

Emergence of a Relaxor Phase and Dimensional Tuning in Mixed 2D Hybrid Perovskites

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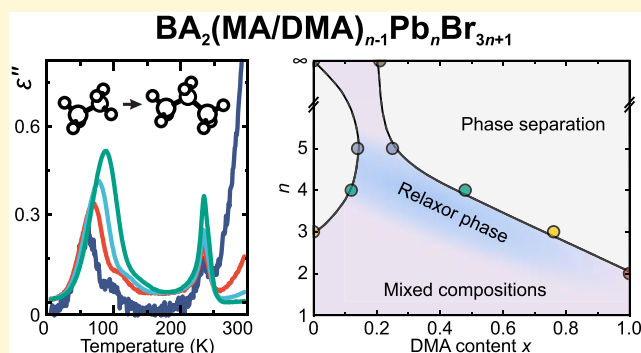


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ABSTRACT: Mixing of molecular cations in hybrid lead halide perovskites offers a powerful route to tailor their optoelectronic functionality, structural stability, and phase transition behavior. While such compositional engineering has been extensively studied in three-dimensional perovskites, its impact on low-dimensional analogues remains largely unexplored. Here, we investigate cation mixing in the Ruddlesden–Popper $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ two-dimensional perovskites using a comprehensive multitechnique approach. We show that substituting methylammonium (MA) with dimethylammonium (DMA) transforms the long-range ferroelectric phase into a state characterized by frustrated electric dipoles. Broadband dielectric measurements reveal that this state is a relaxor phase, which was previously unobserved in three-dimensional hybrid perovskites. Remarkably, cation mixing also governs perovskite dimensionality, enabling stabilization of thick-slab members up to $n = 5$ in single-crystal form. These results establish cation mixing as a versatile tool for controlling both polar order and dimensionality in two-dimensional hybrid perovskites.



INTRODUCTION

Hybrid perovskites have emerged as a highly promising class of materials for photovoltaic and optoelectronic applications.^{1–4} Solar cells based on three-dimensional (3D) lead halide hybrid perovskites, such as MAPbX_3 ($X = \text{I}, \text{Br}, \text{Cl}$), have achieved power conversion efficiencies exceeding 25%, rivaling established silicon-based technologies.^{3,5–9} These materials adopt the perovskite architecture, which consists of corner-sharing lead-halide octahedra that form extended 3D networks containing small organic cations such as methylammonium (MA), formamidinium (FA), and others.^{8–12}

In parallel to the 3D perovskites, considerable attention has been devoted to lower-dimensional hybrid perovskite structures, in which the perovskite motifs are separated by bulky organic spacer cations, giving rise to unique and highly tunable properties.^{12–15} A prominent example of this class is the family of two-dimensional (2D) Ruddlesden–Popper (RP) perovskites described by the general formula $\text{A}'_2\text{A}_{n-1}\text{Pb}_n\text{X}_{3n+1}$ ($n \geq 2$), where A denotes a small “perovskitizer” cation, and A' is a large monovalent spacer cation.^{16–19} In these structures, the organic spacer cations separate slabs of the perovskite framework consisting of n octahedral layers. Tuning the dimensionality in these systems through controlled variation of n is synthetically demanding, and the growth of larger single crystals has usually been restricted to $n = 3$,^{12,17,20} with very

few known $n = 4$ analogues,^{21,22} whereas higher values up to $n = 7$ can be achieved in microcrystals, thin films, and crystals with a large lateral size but a small thickness of about 500 nm.^{23–26}

Beyond their optoelectronic applications,^{15,21,27} 2D perovskites also exhibit phenomena that are absent in 3D analogues, including ferroelectric phase transitions that enable reversible switching of macroscopic electric polarization under an external electric field.^{12,17,20,28} This behavior allows the design of dielectric and piezoelectric responses, opening avenues for piezoelectric sensors,^{29,30} nonlinear optics,^{31,32} and dielectric switches,^{33,34} and other multifunctional devices that combine optoelectronic and ferroic functionalities.

