# First evidence of macroscale single crystal ion exchange found in lead halide perovskites

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#### Abstract

Ion exchange is classified as a reaction that may be performed among nanocrystals. Here, we discovered that methylammonium lead bromide macroscale perovskites' single crystals may exchange ions with the environment while maintaining their original morphology. Iodide replaced bromide and was detected even in the very center of a previously pure macroscale MAPbBr<sub>3</sub> single crystal. Additionally, the entrance of chloride into the crystal is energetically favorable and most bromides were exchanged, yet kinetic factors hindered  $Cs^+$  entry and  $Pb^{2+}$  by  $Sn^{2+}$  substitution. Furthermore, grinding different single crystals together revealed swift I/Br exchange. Clear differences in comparison with nanomaterials, along with density functional theory calculations, shed light on the nature of ion-exchange reactions in perovskites' single crystals. This work provides first evidence of these halide exchange reactions in macroscale perovskite single crystals. These results offer a new perspective on ion-exchange reaction and pave a path toward synthesis of inhomogeneous single crystals.

#### K E Y W O R D S

energy materials, environmental science, ion-exchange reactions, perovskite, single crystals, solid-state chemistry

#### **1** | INTRODUCTION

Perovskite materials have attracted a great extent of research due to their exponentially increasing use in the field of solar cells.<sup>1-3</sup> Ion mobility inside the perovskite was attributed as the cause for the large measured, direction switchable, photocurrents in symmetric electrodes of heterojunction perovskite solar cells (PSCs).<sup>4,5</sup> Although photocurrent direction has been switched in optoelectronic devices earlier, a switchable donor/acceptor was used next to the photosensitizing materials.<sup>6,7</sup> Another characteristic of perovskite is its ability to contain in a single crystal more

than one type of ion in the same crystallographic unit cell position.<sup>8</sup> Single crystals containing different ratios of Br<sup>-</sup> to I<sup>-</sup> and of Cl<sup>-</sup> to Br<sup>-</sup> were identified and revealed combined optical properties with structural dominance of the major element of the lattice.<sup>9</sup> Ions' coexistence paved the way toward profusion of perovskite compositions to be used in PSCs. Optimization of photovoltaic properties and stability by compositional changes is currently the main topic of perovskite solar energy conversion research.

Ion-exchange reactions were extensively investigated and identified in nanometric materials such as chalcogenides<sup>10-12</sup> and metal organic frameworks.<sup>13,14</sup> All-inorganic

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perovskite  $CsPbX_3$  (X = Cl, Br, I) nanocrystals have shown very swift halide exchange, simply by mixing two compositions in solution.<sup>15</sup> These reactions average the halide content in a matter of minutes and give path for bright emitters that are tunable across the visible spectrum. Halide salts can react with CsPbX<sub>3</sub> nanocrystals in solution as well.<sup>16,17</sup> In addition, methylammonium lead halide (MAPbX<sub>3</sub>) nanocrystals have shown similar interparticle exchange.<sup>18</sup> Also, thin multicrystalline films of perovskite exhibit fast halide and metal exchange in salt solutions for tens of nanometers thick films.<sup>19-21</sup> These reactions are completed within seconds or minutes with the exception of MAPbBr<sub>3</sub> with MAI, which was slower and incomplete.<sup>22</sup> Cation exchange in thin films of perovskite was comparably slow and took several hours to progress.23

All three aforementioned qualities, namely, fast ion migration, coexistence of different ions in the same crystallographic site, and swift surface ion exchange, characterize lead halide perovskites. This has brought us to contemplate whether macroscale perovskite single crystals may also perform ion-exchange reactions with their environment. Following this rationale, MAPbBr<sub>3</sub> single crystals were reacted in solutions of different ions and solvents. It was found that specific combinations of salts and solvents prevented the degradation of the crystals in an environment of polar solvents. These combinations such as SnBr<sub>2</sub> in 2-methoxyethanol, CsBr in methanol, and MACl or MAI in ethanol were further investigated as possible conditions to allow single crystal ion exchange. Additionally, solid-phase grinding of different perovskite single crystals allowed insight into the ion-exchange possibilities and mechanisms in solids. The results differ greatly from nanocrystal and thin film ion exchange and are indicative of the conditions that allowed the same crystals to change composition while retaining their morphology and structure.

