskite absorber or ETL. The reference devices showed an average level of PCE ~17.6 %, and incorporation of MX to the absorber and ETL films increased efficiency to 19.2%. However, the devices with MX incorporated just to ETL demonstrated a decrease in performance. Thus, we assume that energy level shifting with the incorporation of MX should be done in parallel for perovskite and ETL to align Fermi levels at the higher position. The changes in the work function in MX doped films were measured and confirmed by ultraviolet photoelectron spectroscopy. Halide perovskite films doped with Mxenes showed a significant gain of the PL that corresponds to the passivation of non-radiative defect centers. The improvement in the PSCs performance manifested in the increase of  $J_{sc}$  and higher EQE level in the near-infrared region, which represents the quality of electron collection. The recombination current measurements demonstrated an improved lifetime of the charges. This effect has been modeled in drift diffusion calculations.

This work demonstrates prospective way for further optimization of PCS operation with interface engineering.

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## Ni Doping in CsPbX<sub>3</sub> Nanocrystals via Post-Synthesis Anion- Cation Co-Exchange

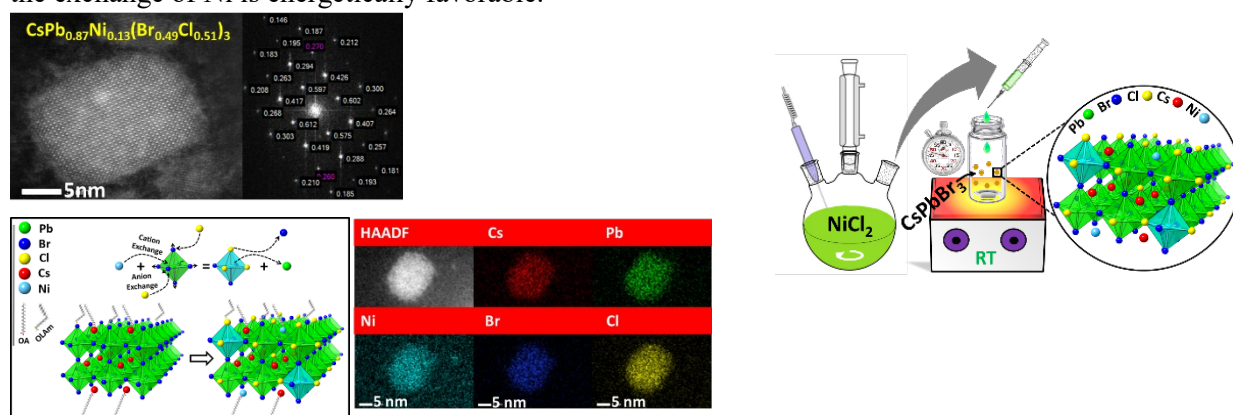
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In the last decade perovskite nanocrystals (NCs) burst into the consciousness of the scientific community as a new class of semiconductors and became the material class at the forefront of research efforts. Particularly, the topic of doping arose in recent years, involving doping or alloying by magnetic ions, which induced changes in the optical and magnetic properties.

In this work a novel dynamic cation exchange strategy driven by a simultaneous anion exchange was implemented<sup>1</sup> to incorporate Ni<sup>2+</sup> ions into CsPbBr<sub>3</sub> perovskite nanocrystals<sup>2</sup> at room temperature and ambient conditions. Ni is especially interesting as a dopant, as it combines an electron spin of S=1, a lack of nuclear spins (with the exception of <sup>61</sup>Ni with a low natural abundance of < 1%) and relatively weak spin-orbit coupling compared to Pb. Magnetic dopants in semiconducting materials induce spin-exchange interactions with the host carrier's spins, mostly leading to a giant magnetization within the host lattice. The lack of spin-orbit and nuclear spin coupling of the Ni dopants should preserve this giant magnetization and consequently the carrier's spin coherency for a length of time. Long spin coherence time is the holy-grail of spin-based devices.

