

Thermal and Structural Characterization of Methylammonium- and Formamidinium-Halide Salts

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Four organic halide salts of interest to alloyed perovskite solar cell fabrication are characterized using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), powder x-ray diffraction (XRD), and thermogravimetric analysis. The chemical and crystal structures of methylammonium iodide (MAI), methylammonium bromide (MABr), and formamidinium iodide (FAI) are confirmed, and the experimental ATR-FTIR spectrum and XRD pattern of formamidinium bromide (FABr) are presented. The enthalpy, ΔH_{vap} , and entropy, ΔS_{vap} , of vaporization are quantified for each salt and are used to estimate their vapor pressures in the temperature range of 150–300 °C. MAI, MABr, and FAI have similar vapor pressures in this temperature range, while FABr has a higher vapor pressure in the temperature range of 150–240

 $^{\circ}$ C. This data provides a foundation for achieving effective control of vapor phase concentrations for vapor processing of alloyed perovskite solar cells.

1 Introduction

Hybrid perovskite materials have attracted substantial interest over the past decade due to their impressive solar cell power conversion efficiency and increasingly promising stability.^[1, 2, 3] Many improvements have been attributed to the effects of alloying methylammonium lead triiodide (MAPbI_s) with formamidinium (FA), cesium, and bromide. Incorporating these components into the material allows the perovskite's electronic, optical, and structural properties to be tuned, resulting in improved stability and increased stabilized power output of the solar cell.^[4, 5, 6] This in turn increases the commercial viability of perovskite solar cells, even though some questions regarding manufacturing remain unanswered. While a variety of viable solution and vapor processes exist for high-throughput perovskite production, some unresolved issues remain with producing and validating complex stoichiometries that contain multiple components, such as $Cs_x (MA_yFA_1 - y)_{1-x}Pb(I_1 - yBr_y)_3$.^[5]

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Here we focus on the challenge of incorporating alloys in vapor processes. While there are many vapor deposition processes, most fall into one of two categories: single-step processes such as co-evaporation,^[7, 8, 9] and sequential, deposition-plus-reaction processes.^[10, 11, 12, 13] In co-evaporation systems, it has proven difficult to control the flux of volatile organic reactants such as methylammonium iodide (MAI) using, for example, quartz crystal microbalance (QCM) technology.^[11, 14, 15, 16] This is due to the high vapor pressure and low sticking coefficient of MAI, such that it does not obey line-of-sight mass transport nor does it deposit uniformly on the QCM surface.^[17] Some have tried to circumvent this problem by depositing the perovskite at a fixed system pressure and assuming that the measured pressure is equal to the volatile organic salt's partial pressure.^[14, 15, 16] While this approach might suffice to produce simple perovskite chemistries, such as MAPbI₃, for complex stoichiometries containing MA, FA, Cs, and Br, its usefulness is limited due to a lack of control over each species' flux. Similar problems arise in sequential, deposition-plus-reaction processes, where a PbI₂ precursor film is reacted with ambient MAI vapor at a fixed temperature over a period of time.^[10, 13] Here, there is limited understanding of the rate of the MAI delivery as well as intrinsic reaction kinetics. Again, while this approach may be used to produce perovskites with simple stoichiometries, it is difficult to determine the composition of alloyed perovskite films without an understanding of species-specific fluxes to the sample surface. Without this knowledge, scaled-up vacuum deposition processes are significantly harder to design and implement.

A central problem with these two approaches is a lack of information on the vapor pressures (p_{vap}) of the organic precursor salts used to alloy the perovskite film (MABr, FAI, and FABr). With known vapor pressures, the flux of each species may be evaluated from measured temperatures, using standard transport phenomena calculations, and the final composition may be estimated from the flux ratios.^[18, 19, 20] In this article, the enthalpy (ΔH_{vap}) and entropy (ΔS_{vap}) of vaporization for MAI, MABr, FAI, and FABr are evaluated using thermogravimetric analysis (TGA). Using a Clausius-Clapeyron fit, the vapor pressure of each species is quantified over the temperature range T = 150-300 °C. The syntheses of MAI, MABr, and FAI are confirmed using attenuated total reflectance spectroscopy Fourier transform infrared spectroscopy (ATR-FTIR), and powder X-ray diffraction patterns (XRD) are presented for each salt. To the best of our knowledge, as of the time of this writing, no X-ray diffraction standards for FAI or FABr exist in the International Centre for Diffraction Data (ICDD) database. We validate our methods by comparing ATR-FTIR spectra,^[21] XRD patterns, and thermodynamic properties of MAI^[22] with literature and then apply them to MABr, FAI, and FABr.