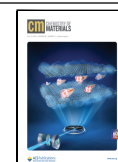
In 3D hybrid perovskites, molecular cation mixing has been shown to significantly enhance photovoltaic performance and stability, and a wide range of organic cations has been proposed and investigated at both the fundamental and device levels.^{12,35–38} Such mixing can disrupt long-range structural

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ordering, suppress structural phase transitions, and introduce molecular cation frustration, giving rise to glassy dynamics of electric dipoles.^{12,39–44} However, neither direct evidence of dipole freezing nor a ferroelectric relaxor phase^{45,46} has been reported in 3D hybrid perovskites, reflecting their intrinsically nonferroelectric nature.^{47–51} In contrast, in 2D hybrid perovskites, where ferroelectric order is frequently observed, the impact of molecular cation mixing on dipolar dynamics and phase behavior remains poorly explored.^{52,53} Here, of particular interest is the relaxor phase, which in classical inorganic systems has enabled a broad range of applications, including transducers, actuators, sensors, high-energy-density capacitors, and electro-optical devices.^{45,46}

Here, we employ a multitechnique approach to investigate the effects of molecular cation mixing in the ferroelectric 2D hybrid perovskite family $\text{BA}_2(\text{MA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ (BA = butylammonium),^{17,20} where we replace the MA cation by the bulkier dimethylammonium (DMA). The choice of DMA is motivated by its relatively large electric dipole moment¹² and by its ability to significantly alter structural phase transitions in 3D hybrid perovskites.^{41,54} We show that DMA incorporation in 2D compounds affects phase transitions and introduces molecular cation frustration, leading to the formation of a relaxor phase. Moreover, cation mixing enables access to high-*n* single crystals, providing a unique and efficient route to tune the dimensionality of layered hybrid perovskites.

■ EXPERIMENTAL SECTION

Sample Synthesis

All reagents were purchased from Sigma-Aldrich and used without further purification (PbBr_2 99%, HBr 48% in H_2O , 2.0 M solution of methylamine (MA) in methanol, 2.0 M solution of dimethylamine in methanol).

In order to grow $\text{BA}_2\text{MA}_{1-x}\text{DMA}_x\text{Pb}_2\text{Br}_7$, 4.5 mmol of PbBr_2 was dissolved in 20 mL of HBr under stirring. Then, 4 mmol of butylamine and a solution containing dimethylamine and methylamine (different ratios with *x* from 0 to 1, step 0.1, and 3 mmol altogether) were added, and the solution was heated to 90 °C. The solution was then cooled to room temperature at a rate of 5 °C/h and left at room temperature. Light-yellow plate-like crystals, which grew at the bottom of the vial, were separated from the mother liquid after 3 days and dried at room temperature.

The same synthesis method was used for the synthesis of other compounds, where the amount of PbBr_2 (MA+DMA) was increased to 7 mmol (5 mmol), 10 mmol (7 mmol), and 12 mmol (9 mmol) for the *n* = 3, *n* = 4, and *n* = 5 phases, respectively. The phase purity and composition of the obtained samples were verified using XRD and NMR methods. All compositions reported in this work were determined from the NMR analysis. Only samples exhibiting a high phase purity were selected for further studies.

NMR

¹H NMR experiments were carried out at 14.1 T on a Bruker Avance Neo NMR spectrometer operating at 600.3 MHz using a 5 mm Bruker ¹H–¹³C-BB TBI probe. The temperature was stabilized at 298 K. A pulse sequence employing $\pi/6$ excitation was used with the following parameters: 5 s repetition delay and 64 scans accumulated. Samples were dissolved in DMSO-*d*₆ (99.96% D atom, from Sigma-Aldrich), which was also used for the lock signal. For signal assignment of different molecular motifs, a ¹H–¹H correlation spectroscopy (COSY) experiment was performed on a selected sample (see Figure S1), where 16 scans were collected for 1024 increments.