The present work describes a thorough investigation of the doping mechanism into perovskite nanocrystals and characterization of the produced structures and composition, using electron microscopy and spectroscopic techniques. The doping of CsPbBr<sub>3</sub> NCs with Ni<sup>2+</sup> ions was carried out using ion exchange procedures, involving post-treatment with either NiCl<sub>2</sub>, PbCl<sub>2</sub>, PbBr<sub>2</sub> or NiBr<sub>2</sub> precursors at room temperature. The reaction with NiCl<sub>2</sub> was utilized for the anion-cation co-exchange in order to achieve a uniform Ni incorporation into the lattice, and the use of all other reagents was dedicated to control experiments. The results indicate the essential need for co-exchange of cation and anion, enabling integration of Ni<sup>2+</sup> ions with a concentration from < 1% to about 12%. The observations revealed a uniform distribution of the Ni ions across the nanocrystals. Moreover, the nanocrystals exhibit improved luminescence quantum yields beyond those of the non-doped CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub>. The observations were corroborated by a theoretical density functional theory calculation, confirming that the exchange of Ni is energetically favorable.



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## Photostimulated Defect Formation in Doped and Undoped CsPbBr<sub>3</sub> Perovskite

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The CsPbBr<sub>3</sub> perovskites have great potential in photonics and optoelectronics applications and provide a very promising alternative to organo-metal halide perovskites, taking into account their better long-term stability and impressive radiative efficiency. [1] It has been demonstrated that tuning the optoelectronic properties of perovskites is possible via inclusion or partially replacing Pb with a monovalent cation Ag.

Study the impact of lead substitution by silver cations at concentrations of 0, 0.3, 0.5, 1, and 1.5 at% on absorption and photostimulated defect formation of dispersed CsPbBr<sub>3</sub> perovskites were examined via diffuse reflectance spectroscopy. In this article, Ag<sup>+</sup> Doping does not affect the forbidden band gap in perovskite.

The essential response demonstrated by CsPbBr<sub>3</sub> perovskites to irradiation in intrinsic absorption spectral region is photostimulated generation of new defect states. Their formation results in appearance of new corresponding absorption bands in extrinsic absorption spectral region. [2] The analysis of kinetics of photostimulated defect accumulation infers that two different mechanisms are realized: typical for both photoresistant and photosensitive solids. In former case the photostimulated defect formation occurs due to charge carrier trapping by existing defects in perovskites while in latter scenario new lattice defect states are formed due to electronic excitation dissipation. It has been demonstrated that efficiencies of both defect formation photoprocesses are dependent on Ag dopant concentration.

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## Unexpected structural diversity of formamidinium bromoplumbates: novel 2D and 1D low-dimensional phases and solvates

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The outstanding optical and electronic properties of organo-inorganic haloplumbates with a perovskite structure provided an unprecedented surge of interest as a new generation of semiconductor materials for efficient photovoltaic and optoelectronic devices. One of the most important features of this innovative class of semiconductors is the extraordinary tunability of their optoelectronic parameters through adjusting the connectivity of the inorganic anionic framework [1]. In most cases the dimensionality of its inorganic framework is controlled via introducing bulk organic cations acting as a template for the structure [2]. However, the small cations like guanidinium and cesium are also known to form low-dimensional phases (2D, 1D, 0D) in the case of excess of organic halides [3, 4].

In this research, we carried out the first systematic study of low-dimensional phases, which crystallize from dimethylsulfoxide (DMSO) and dimethylformamide (DMF) solutions of FAPbBr<sub>3</sub> perovskite with different FAPbBr<sub>3</sub> excess. We revealed that a three novel phases of layered (2D) layered perovskites can be crystallized from DMF solutions with FAPbBr<sub>3</sub>/PbBr<sub>2</sub> ratio about 2-2.5. All three phases have the same general formula FA<sub>2</sub>PbBr<sub>4</sub>, but differ in structure. The first phase (FA<sub>2</sub>PbBr<sub>4</sub>-I) grows from solution in form of thin transparent plate-like crystals with yellowish tint. It possesses a unique “eclipsed” structure with unusually short interlayer distance and the most undistorted inorganic lattice among all the (110) bromoplumbate perovskites known so far. The second phase (FA<sub>2</sub>PbBr<sub>4</sub>-II) is apparently more stable than the first phase and usually formed via dissolution-recrystallization of the FA<sub>2</sub>PbBr<sub>4</sub>-I. This phase possesses an eclipsed structural motif, which is usual for layered perovskites, and relatively distorted [PbBr<sub>6</sub>] octahedra. The third phase (FA<sub>2</sub>PbBr<sub>4</sub>-III) is unusual (210)-oriented layered perovskite, appearing as well-shaped optically transparent isotropic crystals. In addition, we firstly found a new phase FA<sub>3</sub>PbBr<sub>5</sub> with 1D structure containing the chains of corner-sharing [PbBr<sub>6</sub>] octahedra.