2 **Results**

2.1 ATR-FTIR spectroscopy

ATR-FTIR spectroscopy was carried out on powders of each MA- and FA-salt, and the spectra are shown in **Figure 1**. Peak positions and assignments for MAI and MABr are provided in Table S1. The measured peaks for each CH_3 , C–N, and NH_3 mode are consistent with previous reports and confirm the synthesis of MAI and MABr.^[21, 23] Notably, the MABr peaks are shifted toward higher wavenumber than the MAI peaks, likely due to different hydrogen bonding interactions between the halides.^[24]









Peak positions and assignments for FAI and FABr are listed in Table S2, and are consistent with previous reports.^[23, 24] The appearance of asymmetric NH_2 stretching vibrations > 3000 cm⁻¹, and the NCN stretch at $\approx 1690 \text{ cm}^{-1}$, confirms the formation of the formamidinium salt. The FABr spectrum is nearly identical to that of FAI with strong absorptions of NH_2 > 3000 cm⁻¹ and NCN $\approx 1700 \text{ cm}^{-1}$ which confirm its structure. As with the MAI salts, many of the FABr absorption peaks appear to be shifted to higher wavenumber.^[24] It is possible that some NH₄I or NH₄Br may be present as a degradation side product of FAI or FABr, respectively,^[25, 26, 27] but, due to the overlapping absorption of NH vibrational modes at $\approx 1390 \text{ cm}^{-1}$, 3050 cm⁻¹, and 3100 cm⁻¹, their presence cannot be confirmed using ATR-FTIR spectroscopy.^[28]

2.2 X-ray diffraction analysis

Figure 2 shows powder XRD scans carried out on each of the MA- and FA-salts. The MAI and MABr patterns have a near-perfect match to their reference patterns in the ICDD (00-010-0737 and 00-010-0699, respectively). This corroborates the match to published ATR-FTIR spectra and confirms each species was synthesized successfully.

In the absence of FAI or FABr standards in the ICDD, it is difficult to confirm the structure of these materials. However, several published patterns for FAI can be used for comparison.^[29, 24] Previous work on theoretical and single crystal diffraction patterns suggests that FAI can exist in up to three different phases depending upon the temperature of the sample, although it is thought to exist in the monoclinic space group $P2_1/c$ at room temperature.^[29] Several characteristic diffraction peaks for FAI were observed to be in agreement with literature and are listed in Table S3.^[29] However, several of these peaks are difficult to distinguish from the background due to the strong reflection at $2\theta = 25.7^{\circ}$. It is possible that a spurious orientation effect may have been introduced during the powder pressing process due to strong hydrogen bonding within the FAI crystals,^[24] resulting in the strong reflection at $2\theta = 25.7^{\circ}$.

As for the FABr sample, assigning a crystal structure is beyond the scope of this work; nevertheless, for completeness, the experimental data are provided. One might expect a similar structure to FAI, with shifted peak positions due to the smaller Br atoms, however, due to the temperature dependence of the FAI structure,^[24, 29] this might not be the case. It is worth mentioning that several of the measured diffraction peaks of the FABr sample align with the XRD pattern of cubic NH_4Br (ICDD 00-001-0974) and are marked in Table S3 of the Supplementary Information. These NH_4Br peaks have lower intensities than the FABr peaks and likely indicate that a trace amount of NH_4Br is present in the sample purchased from Sigma Aldrich.

2.3 Thermogravimetric analysis

Single-pass TGA scans on each MA- and FA- salt are shown in **Figure 3**. All four salts lose mass in a single, broad step, although there are small kinks in the FAI and FABr curves at T $\approx 250-255$ °C, which are thought to correspond to the melting point of these substances.^[29] Here, FABr begins evaporating at the lowest temperature with MAI, MABr, and FAI starting to evaporate around the same temperature. MAI appears to finish evaporating first, at a temperature around 340 °C, followed by MABr at 360 °C, and both FAI and FABr around 400 °C. While trace NH₄Br was observed in the XRD pattern of FABr, it does not appear to affect the rate of mass loss likely due to its high vapor pressure[30] and low concentration.