PXRD

PXRD measurements were performed at room temperature on finely ground samples in reflection geometry using a PANalytical X'Pert

PRO diffractometer equipped with a PIXcel ultrafast line detector and 0.04 rad Soller slits employing Cu K α radiation (λ = 1.5406 Å). Data were collected over the 2θ range of 3–70° with a step size of 0.026°. The analysis was carried out using the HighScore Plus software package. Lattice parameters were refined by least-squares fitting of the peak positions.

DSC

Differential scanning calorimetry (DSC) measurements were carried out by using a Mettler Toledo DSC 3 instrument under a nitrogen atmosphere. Heating and cooling scans were conducted at a rate of 5 K/min with sample masses of approximately 20 mg for all of the compositions.

Heat Capacity

Heat capacity measurements were performed using a commercial Physical Property Measurement System (PPMS) employing the thermal relaxation method. Methodological details are provided in ref 55. Due to limitations in thermal coupling between the sample and the measurement platform, two separate experimental runs were carried out for each sample using different greases optimized for distinct temperature ranges: 2–275 K and 250–375 K. In each run, the measured sample consisted of either a single crystal or several small crystals to ensure an efficient thermal response. The sample masses ranged from 1.5 mg to 4.6 mg.

Raman Spectroscopy

Room-temperature Raman spectra were measured for powder samples using a Bruker FT 100/S spectrometer with YAG:Nd laser excitation (λ_{exc} = 1064 nm) and 2 cm^{−1} spectral resolution.

Optical Absorption

Room-temperature diffuse reflectance spectra of the powder samples were measured using a Varian Cary 5E UV–vis-NIR spectrophotometer.

SHG

Second harmonic generation (SHG) measurements were performed using a laser system comprising a Coherent Astrella Ti: Sapphire regenerative amplifier (800 nm, 75 fs, 1 kHz) pumping a TOPAS Prime optical parametric amplifier (OPA). The OPA output was tuned to 1500 nm and was used unattenuated and unfocused, delivering a fluence of 0.26 mJ/cm² at the sample. Single crystals of the studied samples were mechanically crushed. The powders were packed uniformly between microscope glass slides, sealed, and mounted on a horizontal sample holder. Identical excitation parameters and geometric configurations were maintained for all samples. Signal collection was performed in the reflection mode. Specifically, the 1500 or 1550 nm laser beam was directed onto the sample at a 45° incident angle. Signal collection optics consisted of a ϕ 25.0 mm plano-convex lens (*f* = 25.4 mm) coupled to a 400 μm , 0.22 NA optical fiber and positioned perpendicular to the sample plane. The distance between the lens front surface and the sample plane was 30 mm. SHG spectra were acquired using an Ocean Optics Flame-T CCD spectrograph (200 μm entrance slit). Temperature control of the sample was performed using a Linkam LTS420 Heating/Cooling Stage. Temperature stability was 0.1 K.

Dielectric Spectroscopy

Broadband dielectric spectroscopy measurements on pellet samples in the 100 Hz–1 MHz frequency range were carried out using an HP4284A LCR meter. The complex dielectric permittivity was calculated from the measured capacitance and loss tangent of pressed pellet samples using a flat capacitor model. For experiments in the microwave (GHz) frequency range, the complex reflection coefficient was measured by using an Agilent 8714ET vector network analyzer. The real and imaginary parts of the complex dielectric permittivity were then calculated using a multimode capacitor model.⁵⁶ Temperature-dependent dielectric spectra were recorded on cooling at a rate below 1 K/min. Silver paste was used for the sample electrodes.