In the case of DMSO solutions we observed the crystallization of two novel adduct phases: FAPbBr<sub>3</sub>•DMSO and FA<sub>2</sub>PbBr<sub>4</sub>•DMSO. The FA<sub>2</sub>PbBr<sub>4</sub>•DMSO solvate consists of isolated chains of corner-sharing octahedra, whereas FAPbBr<sub>3</sub>•DMSO possesses layered motif with alternating corner- and edge-shared arrangement of [PbBr<sub>6</sub>] octahedra. It is worth noting, that both DMSO adducts have a relatively short direct Pb<sup>2+</sup>–O coordination bond. This feature might explain high stability of the adducts as thin films and single crystals at room temperature.

The FA<sub>2</sub>PbBr<sub>4</sub> layered perovskites and other obtained phases were characterized by means of X-ray diffraction, diffuse reflection spectroscopy and photoluminescence spectroscopy. Remarkably, FAPbBr<sub>3</sub>•DMSO adduct exhibits broad photoluminescence at 620 nm with FWHM around 230 nm, that makes it a perspective material for white-light emitters.

Therefore, we discover 4 low-dimensional lead bromide phases, which form from FAPbBr<sub>3</sub>-excessive FAPbBr<sub>3</sub> solutions and can exhibit intriguing luminescent properties per se or

acts as a wide bandgap passivating capping layer in 3D perovskite films. In addition, we revealed the DNSO adduct phases, which is important for formamidinium lead perovskite thin film processing and also show uncommon broad photoluminescence.

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## Ex-situ photoluminescence studies of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films recrystallized in iodine atmosphere

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Recently our group showed that perovskite can chemically absorb iodine to form reactive polyiodide melts (RPM) [1-2], which promotes the recrystallization of perovskite grains. However, no detailed studies of the effect of this approach on semiconductor properties of perovskite have been conducted.

In the present work, we aimed to establish the impact of iodine treatment on luminescent properties of thin films of hybrid organic-inorganic perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .

Photoluminescence spectroscopy was chosen because it proved to be a versatile tool for diagnosis of wide range of semiconducting materials due to its simplicity in terms of instrumental implementation, sample preparation and high sensitivity to minor changes in structure and composition of the material.

For the experiments perovskite thin films were deposited from polar solvents (DMF/DMSO) using chlorobenzene as an antisolvent, treated with iodine ( $p(\text{I}_2) \sim 0.3$  mbar) for varying periods of time and annealed to remove an excess of iodine.

Using XRD, we confirmed that phase assemblage of iodine-treated samples was retained, i.e. no decomposition occurred upon such a treatment. Scanning electron microscopy images showed significant increase of the average grain size due to RPM-induced recrystallization. Steady-state photoluminescence revealed that the longer the exposure to iodine gas leads to an increase of the half-widths of the emission bands, as well as luminescence intensity and redshift of the emission peak.

An important part of the results presented in this work is the demonstration of the influence of iodine vapor treatment duration on the luminescent properties of the perovskite-based materials.

Based on available reports on luminescence of halide perovskites and fundamental concepts of solid-state physics, we suggest the observed redshift of the PL band maximum occurs due to changes in the concentration of surface states.

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## Surface stabilization of perovskite solar cells by MOF, COF and polymer films: *ab initio* studies

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The development of perovskite solar cells enabling their large-scale implementation encounters two major obstacles in place: the toxicity of lead and the stability towards the external influences / durability issues. This talk aims at describing the ways of interaction between experimentalists and theoreticians in the quest for complex solutions to lead toxicity problem<sup>1</sup> and surface stabilization of perovskite<sup>2</sup>. In particular, an application of sulfur-containing compounds for coating, including Metal-Organic Frameworks (MOF)<sup>1</sup>, Covalent Organic Frameworks (COF) and polymers<sup>3</sup>, which, on the one hand, allow for binding lead and prevent its leakage, and, on the other hand, enable protection of perovskite layer from the external chemical agents, is considered as a two-in-one solution to address these challenges. Thus, in this talk the methodology of the joint theoretical and experimental search of stable functional coatings for application in perovskite solar cells is presented. Modeling of these systems is accomplished from the first principles, including Density Functional Theory (DFT) based molecular dynamics simulations. The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University<sup>4</sup>.