#### 2 | RESULTS AND DISCUSSION

Lead halide perovskites are composed of vertices-sharing halide octahedrons with lead cation at their center and cations such as MA<sup>+</sup> in the complementarily formed network of cuboctahedral voids. Figure 1A schematically illustrates the perovskite structure of MAPbBr<sub>3</sub> and the ion-exchange reactions, which were investigated in this work. MAPbBr<sub>3</sub> was chosen as a model due to the large clear single crystals it forms, the medium radius of bromide among the other halides, and its absorbance in the middle of the visible spectrum. The exchange of bromide with iodide or chloride was investigated alongside the cation exchange of MA<sup>+</sup> with Cs<sup>+</sup> and the metal exchange of Pb<sup>2+</sup> with Sn<sup>2+</sup>. Single crystals of MAPbBr<sub>3</sub> were synthesized by vapor-assisted crystallization. The 2 to 5-mm cubic crystals appeared after a N,N dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) solution of MAPbBr<sub>3</sub> was in contact with ethanol vapors for 3 days. In order to isolate one ion to be exchanged, salts composed of one existing and one introduced ion as MAI or MACl were utilized. It was found that certain concentrations of MAX in solvents such as ethanol or isopropanol prevented the degradation of the perovskite crystals. Such stabilization was suspected to be caused by ion exchange on the surface. The absorbance of the crushed MAI/MACl-treated MAPbBr3 single crystals and the absorbance of pure MAPbBr<sub>3</sub> single crystal are presented in Figure 1B.

MAPbBr<sub>3</sub> single crystals in MAI ethanol solution changed color to black on their margins, and the crystals maintained their initial morphology (Figure 2A,B). Alternative chloride exchange of MAPbBr<sub>3</sub> was performed in ethanol solution of MACl under ambient conditions. A hypsochromic shift of the crystal absorbance to shorter wavelengths (Figure 1B) indicates the high percentage substitution of bromide with chloride (Figure 2C,D).



**FIGURE 1** Single crystal ionexchange illustration and absorbance of reacted specimens. A, Schematic illustration of MAPbBr<sub>3</sub> crystal structure and the investigated ion-exchange reactions. B, Normalized absorbance of crushed pure MAPbBr<sub>3</sub> single crystals (red curve) vs the crystals treated with 10 mg/mL MACl/MAI ethanol solution for 10 days (yellow and black curves, respectively). The MAI solution was heated to 70°C

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Further optical microscopy and scanning electron microscopy (SEM) images of similar crystals show the entrance of chloride toward the center of the crystals (Figure S1A-E). Also massive substitution may result in hollow perovskite crystals due to the smaller chloride radius. Alternatively, using isopropanol as a more moderate solvent slowed down the reaction and resulted in very unique crystals with yellow edges and orange faces (Figure S1F-G).

In order to characterize the insertion of chloride toward the center of the crystals, an MACl-treated MAPbBr3 crystal was cleaved down the middle. Optical microscopy of the revealed surface showed that the yellow chloride-rich perovskite front moved toward the center of the crystals from its margins (Figure 3A). This approximately 2-mm size crystal was suspended for 3 days in MACl ethanol solution. Other small specimens that were allowed to react further became yellow altogether. An energy-dispersive spectroscopy (EDS) line analysis across the new crystal face is presented on top of the crystal SEM image in Figure 3B. Across the line scan, the chloride-to-bromide ratio at the edges of the sample was ca. 83%, decreasing to close to nil in the middle. Although bromide and chloride displayed opposite trends, the lead concentration remained steady across the sample. Close-up SEM image of the yellow cleaved face exposed crossed "Lego-like" patterns of the breakage (Figure 3C). In addition, a similarly treated crystal (ca. 4 mm size) was examined as a whole using a powder

X-ray diffractometer (Figure 3D). The results show five notable successive peaks from the (1,0,0), (2,0,0), (3,0,0), (4,0,0), and (5,0,0) facets. These two findings are indicative of the single crystalline nature of the chlorine-rich perovskite. This is affirmed by the high signal-to-noise ratio of the X-ray diffraction (XRD) measurement. Cracks may be caused due to the smaller volume of the chloride vs bromide, yet lattice orientation remains equivalent throughout the substance. These cracks are more pronounced after longer MACl exposure (Figure S2) and hinder single-crystal XRD structure determination.