Figure 3: Single-pass TGA curves for each MA- and FA-salt. Scans take place from 25 °C to 500 °C at 10° Cmin⁻¹ under a N₂ flow at 50 mLmin⁻¹.

Since mass loss occurs in a single step, the thermodynamic properties of vaporization (ΔH_{vap} and ΔS_{vap}) can be determined using the method described in section 5. This method was applied to each MA and FA salt, and the rates of mass loss are shown in Figure S1 of the Supplementary Information. In general, the data indicates a linear rate of mass loss for each salt. While there is some curvature to the measured mass of MAI at 300°C, this divergence from a linear rate of mass loss can be attributed to depletion of the MAI powder and small deviations in the holding temperature during the experiment.

The average rate of mass loss, \dot{m}_{sub} , was evaluated from the mass loss profiles at each temperature for each salt and used for further analysis. Equations (S1)–(S4) were applied to produce the mass loss plots shown in Figure S2 and calculate ΔH_{vap} and ΔS_{vap} . The fitting parameters are shown in Table S4 with R^2 -values > 0.986 and R^2_{adj} -values > 0.983 indicating reasonably good agreement between the model and the data without over-constraining the model. This justifies the use of the slope and the intercept to extract the thermodynamic data for each salt. Values of ΔH_{vap} and ΔS_{vap} determined from Figure S2 are presented in **Table 1**. These results show that the volatility of the salts increase in order of MAI, MABr, FAI, and FABr, with FABr being significantly more volatile than the others. In previous work on MAI,^[22] the extrapolated thermodynamic parameters were $\Delta H_{vap} = 105 \pm 5$ kJ mol-1 and $\Delta S_{vap} = 210 \pm 14$ J mol-1 ($T_{sub} = 247 \pm 26^{\circ}$ C). There is good agreement between ΔH_{vap} presented here and from literature, but ΔS_{vap} differs by ≈ 60 J mol-1K-1. This deviations may be due to differences in measurement protocol, such as total mass of the MAI sample or different N₂ flow rates. Nevertheless, the agreement in ΔH_{vap} confirms the validity of this method and suggests that the values of ΔH_{vap} for MABr, FAI, and FABr are accurate.

Salt	ΔH_{vap} [kJ mol ⁻¹]	ΔS_{vap} [J mol ⁻¹ K ⁻¹]
MAI	96,6	153,12
MABr	89,1	141,1
FAI	86,1	136,3
FABr	47,3	70,5

Table 1: Enthalpy and entropy of vaporization for each MA- and FA-salt, where the error barsrepresent the 95% confidence interval for each value.

The calculated vapor pressure of each MA- and FA-salt is plotted vs 1/T in Figure 4. There is significant overlap between MAI, MABr, and FAI, indicating that their vapor pressures are approximately equal across the range of temperatures tested. FABr deviates from the other salts at lower temperature, with a higher vapor pressure in correspondence with its higher volatility.



Figure 4: Vapor pressure fits for each salt. The error bars represent the 95% confidence intervals of each sample.

3 Discussion

The absence of secondary mass loss events in the single-pass TGA scans indicates that the powders do not undergo decomposition prior to evaporation. We note that both MAI and FAI have been documented to decompose on evaporation.^[17, 31, 32] Therefore, the vapor pressure can be used

to quantify the partial pressure of each decomposition product. For example, in the case of MAI, the proposed degradation pathways are

$$CH_{3}NH_{3}I(s) \rightarrow [\Delta]CH_{3}NH_{2}(g) + HI(g)$$
(1)

$$CH_3NH_3I(s) - > [\Delta]CH_3I(g) + NH_3(g)$$
(2)

where equation 2 is thought to be favored at temperatures below $350 \degree C$.^[17, 31] For the case of FAI, the proposed degradation pathways are^[31, 32]

$$CH(NH_{2})2I(s) -> [\Delta]1/3(HCN)_{3}(g) + NH_{3}(g) + HI(g)$$
(3)

$$CH(NH_{2})2I(s) -> [\Delta]HCN(g) + NH_{3}(g) + HI(g)$$
(4)

$$CH(NH_{2})2I(s) -> [\Delta]CN_{2}H_{5}(g) + HI$$
(5)

where equation 3 is thought to be favored below $350 \,^{\circ}$ C.^[31] In either case, the products of a given degradation pathway form according to the stoichiometry of the decomposition process, with the sum of the partial pressures of each degradation product equal to the vapor pressure of the salt in question multiplied by its stoichiometric coefficient. However, while the degradation pathways of MAI and FAI are well-documented,^[17, 31, 32] those of MABr and FABr are not as well-established. It is likely that these bromide salts have similar degradation pathways to their iodine counterparts.