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# Ion diffusion through the Blocking Layers of Perovskite solar cells - Device level Electrochemistry

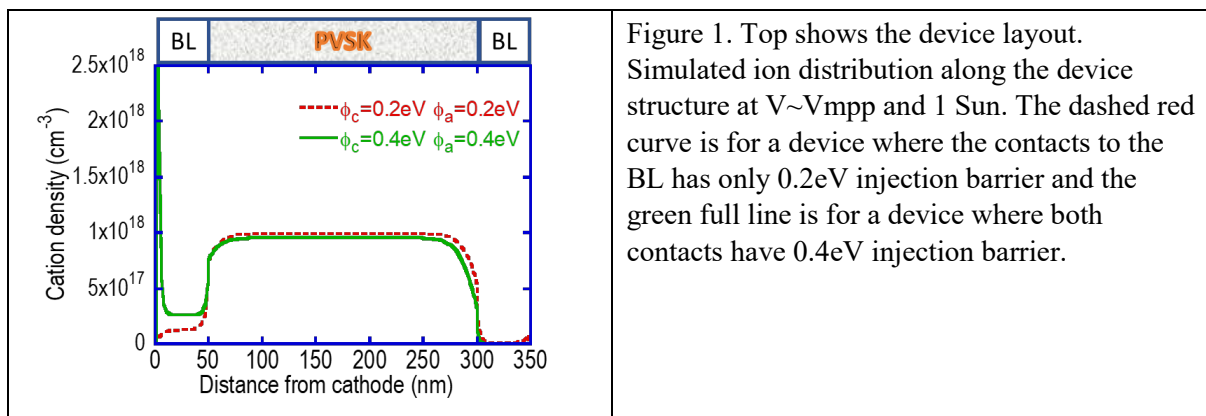
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Defect chemistry plays a major role in the operation of perovskites cells. On one hand they are behind the remarkable self-healing,[1] while on the other they dictate the level of traps, non-radiative recombination,[2] as well as promote ion migration.[3] Moreover, once ions reach the electrodes the device degradation is accelerated.[4, 5] Combining the various reports it seems that if the perovskite would not lose its constituents it would self-heal and if it do lose them it is game-over. We claim that ion migration into the blocking layer is the most important electrochemical process standing in the way of long-term stability. As we will show at the presentation, a significant part of the electrochemistry behind ion leakage and consequently electrode reactions, is captured by a semiconductor device model that accounts for mixed electronic-ionic conduction.[6] Moreover, it is possible to design the device to mitigate this ion leakage.

As an example, Figure 1 shows the ion distribution under light and forward bias for two devices. While the device structure can compensate for loss of  $V_{bi}$ , the ions release is much more pronounced for the device with lower  $V_{bi}$ .



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## **Making sense of approaches addressing toxicity of hybrid lead halide perovskites**

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Photoconversion efficiency (PCE) of Pb-based hybrid perovskite solar cells demonstrated an unprecedented growth during the last decade to more than 25%. Excellent optoelectronic properties of hybrid lead halide perovskites, such as defect tolerance and long carrier lifetime, encourage application of these materials also in other types of optoelectronic devices, such as LED, photosensors, photo-memristors, lasers and etc. However, the issue of Pb toxicity still remains a significant obstacle that can hinder commercial potential of hybrid perovskites. The frequently expressed opinion that Pb toxicity can be simply neglected, because even a complete dissolution of the perovskite layer from a compromised module can increase Pb concentration in already contaminated urban soil by only a factor of 2, is a dangerous simplification that neglects high bioavailability of  $\text{PbI}_2$  and neurotoxicity Pb. According to the World Health Organization, the blood Pb level for children should not exceed 5 micrograms per liter, which is the amount of Pb contained in only 5 mm x 5 mm area of a perovskite absorber layer. Although the issue of Pb toxicity can be, perhaps, addressed through implementation of mandatory end-of-life recycling programs that could, conditionally, justify exemption from ROHS regulations in the case of utility-level solar power stations located in non-residential areas, the developmental neurotoxicity of Pb should be considered extremely seriously in the case of building integrated perovskite PV systems. This is especially true for flexible optoelectronic devices that are frequently proposed as promising for consumer electronics and even for wearable electronic devices. In this presentation I am going to critically review approaches addressing toxicity of hybrid lead halide perovskites and discuss prospects for development of non-Pb semiconducting halides as well as approaches aimed on deactivation of Pb in compromised PV modules.