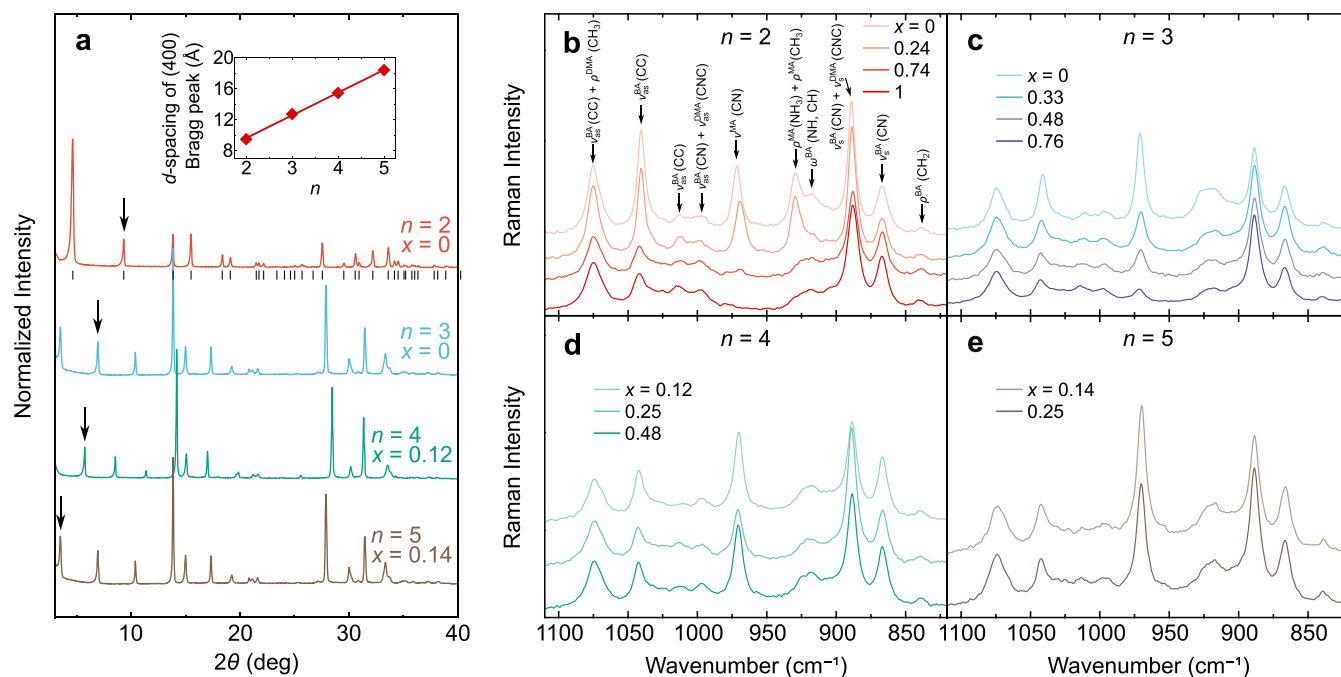


Figure 1. Characterization of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$. (a) Room-temperature PXRD patterns of selected samples with the lowest DMA concentration for different n values. Arrows indicate reflections corresponding to the perovskite-slab stacking periodicity. Black tick marks indicate simulated Bragg reflections for $\text{BA}_2\text{MAPb}_2\text{Br}_7$. The inset highlights the systematic increase in basal plane spacing, confirming successful growth of crystals with n up to 5. (b) Room-temperature Raman spectra of the studied mixed compounds with different values of n . Arrows mark molecular vibrations assigned to different molecular cations.