In the case of MAI-treated MAPbBr<sub>3</sub> single crystals, the crystals retained their shape and morphologies during the reaction while changing the color of the fringes to black (Figure 2B). A powder XRD measurement over the face of the intact crystal indicated a single crystal pattern similar to MAPbI<sub>3</sub> (Figure S3A). After cleaving a similar crystal sample in the middle, a wavelength-dispersive spectroscopy (WDS) elemental line scan across the crystal was performed in order to obtain the contents of iodide in the bulk of the crystal (Figure 4A). High mass percentages of iodide were detected on the sides, and up to 4% of iodide was detected in the bulk of the crystal. In addition, the cleaved face SEM of the crystal showed smooth surface with extruding squares, which were more prevalent and more close to the margins of the crystal, compared with the center bulk (Figure S3B,C). These features were not detected on other perovskite crystals and may be 4 \_\_\_\_WILEY\_EcoMat



**FIGURE 4** Br/I ion exchange and calculated energies for mixed halide compositions. A, Iodide weight percent as detected by WDS line scan over the middle-cleaved face (see inset illustration) of MAI-treated MAPbBr<sub>3</sub> single crystal in ethanol solution of 10 mg/mL, 60 days treatment. The inset graph is a close up of the curve, emitting the very edges of the crystal. B, Calculated total energy curves of MAPbX<sub>3</sub> (X = Cl, Br, I) as a function of the lattice constant, relative to the total energy of the optimized lattices, for two cases: all cell vectors (Rx = Ry = Rz) are variables (solid lines), and in the case in which the base vectors Rx = Ry values are fixed at the value optimal for MAPbBr<sub>3</sub>, while Rz is a variable. The total energies of MAPbCl<sub>3</sub> and MAPbI<sub>3</sub> at the unit cell size optimal for MAPbBr<sub>3</sub> are  $E_1 = 0.22$  eV and  $E_2 = 0.45$  eV. WDS, wavelength-dispersive spectroscopy

attributed to the pressure caused by the large radius iodide, which entered the lattice.

Density functional theory (DFT) calculations are detailed in Supporting Information. These calculations revealed an energetic preference for chloride to exchange bromide in the MAPbBr<sub>3</sub> lattice, but approximately 0.5 eV cost for the iodide substitution. Nevertheless, vacancies of bromide in the crystal were found to encourage both exchanges to take place. Such perovskite vacancies were shown to move toward the surface<sup>24</sup> and their

mobility was investigated as well.<sup>25</sup> Since the ionexchange reactions progress from the edges of the crystal inwards, a gradient of the local cell unit is formed across the single crystal lattice. The total energy curves as functions of the lattice constant were calculated by means of DFT. They are drawn, relative to the system energy of the optimized unit cell for MAPbX<sub>3</sub> (X = Cl, Br, I), as solid lines in Figure 4B. The dashed lines represent the corresponding curves obtained for the structures with two lattice vectors fixed at the value optimal for MAPbBr<sub>3</sub>. Through ion-exchange reactions, the introduced ion forms a gradient of concentrations, thus inducing a gradient of the lattice constants across the crystal. However, the pure MAPbBr<sub>3</sub> phase in the crystal interior fixes the size of the planar base of the doped unit cells. The energetic cost of the iodide poor substrate strain, acting on the iodide rich phase, is another reason for the limited exchange. Yet, the tension caused by this substrate may cause microscopic cross-patterned cracks and the "Lego-like" breakage patterns.