## New pigeonholing approach for selection of solvents relevant to lead halide perovskites processing

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One of the key factors for achieving high power conversion efficiency (PCE) by perovskite solar cells (record PCE = 25.5% in 2020)<sup>1</sup> is the development and optimization of the most widely used solution deposition methods. Sequential deposition of PSC components requires the use of a set of technologically relevant solvents including those that are inert to the underlying sandwich of preliminary deposited materials and, at the same time, play the role of good solvents for the dissolution and deposition of the target material. At the moment, a universal approach that could effectively categorize solvents based on their type of interaction with organo-inorganic perovskites is missing. The development of this approach can also help in searching of new solvent mixtures for precise deposition of perovskite solar cell materials.

In this work we propose an approach<sup>2</sup> for the search and selection of solvents using three parameters that fully reflect the three main types of interaction in the perovskite solution: hydrogen bonding (hydrogen bonding parameter of Hansen), donor-acceptor interactions in Pb<sup>2+</sup>-solvent complexes (donor number), and ion-dipole interactions of charge complexes with the solvent (dipole moment) (fig. 1a.). This approach allowed to divide solvents into separate groups that correspond to the type of their effect on lead halide perovskites: neutral (low values of all parameters); AX-selective solvents, dissolving only the organic part of perovskite (donor number and dipole moment are low,  $\delta_{HB} > 10$  (MPa)<sup>1/2</sup>); strong solvents (all parameters are high), and weak solvents (all parameters are relatively average). The proposed model was experimentally verified for a group of neutral and weak solvents which parameters are quite close (e.g. ethyl acetate (previously considered neutral) and tetrahydrofuran (previously considered weak)).

After a long (12 hours) exposure of MAPbI<sub>3</sub>, MAPbBr<sub>3</sub>, and FAPbBr<sub>3</sub> films in group of solvents samples were studied using X-ray diffraction and SEM. It was found that soaking in ethyl acetate, dioxane, nitrobenzene, acetone, benzonitrile leads to recrystallization of MAPbI<sub>3</sub> and MAPbBr<sub>3</sub> films, classifying these solvents to the group of weak. It was also found that vapors of the weak solvents can lead to an increase in both photoluminescence intensity and lifetime of charge carriers, which apparently indicates the passivation of the defects on the perovskite surface by solvent molecules.

Summing up, the developed approach shows a great coherence with literature data and experimental results, and allows to predict the type of more than 30 new solvents which can be used for further more precise development of solution-based approaches for halide perovskites and/or charge-transporting materials coating.

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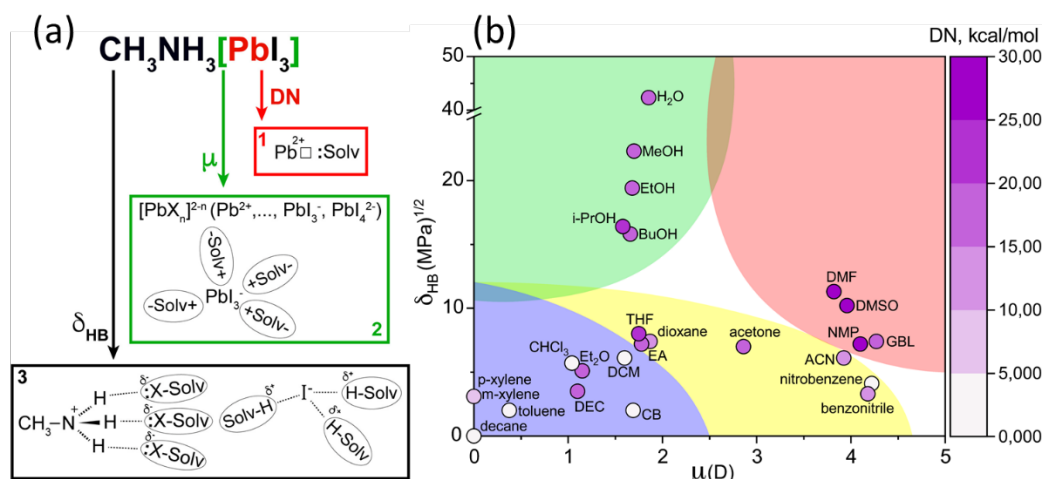