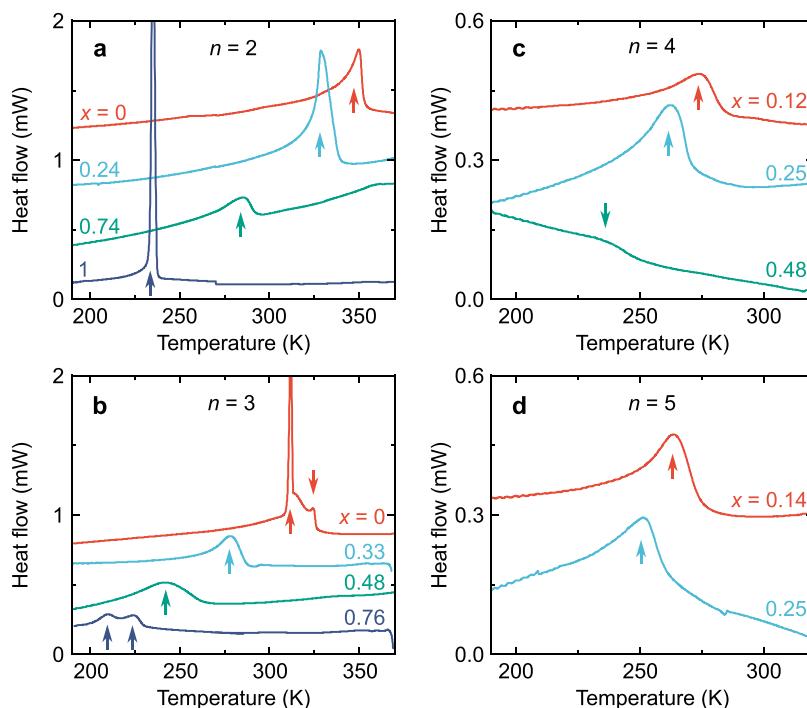


Figure 2. Calorimetry of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$. DSC traces of the studied mixed compounds for (a) $n = 2$, (b) $n = 3$, (c) $n = 4$, and (d) $n = 5$. Arrows indicate phase transition points.

■ RESULTS

Sample Characterization

Crystals of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ were grown across a range of DMA fractions x , initially targeting the $n = 2$ and $n = 3$ members. The resulting samples were characterized by room-

temperature powder X-ray diffraction (PXRD) and Raman spectroscopy (Figure 1), and the DMA content was quantified by ^1H NMR (Figure S1, Supporting Information). For $n = 2$, the PXRD pattern of nonmixed $\text{BA}_2\text{MAPb}_2\text{Br}_7$ ($x = 0$, Figure 1a) shows multiple reflections consistent with its orthorhombic symmetry,¹⁷ while the corresponding Raman spectrum (see

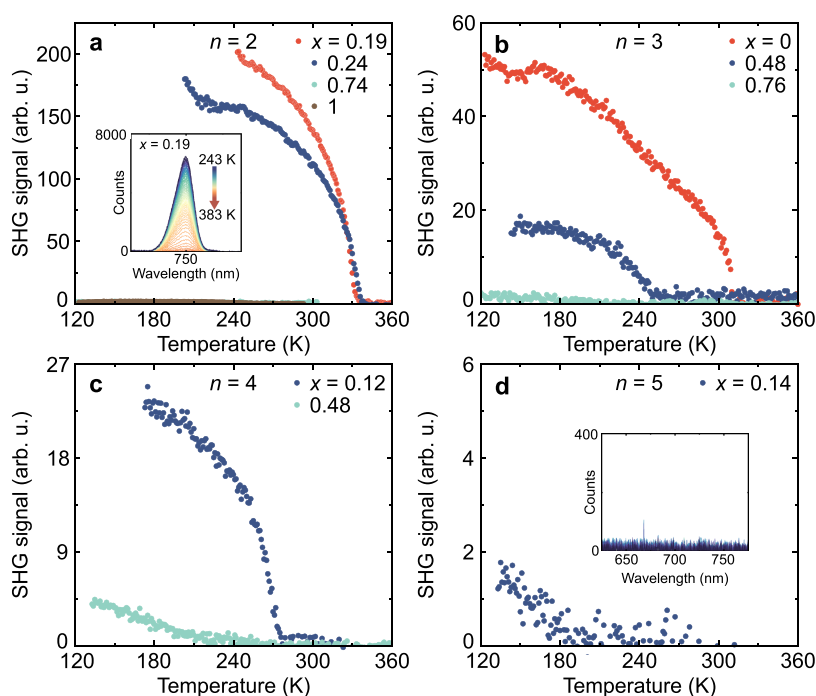


Figure 3. Nonlinear optical properties of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{PbBr}_{3n+1}$. SHG response of the selected mixed compounds for (a) $n = 2$, (b) $n = 3$, (c) $n = 4$, and (d) $n = 5$. Inset in (a) highlights a strong SHG signal for the weakly mixed $n = 2$ compound ($x = 0.19$), while the inset in (d) shows no SHG response for the $n = 5$ compound ($x = 0.14$), indicating its centrosymmetric origin.