Solid-phase direct reactions between MAPbBr3 and MAPbI<sub>3</sub> single crystals were performed by grinding EcoMat\_\_\_\_WILEY\_

5

the two compounds together. Pestle and mortar grinding of several mass ratios of the pure halide crystals rendered the intermediate colored powders in Figure 5A. Absorbance curves for these powders revealed patterns which diverge from the superposition of pure MAPbBr<sub>3</sub> and MAPbI<sub>3</sub> absorbance patterns (Figure 5B, dotted lines). Ion-exchange interactions lend the powders absorbance similar to halide mixture of a range of MAPb $(Br_xI_{1-x})_3$  homogeneous perovskite powders. Additional 70°C treatment for 24 hours added to the homogeneity of the powders. The moderate absorbance slopes that indicate highly inhomogeneous mixture turned much sharper after the treatment (Figure 5B solid lines). Complementary powder XRD measurements for the unheated ground crystals were performed (Figure 5C). The observed shifts of the peaks' position of each phase toward the other directly indicate of ion exchange between MAPbBr<sub>3</sub> and MAPbI<sub>3</sub>. In addition, the integration of the peaks' ratio tends to lean toward the major phase (Table S1). Finally, the powder XRD curves of the same samples after the heating treatment are depicted in Figure 5D. Here, as the same trends sharpen, the 1:1 ratio curve (curve 5) unveils



FIGURE 5 Optical and powder XRD characterization of co-ground MAPbBr<sub>3</sub> and MAPbI<sub>3</sub> single crystals. For all sections, the mass percentage of MAPbI<sub>3</sub> in samples 1 to 7 is 0, 5, 10, 20, 50, 80, and 100, respectively. A, Appearance of the co-ground samples. B, Absorbance of the samples-dotted lines represent the co-ground samples and solid lines represent the same samples after 70°C treatment for 24 hours. C, Powder XRD curves of the samples. D, Powder XRD curves for the samples after the heating treatment, as shown in B. XRD, X-ray diffraction

completely chaotic phase mixture between cubic and tetragonal because of I/Br exchange. The calculated energy for the entrance of bromide to MAPbI<sub>3</sub> is in the range of -0.48 to -0.54 eV (see Supporting Information for DFT calculations). Therefore, the suggested vacancies-assisted mechanism is combining the entrance of iodide to the MAPbBr<sub>3</sub> vacancies with the movement of bromides to replace iodides in MAPbI<sub>3</sub>. Elevating temperatures were shown to promote vacancies in perovskites and also to raise the energy of the reactants and thus advance the reactions forward.

Two additional ion-exchange reactions were examined in order to find out whether the cation or the metal ion can be replaced. Single crystals of MAPbBr<sub>3</sub> were dipped in methanol solution of CsBr and did not show signs of degradation (Figure S4). Stabilizing conditions were found for SnBr<sub>2</sub> in 2-methoxyethanol as well. Elemental analyses detected that caesium was not detected in the crystals by measurable quantities even after a heating treatment. Nonetheless, Sn<sup>2+</sup> ions were detected on the very edges of the treated crystals, but not in the bulk (Figure S5). Both reactions were calculated to have reasonable energy differences of 0.28 and -0.054 eV for Sn<sup>2+</sup> and Cs<sup>+</sup> exchanges, respectively. Yet, the vacancy mobility activation energies of these species were reported to be high, which may hinder the progression of these reactions.<sup>25</sup>

#### 3 | CONCLUSION

In conclusion, it was established that the right combination between salt and solvent can result in ion-exchange reactions on the surface of perovskite single crystals. The introduced ions migrate according to the lattice ion migration and physical properties. As the propagation of the reactions is directional from the margins inwards, anisotropic crystals may be formed and further investigated along with the ion migration properties of perovskite. Furthermore, the preparation of otherwise inaccessible perovskite crystal compositions and morphologies can be achieved. Additionally, the integration of various additives can be investigated using this method.

#### 3.1 | Experimental section

#### 3.1.1 | Materials and methods

#### Materials

Hydrochloric acid 37%, hydrobromic acid 48% (99.99% pure), hydroiodic acid 57% (99.99% pure), PbBr<sub>2</sub> 99%, PbI<sub>2</sub> 99%, CsBr 99.99%, SnBr<sub>2</sub>, methanol anhydrous 99.8%, 2-methoxyethanol anhydrous 99.8%, and isopropanol

anhydrous 99.5% were purchased from Sigma. Methylamine 40% in methanol was purchased from TCI Ltd. Ethanol extra dry 99.5%, DMSO extra dry, and *N*,*N* dimethylformamide (DMF) extra dry 99.8% were purchased from Acros Organics.