Figure 1. (a) Schematic illustration of three main types of perovskite interaction with solvents: (i) – complexation of  $Pb^{2+}$  with Lewis bases (pink rectangle); (ii) – ion-dipole interaction of  $[PbX_n]^{2-n}$  ions with solvent dipoles (green rectangle); (iii) – hydrogen bonding of  $A^+/X^-$  with corresponding solvent groups (black rectangle). (b) Set of solvents drawn in  $\delta_{HB} - \mu$  coordinates with color mapping by DN values. Green, red, yellow, and blue areas highlight four basic regions of the plot corresponding to AX-selective solvents, strong solvents, weak solvents, and inert solvents, respectively.

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## Optical properties and electronic structure of a new copper-based X-ray scintillator $\text{MACu}_2\text{I}_3$

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Hybrid organic-inorganic compounds became the materials of extremely intense research. While hybrid lead halide perovskites revolutionized the photovoltaics due to their outstanding properties, other hybrid compounds based on non-toxic metals also drew attention owing to their structural versatility. A particular interest has been attracted to halocuprates (I) because of their highly intense luminescence and potential applications in scintillators, photodetectors and LEDs [1, 2].

In this study, the new hybrid organic-inorganic compound  $\text{MACu}_2\text{I}_3$  was synthesized using two independent techniques: mechano-synthesis and crystallization from acetonitrile. Its crystal structure was determined by single crystal X-ray diffraction. It was found that the target compound  $(\text{MeNH}_3)\text{Cu}_2\text{I}_3$  crystallizes in a monoclinic unit cell with a structure containing infinite double-chained  $\{[\text{Cu}_2\text{I}_3]^{-}\}_{\infty}$  anions and isolated  $\text{MA}^{+}$  cations [3].

The diffuse reflectance spectrum of the of  $\text{MACu}_2\text{I}_3$  showed that it has a steep absorption edge at 3.62 eV and three maxima in the UV absorption region at 325, 316, and 301 nm which can have excitonic origin due to the low electronic dimensionality and quantum confinement. It was found that  $\text{MACu}_2\text{I}_3$  does not exhibit intrinsic photoluminescence but demonstrate yellowish-orange X-ray luminescence under exposure to the radiation with  $\lambda = 0.9699 \text{ \AA}$ .

The electronic structure of  $\text{MACu}_2\text{I}_3$  was analyzed using DFT method based on the obtained crystallographic data. The electronic structure, including density of states for  $\text{MACu}_2\text{I}_3$  was calculated using 6 different functionals, with the best agreement between the calculation (3.44 eV) and experimental data (3.62 eV) obtained for the HCTH functional. It was found that  $\text{MACu}_2\text{I}_3$  is a direct semiconductor with a bandgap at the  $\Gamma$  point with the VBM composed mainly of Cu 3d orbitals and I 5p orbitals and the CBM composed of Cu 4s and I 5p orbitals.

The research was financially supported by Russian Foundation for Basic Research (Project No. 20-33-70265).

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## Hybrid perovskites photodegradation and accompanying chemical corrosion of metal electrodes in perovskite solar cells

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Long-term stability of hybrid perovskites (HPs) is the most critical problem nowadays in perovskite photovoltaics. Determination of the main degradation mechanisms under different exploitation factors (heat, humidity, oxygen, light, electrical bias) is essential for successful search and development of approaches to improve stability of light-harvesting perovskite materials and perovskite solar cells (PSCs) as a whole device. A large amount of reports discloses processes taking place during HPs degradation under heat, oxygen, and humidity. On the other hand, light-induced perovskite degradation mechanism is still under debate due to the complexity of processes occurring under light irradiation.