Figures 1b and S2) displays bands associated with MA and BA molecular vibrations.¹⁹ Upon DMA incorporation, the intensity of the MA-related bands gradually decreases and completely disappears for $\text{BA}_2\text{DMAPb}_2\text{Br}_7$ ($x = 1$), which is consistent with the replacement of MA by DMA. DMA-specific bands could not be resolved due to their spectral overlap with BA vibrations. We also performed optical absorption measurements on the obtained compounds, which show a gradual increase in the band gap and exciton energy with increasing DMA content (Figure S3), further confirming successful cation mixing. The $n = 2$ crystals were obtained across the full compositional range ($0 \leq x \leq 1$), and selected compositions with $x = 0, 0.19, 0.24, 0.74, 0.84$, and 1 were chosen for further studies.

The characterization results of the obtained $n = 3$ crystals are also presented in Figure 1, showing a similar behavior. However, here, the full compositional range was not accessible, limiting the DMA content to $0 \leq x \leq 0.76$ due to the preferential formation of the $\text{BA}_2\text{DMAPb}_2\text{Br}_7$ phase for high DMA concentrations. For further studies, we selected compositions with $x = 0, 0.07, 0.33, 0.43, 0.48$, and 0.76.

Surprisingly, the continued cycling of the growth process enabled the formation of crystals with $n = 4$ and 5 (Figure 1), representing the largest slab thicknesses reported to date for single-crystal 2D hybrid perovskites. For these higher n values, crystals were obtained only for mixed compositions within narrow DMA ranges ($n = 4: 0.12 \leq x \leq 0.48$, $n = 5: 0.14 \leq x \leq 0.25$), revealing previously unreported compositional control over the dimensionality in these systems. Note that when attempting to synthesize nonmixed MA compounds with $n = 4$ or 5, we consistently obtained a mixture of the $n = 3$ phase and MAPbBr_3 . For DMA, even the $n = 3$ phase could not be stabilized, as a mixture of the $n = 2$ phase and DMPbBr_3 was formed.

Phase Transition Properties

We investigated the phase transition properties of the obtained compounds to determine whether the transitions and dipole ordering in $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{PbBr}_{3n+1}$ are affected by molecular cation mixing, which is frequently observed in 3D perovskites.¹² For instance, a strong suppression of phase transitions was reported in the related $\text{MA}/\text{DMPbBr}_3$ ($n = \infty$) mixed system upon introduction of the larger DMA cations.^{12,41,54} To probe these effects in 2D perovskites, we employed multiple complementary experimental techniques including differential scanning calorimetry (DSC), heat capacity C_p , second harmonic generation (SHG) measurements, and broadband dielectric spectroscopy.

The DSC results for the studied samples are presented in Figure 2, showing a pronounced effect of DMA incorporation on the phase transition behavior. With increasing DMA content, the transition temperatures decrease substantially, and the thermal anomalies broaden. However, in contrast to the 3D case,⁴¹ a complete suppression of the transitions is not observed. In some instances, closely spaced transitions appear even in the nonmixed compounds (e.g., $n = 3$), suggesting a complex nature of the ordering. Notably, these transition doublets were reproduced across different synthesis batches and were also observed in the heat capacity (Figure S4) and dielectric data (Figure 4).