#### Methylammonium iodide/bromide/chloride synthesis

Hydroiodic/hydrobromic/hydrochloric acid (10% molar excess) was added dropwise to a methylamine solution (40% in methanol) and stirred for 2 hours in an ice bath. The precipitate was recovered using a rotatory evaporator at 60°C. The solid was then dissolved in ethanol and recrystallized using ether and filtered three times. Finally, the resulting MAI/MABr/MACl powder was dried in a vacuum oven at 70°C overnight.

# Methylammonium lead bromide/iodide single crystal growth

MAPbBr<sub>3</sub> single crystals were grown through an antisolvent-assisted crystallization method. Typically, an equimolar solution of PbBr<sub>2</sub> and MABr (1 M, in 825  $\mu$ L DMF, 175825  $\mu$ L DMSO) was placed on a hot plate (70°C) in an inert atmosphere glovebox for 2 hours. Subsequently, the solution was placed in a 4 mL vial, which was in turn placed in an 18 mL vial, containing ethanol (ca. 4 mL). Clear single crystals of MAPbBr<sub>3</sub> appeared after 2 days at room temperature and were allowed to keep growing to their maximal size for another 1 to 2 days. A typical sample is shown in Figure S7. MAPbI<sub>3</sub> single crystals were grown utilizing a previously reported inverse temperature crystallization method.<sup>26</sup>

#### Ion-exchange reactions of MAPbBr<sub>3</sub> single crystals

After drying the methylammonium lead bromide single crystals, they were placed in a vial filled with an ethanol solution of methylammonium chloride or methylammonium iodide (10 mg/mL) for the chloride/ iodide ion exchange. Alternatively, MAPbBr<sub>3</sub> single crystals were dipped in an isopropanol solution of MACl (10 mg/mL) for the isopropanol chloride reaction. For the Cs<sup>+</sup> reaction, MAPbBr<sub>3</sub> single crystals were dipped in CsBr methanol solution (10 mg/mL) and the vial was placed on a hot plate at 70°C. For the Sn<sup>++</sup> substitution, the crystals were reacted inside an inert atmosphere glovebox with SnBr<sub>2</sub> 2-methoxyethanol solution (10 mg/mL).

#### Absorbance measurements

Perovskite crystals were crushed between two microscope glasses by hand. Afterwards, the specimen absorbance was measured in an integrating sphere spectrophotometer (Varian Cary 5000 UV-Vis-IR spectrophotometer DRA-2500).

#### Powder XRD measurements

The crystals were ground using an agate mortar and pestle and then placed on a quartz holder. Subsequently, the measurements were carried out on a D8 Advance diffractometer (Bruker AXS) with a secondary graphite monochromator.  $2\theta$  diffractions were recorded at room temperature with CuKa radiation ( $\lambda = 1.5418$  Å) at a tube voltage of 40 kV, a tube current of 40 mA, a step size of  $0.02^{\circ}$ , and a counting time of 1 second per step. For the extraction of crystalline parameters, TOPAS V3.0 software and EVA software were used. The same measurement procedure was performed for intact single crystals as well. The penetration depth through the crystal was calculated to be ca. 15 µm.

#### Electron microscopy and elemental analysis

SEM images were taken using an extra high-resolution SEM Magellan 400L (FEI), and the EDS line scans were performed using a silicon drift detector Oxford X-Max on the INCA 450 platform (5 keV). WDS analyses were performed over an electron probe microanalyzer (EPMA) instrument (JEOL Superprobe JXA-8230), and the line measurements were performed using a WDS detector for 200 consequent measurements.

#### DFT calculation methods

DFT calculations were performed using the Quantum ESPRESSO package.<sup>27</sup> This code is based on the plane waves and the pseudopotentials for the atomic cores. The gradient-corrected Perdew-Burke-Ernzerhof parametrization of the exchange-correlation functional was used. The energy cutoffs of 60 Ry for the plane waves and 300 Ry for the density were set. The uniform k-mesh with the  $8 \times 8 \times 8$  grid was sufficient to converge the total energies. The atomic structures were optimized using the Broyden-Fletcher-Goldfarb-Shanno algorithm,<sup>28</sup> until the atomic forces were smaller than 1 meV/Å.

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#### **CONFLICT OF INTEREST**

The authors declare no conflicts of interest.

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8

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#### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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