In this work, we provided a detailed study of photodegradation of conventional 3D hybrid perovskites with a various composition of cation “A” in APbI<sub>3</sub> (A: MA, FA/Cs, MA/FA, MA/FA/Cs). We also expanded the current research onto a homologous row of layered 2D perovskites BA<sub>2</sub>MA<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (BA = butylammonium) with Raddlesden-Popper crystal structure, considered as a more stable light-harvesting material for PSCs. Additional attention in this work was paid to the study of chemical corrosion of metal electrodes (Au, Cu) due to the reaction with iodine-containing perovskite decomposition products.

According to the results of in-situ Raman spectroscopy visible light irradiation ( $E_{\text{light}} > E_{\text{g(perovskite)}}$ ) causes intensive perovskite degradation with the release of volatile polyiodide species (characteristic vibrations at 108-110, 145, and 165-169 cm<sup>-1</sup>). Cation composition in 3D perovskites has no significant effect on the detected by Raman spectroscopy decomposition products – molecular iodine and liquid polyiodide melts with methylammonium (MAI<sub>x</sub>) and/or formamidinium (FAI<sub>x</sub>). [1] Light-induced degradation of layered perovskites also proceeds with the formation of polyiodides which were detected by optical absorption spectroscopy of heptane solvent used as an inert non-polar medium during visible light irradiation of 2D HPs. This similarity in photodegradation products between 2D and 3D counterparts highlights the same nature of light-induced decomposition mechanism originating from PbI<sub>6</sub> inorganic sublattice rather than from organic components of these hybrid materials.

The release of highly reactive polyiodide melts as one of the HPs photodegradation products determined the need for the investigation of metal electrodes and some electron- and hole-conducting materials (ETMs and HTMs respectively) stability to chemical corrosion by polyiodide species. The most widely used materials spiro-OMeTAD and PCBM both showed complete instability to MAI<sub>x</sub>, while poly(triaryl)amine (PTAA) as well as copper phthalocyanine (CuPc) oppositely demonstrated superior durability. Analysis of gold and copper electrodes showed a poor stability of both metals to polyiodide-assisted corrosion with formation of newly found complex phases MA<sub>2</sub>Au<sub>2</sub>I<sub>3</sub> [2] and MACu<sub>2</sub>I<sub>3</sub> [3] respectively. However, in the case of copper a one more corrosion product – CuI is formed. The resulting CuI and MACu<sub>2</sub>I<sub>3</sub> phases proportion depends on the reaction temperature and on the presence

of lead derivatives in the reaction zone. Formation of these compounds during metal corrosion can deteriorate a thin metal layer causing shunts in the working under continuous illumination perovskite solar cells.

Summing up, light-induced decomposition of hybrid lead-halide perovskites with either perovskite 3D or layered 2D crystal structure is accompanied by the formation of highly reactive polyiodide melts with small and/or bulky organic cations (e.g.  $\text{MA}^+$ ,  $\text{FA}^+$ ,  $\text{BA}^+$ , etc.). The presence of such melts inside PSCs even locally could cause chemical corrosion of a wide range of materials inside PSCs (e.g. spiro-OMeTAD, PCBM, Au, Cu, etc.) leading to a device break down.

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## Solution-based iodine-treatment as a new method of morphology improvement of thin film hybrid organo-inorganic halide perovskites