The data presented here allows researchers to quantify the vapor pressure of MAI, MABr, FAI, and FABr and calculate the partial pressure of each degradation product for vapor phase perovskite processing. By controlling source temperatures, an appropriate amount of each species can be delivered to the substrate in both batch and continuous processes. This should improve the understanding of vapor phase deposition and reaction processes and allow more precise control over the deposited perovskite's stoichiometry. The concentration data and models developed from this data will serve as a cornerstone for the design of scaled-up vapor-phase perovskite processing systems.

4 Conclusion

The organic halide salts MAI, MABr, FAI, and FABr were characterized using ATR-FTIR, XRD, and TGA to confirm their identities, provide experimental diffraction patterns, and to evaluate the equilibrium vapor pressure parameters ΔH_{vap} and ΔS_{vap} . MAI, MABr, and FAI were found to have near-identical vapor pressures over the window of temperatures tested. FABr was found to have a significantly higher vapor pressure than the other salts from 150–240 °C but begins to overlap from 240–300 °C. With this data, the temperature-dependent vapor pressure can be evaluated for any vapor processing system of interest, allowing more precise control over the stoichiometry of alloyed perovskite thin films.

5 Methods

Synthesis of MAX and FAX

MAI and MABr were synthesized based on procedures established in literature.[33, 34] 40 mL hydroiodic acid (57 wt.% in water, Sigma Aldrich) or 31 mL hydrobromic acid (48 wt.% in water, Sigma Aldrich) were added drop-wise to a 38 mL methylamine solution (33 wt.% in absolute ethanol 98%, Sigma Aldrich) in argon and stirred at room temperature for 2 hours. The resulting solution was dried until a white precipitate formed, which was collected and rinsed with diethyl ether (Fisher). The powder was recrystallized twice from ethanol (Decon), rinsed well with diethyl ether, dried, and stored in a dry N_2 desiccator.

For FAI synthesis,^[23] 19.7 g formamidinium acetate (Sigma Aldrich), was added to a beaker of 50 mL HI at 0 °C under argon and stirred for 2 hours. Solutions were then dried at T < 50 °C. The resulting white solids were recrystallized from ethanol twice at T < 50 °C and rinsed well with diethyl ether. Moderate temperatures were used during the purification steps to avoid decomposition of the FA+ ion to NH_3/NH_4^+ .

Due to difficulties in preventing the decomposition of the FA cation during FABr synthesis and in separating synthesized FABr from the side product of NH_4Br , FABr was purchased from Sigma Aldrich (98%), and the ATR-FTIR, XRD, and TGA analyses were performed on the commercial salt.

Measurement procedures

Prior to measurement, all samples were ground to a fine powder using a mortar and pestle in an inert N_2 glovebox.

ATR-FTIR spectra were recorded using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with an ATR element accessory. The ATR attachment was fitted with a ZnSe crystal and powder samples were held in direct contact with the crystal using an attached clamp.

Powder samples were prepared for XRD by pressing the ground powder sample into a platen using a clean glass slide. Powder XRD patterns were obtained using a Rigaku D/Max 2200 scanning x-ray diffractometer with a CuK α X-ray source operating at 40 kV and 40 mA in Bragg-Brentano parafocusing geometry. Scans were carried out from 5–90° at a rate of 0.5° min⁻¹. The XRD sample chamber was filled with Ar to prevent the hygroscopic FABr powder from absorbing moisture.