The nonmixed $\text{BA}_2\text{MAPb}_2\text{Br}_7$ ($n = 2$) and $\text{BA}_2\text{MA}_2\text{Pb}_3\text{Br}_{10}$ ($n = 3$) perovskites are known to be proper ferroelectrics^{17,20,57} and consequently do not possess inversion symmetry in the low-temperature phase. To probe the centrosymmetry properties of the studied compounds, we used temperature-dependent SHG experiments. For $n = 2$ and low mixing levels, our measurements show a clear onset of the SHG response at the phase transition point as the system orders into the ferroelectric phase (Figure 3a). As the DMA content is increased, the response becomes weaker, and compounds with

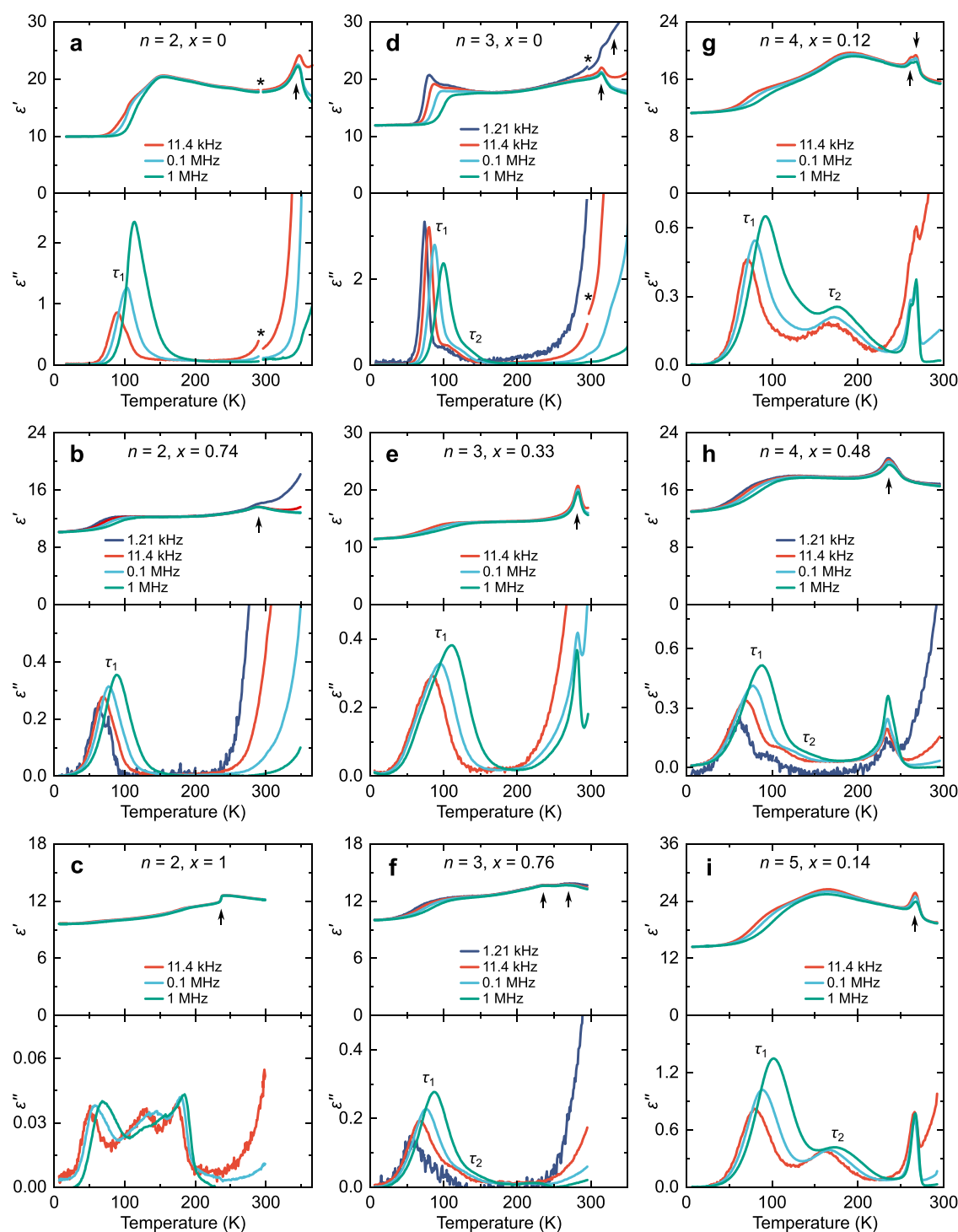


Figure 4. Broadband dielectric response of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_7\text{Br}_{3n+1}$. Temperature dependence of the complex dielectric permittivity of the pellet samples for (a–c) $n = 2$, (d–f) $n = 3$, (g, h) $n = 4$, and (i) $n = 5$ presented at selected frequencies. Arrows indicate resolved phase-transition anomalies. The dielectric relaxations are clearly visible in the low-temperature region for all studied compositions. Asterisks join two separate experimental runs covering the high- and low-temperature regions.

a high DMA content exhibit no SHG signal, indicating the presence of centrosymmetry and thus the absence of ferroelectricity. A similar decrease in the SHG response with increasing DMA is also observed for $n = 3$ and $n = 4$ (Figure 3b,c), while for $n = 5$, SHG is virtually absent even at a relatively low DMA content (Figure 3d). This observation indicates that increasing DMA incorporation progressively suppresses the noncentrosymmetric ordering in the system.

However, elucidating the exact microscopic mechanism underlying this behavior requires advanced structural characterization or sophisticated simulations.

Dynamics of Electric Dipoles

To study the crossover from ferroelectric to nonferroelectric behavior induced by mixing and increasing n , we employed broadband dielectric spectroscopy, which proved to be a powerful tool for probing phase transitions and cation

dynamics in hybrid perovskites and related compounds.^{12,58} In classical ferroelectrics, dielectric spectroscopy is a primary technique for studying dipolar frustration in mixed systems such as dipolar glasses^{59,60} and relaxors.^{45,61}