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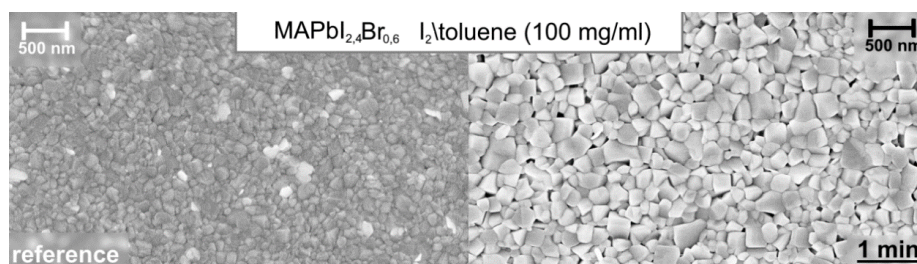
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Recently, hybrid organic-inorganic lead halide perovskites ( $\text{APbX}_3$ , A=methylammonium( $\text{CH}_3\text{NH}_3^+$ ), formamidinium ( $(\text{NH}_2)_2\text{CH}^+$ ), Cs; X= I, Br, Cl) gained a lot of attention of/among scientists around the world, especially due to possible application of these semiconductor materials as an absorber layer in new generation solar cells. The efficiency of such devices recently reached 25,5%, which is almost equal to efficiency of crystalline silicon solar cells. In contrast to traditional materials for photovoltaic application, lead-halide perovskites has significantly lower production cost owing to quite affordable chemical solution fabrication.

However, the quality of hybrid perovskite films after solution deposition procedure is quite poor and requires additional post-treatment procedures. There were suggested several methods for improving properties of lead-halide perovskite materials such as thermal or solvent annealing treatment. Nowadays these steps became essentials for perovskite solar cell fabrication. This post-processing results in an increase of the average grain size and an improvement of the crystallinity of the material.

Within the framework of present research we developed new approach for lead-halide perovskites post-processing, which consists in exposure of thin films of semiconductor in solutions containing molecular iodine. One of the advantages of such technique is the exceptional high rate of semiconductor film recrystallization. It was found that this method is applicable to the most commonly used perovskite materials with composition:  $\text{CH}_3\text{NH}_3\text{PbI}_3$ ,  $(\text{HC}(\text{NH}_2)_2)_{0.75}(\text{CH}_3\text{NH}_3)_{0.25}\text{PbI}_3$ ,  $(\text{HC}(\text{NH}_2)_2)_{0.95}(\text{CH}_3\text{NH}_3)_{0.05}\text{PbI}_{2.85}\text{Br}_{0.15}$ ,  $\text{CH}_3\text{NH}_3\text{PbI}_{2.4}\text{Br}_{0.6}$ . According to X-ray diffraction data, exposure of lead-halide semiconductors to molecular iodine solutions in toluene and decane for a certain period of time results in significant increase in crystallinity of the materials without any changes in phase assemblage. The series of SEM images demonstrated 8-fold increase of the average grain size of lead-halide perovskite thin films.

The results presented in this work indicate that proposed approach of post-processing of lead-halide perovskite thin films may be found promising in production of photovoltaic devices.



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## High-resolution remote thermometry and thermography using luminescent low-dimensional metal-halide perovskites

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While metal-halide perovskites have recently revolutionized research in optoelectronics through a unique combination of performance and synthetic simplicity, their low-dimensional counterparts can further expand the field with hitherto unknown and practically useful optical functionalities. In this context, we present the strong temperature dependence of the photoluminescence (PL) lifetime of low-dimensional, perovskite-like tin-halides, and apply this property to thermal imaging. The PL lifetimes are governed by the heat-assisted de-trapping of self-trapped excitons, and their values can be varied over several orders of magnitude by adjusting the temperature (up to 20 ns °C<sup>-1</sup>, resulting in a thermometric precision of 0.013 °C). Typically, this sensitive range spans up to one hundred centigrade, and it is both compound-specific and shown to be compositionally and structurally tunable from -100 to 110 °C going from [C(NH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>SnBr<sub>4</sub> to Cs<sub>4</sub>SnBr<sub>6</sub> and (C<sub>4</sub>N<sub>2</sub>H<sub>14</sub>I)<sub>4</sub>SnI<sub>6</sub>. Finally, through the implementation of cost-effective hardware for fluorescence lifetime imaging (FLI), based on time-of-flight (ToF) technology, these thermoluminophores have been used to record thermographic videos with high spatial and thermal resolution [1].

We have developed more environmentally stable thermographic luminophores [2] based on Sb<sup>3+</sup> halides that reveal similarly high sensitivity and sustain oxygen impact. The next step in the luminophore development is amorphous thin films that allow conformal coating of arbitrary surfaces and demonstrate micrometre-scale thermography resolution at room temperature by using a confocal microscope with FLI system. That is about an order of magnitude better than achievable by IR methods and allow use of standard optical microscope for visible wavelength range.

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