Thermal analysis was carried out using a TA Instruments Discovery TGA. The TGA pans were scrubbed using ethanol and heated with a blowtorch prior to weight calibration and sample measurement. Scans were performed under a nitrogen flow of 50 mLmin⁻¹. Single pass TGA scans were carried out from 25 °C to 500 °C at a heating rate of 10 °Cmin⁻¹. Incremental isothermal scans were performed by heating a sample from 25 °C to 150 °C at a rate of 25 °C to 150 °C at a rate of 25 °C min⁻¹, holding for a 10 min period, and ramping to the following temperature setpoint. The isothermal temperature setpoints of 150, 200, 225, 250, 275, and 300 °C were used for each sample.

Determining vapor pressure

The following equations are used to determine the enthalpy of vaporization, ΔH_{vap} , and

the entropy of vaporization, ΔS_{vap} , for each species from the TGA measurements and to evaluate their vapor pressures, p_{vap} , with an associated 95% confidence interval. First, according to an expression from Langmuir, p_{vap} , is a function of the rate of mass loss due to sublimation, \dot{m}_{sub} , and temperature, T.^[35]

$$p_{vap} = \frac{\dot{m}_{sub}}{A} \sqrt{\frac{2\pi RT}{M_{w}}}$$
(6)

Here, A is the exposed area of the evaporating species, R is the ideal gas constant, and M_w is the molecular weight.

Next, p_{vap} is related to ΔH_{vap} through the Clausius-Clapeyron equation.

$$\frac{\mathrm{d}\ln p_{vap}}{\mathrm{d}T} = \frac{\Delta H_{vap}}{RT^2} \tag{7}$$

When evaluated as an indefinite integral, the Clausius-Clapeyron equation becomes

$$\ln p = \frac{-\Delta H_{vap}}{RT} + C,$$
(8)

where C is a constant of integration.

Equation (6) and (8) can then be combined to relate \dot{m}_{sub} with ΔH_{vap} .

$$\ln\left(\frac{\dot{m}_{sub}}{A}\sqrt{\frac{2\pi RT}{M_{w}}}\right) = \frac{-\Delta H_{vap}}{RT} + C$$
(9)

For TGA measurements of powder samples, the exposed area, A, is approximated from the 1 cm diameter of the TGA pan. By substituting the appropriate values for M_w , \dot{m}_{sub} , and T, the left-hand-side can be plotted vs. 1/T to give a straight line whose slope m, and intercept C, are used to determine, respectively, ΔH_{vap} and ΔS_{vap} .^[36]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors have no conflict of interest to declare.

Data Availability Statement The data that support the findings of this study are openly available in Mendeley Data at http://doi.org/10.17632/647z57d26b.2, reference number ^[37].

References

[1] Christians J. A., Schulz P., Tinkham J. S., Schloemer T. H., Harvey S. P., Tremolet de Villers B. J., Sellinger A., Berry J. J., Luther J. M., *Nat. Energy* **2018**, *3* 68.

[2] Grancini G., Roldán-Carmona C., Zimmermann I., Mosconi E., Lee X., Martineau D., Narbey S., Oswald F., De Angelis F., Graetzel M., Nazeeruddin M. K., *Nat. Commun.* **2017**, *8*1.

[3] NREL, Best research-cell efficiency chart, URL https://www.nrel.gov/pv/cell-efficiency.html .

[4] Eperon G. E., Stranks S. D., Menelaou C., Johnston M. B., Herz L. M., Snaith H. J., *Energy Envrion. Sci.* **2014**, 7 982.

[5] Saliba M., Matsui T., Seo J., Domanski K., Correa-Baena J., Nazeeruddin M. K., Zakeeruddin S. M., Tress W., Abate A., Hagfeldt A., Grätzel M., *Energy Environ. Sci.* **2016**, *9* 1989.

[6] Noh J. H., Im S. H., Heo J. H., Mandal T. N., Seok S. I., *Nano Lett.* **2013**, *13* 1764.

[7] Gil-Escrig L., Dreessen C., Kaya I. C., Kim B., Palazon F., Sessolo M., Bolink H. J., ACS Energy Lett. **2020**, 5 3053.

[8] Igual-Muñoz A. M., Navaroo-Alapont J., Dreessen C., Palazon F., Sessolo M., Bolink H. J., *Chem. Mater.* **2020**, *32* 8641.

[9] Gil-Escrig L., Momblona C., La-Placa M. G., Boix P. P., Sessolo M., Bolink H. J., Adv. Energy Mater. **2018**, 81.

[10] Harding A. J., Kuba A. G., McCandless B. E., Das U. K., Dobson K. D., Ogunnaike, B. A., Shafarman W. N., *RSC Adv.* **2020**, *10* 16125.

[11] Kam M., Zhu Y., Zhang D., Gu L., Chen J., Fan Z., Sol. RRL 2019, 3 1900050.

[12] Choi W., Na S., Park C., Moon T., Sol. Energy 2019, 178 56.

[13] Leyden M. R., Ono L. K., Raga S. R., Kato Y., Wang S., Qi Y., J. Mater. Chem. A 2014, 2 18742.

[14] Arivazhagan V., Xie J., Yang Z., Hang P., Paravathi M., Xiao K., Cui C., Yang D., Yu X., *Sol. Energy* **2019**, *181* 339.

[15] Hsiao S., Lin H., Lee W., Tsai W., Chiang K., Liao W., Ren-Wu C., Chen C., Lin H., Adv. Mater. **2016**, 28 7013.

[16] Kim B., Choi M., Choi M., Kim J., J. Mater. Chem. A 2016, 4 5663.

[17] Bækbo M. J., Hansen O., Chorkendorff I., Vesborg P. C. K., *RSC Adv.* **2018**, 8 29899.

[18] Bird R. B., Stewart W. E., Lightfoot E. N., *Transport Phenomena*, John Wiley & Sons, Inc., 2 edition, **2007**.

[19] Welty J. R., Rorrer G. L., Foster D. G., *Fundamentals of Momentum, Heat, and Mass Transfer*, John Wiley & Sons, Inc., 6 edition.

[20] Smith D. L., *Thin Film Deposition: Principles and Practice*, McGraw-Hill, Inc., New York, **1995**.

[21] Cabana A., Sandorfy C., Spectrochim. Acta. 1962, 18 843.

[22] Dualeh A., Gao P., Seok S. I., Nazeeruddin M. K., Grätzel M., *Chem. Mater.* **2014**, 26 6160.

[23] Bukleski M., Dimitrovska-Lazova S., Aleksovska S., Maced. J. Chem. Chem. Eng. 2019, 38, 2 237.

[24] Mencel K., Durlak P., Rok M., Jakubas R., Baran J., Medycki W., Cizman A., Piecha-Bisiorek A., *RSC Adv.* **2018**, 8 26506.

[25] Soumpos C. C., Malliakas C. D., Kanatzidis M. G., Inorg. Chem. 2013, 52 9019.

[26] Van Gompel W. T. M., Herckens R., Reekmans G., Ruttens B., D'Haen J., Adriaensens P., Lutsen L., Vanderzande D., J. Phys. Chem. C 2018, 122 4117.

[27] Schaefer F. C., Hechenbleikner I., Peters G. A., Wystrach V. P., J. Am. Chem. Soc. 1959, 81 1466.

[28] Bovey L. F. H., J. Opt. Soc. Am. 1951, 41 836.

[29] Petrov A. A., Goodilin E. A., Tarasov A. B., Lazarenko V. A., Dorovatovskii P. V., Khrustalev V. N., *Acta Cryst.* **2017**, *E73* 569.

[30] -Stull D. R., Ind. Eng. Chem. 1947, 39 517.

[31] Ma L., Guo D., Li M., Wang C., Zhou Z., Zhao X., Zhang F., Ao Z., Nie Z., *Chem. Mater.* **2019**, *31* 8515.

[32] Juarez-Perez E. J., Ono L. K., Qi Y., J. Mater. Chem. A. 2019, 7 16912.

[33] Lee M. M., Teuscher J., Miyasaka T., Murakami T. N., Snaith H. J., *Science* **2012**, *338* 643.

[34] Sawanta S. M., Chang S. S., Chang K. H., NPG Asia Mater. 2015, 7 e208.

[35] I. Langmuir, *PRA* **1913**, *2*, 5 329.

[36] Abrefah J., Olander D. R., Balooch M., Siekhaus W. J., *Appl. Phys. Lett.* **1992**, *60*, 1313 1313.

[37] Harding A., Dobson D., Ogunnaike B., Shafarman W., ATR-FTIR, XRD, and TGA data for methylammonium iodide, methylammonium bromide, formamidinium iodide, and formamidinium bromide characterization, Mendeley Data, V2, doi: 10.17632/647z57d26b.2, **2021**.



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