Figure 4 shows the temperature dependence of the real ϵ' and imaginary ϵ'' parts of the complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ of the selected $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ samples with different DMA concentrations (see Figure S5 for other compositions). For all compounds, the phase transitions are visible as anomalies in the real part of the permittivity. For high levels of mixing, the anomalies become broader and shift to lower temperatures in agreement with the DSC, C_p , and SHG results.

For all studied samples, the dielectric responses exhibit pronounced dipolar relaxations below approximately 200 K, most prominently seen in the imaginary part of ϵ^* (Figure 4). By analogy with 3D hybrid perovskites, we assign these relaxations to the dynamics of the molecular cations.¹² For the nonmixed $\text{BA}_2\text{MAPb}_2\text{Br}_7$ compound ($x = 0$), a single relaxation process (denoted as τ_1) is observed (Figure 4a), which broadens and shifts to lower temperatures upon introduction of DMA cations (Figures 4b and S5). In contrast, the fully substituted $\text{BA}_2\text{DMAPb}_2\text{Br}_7$ ($x = 1$) exhibits multiple overlapping relaxation processes (Figure 4c), likely associated with the motion of the bulkier DMA cations. A similar trend is also observed for the $n = 3$ family (Figure 4d–f), while for the $n = 4$ and $n = 5$ compounds, two well-separated relaxation processes (τ_1 and τ_2) emerge at low temperatures (Figure 4g–i), likely reflecting modified cation dynamics associated with the increased slab thickness.

The most notable observation is that, for highly mixed compositions in which the SHG response is weak or absent, the dielectric relaxations closely resemble those of relaxor ferroelectrics. In particular, the low-temperature flank of ϵ'' for the dominant (τ_1) relaxation becomes nearly frequency independent and collapses onto a single curve (see, e.g., $n = 3$, $x = 0.76$, Figure 4f), which is a hallmark of relaxor behavior.^{45,61} Such dynamics are commonly associated with electric dipole frustration in polar nanoregions, resulting in a broad distribution of relaxation times.

To further investigate the dynamic properties and explore the presence of relaxor-like behavior, we analyzed the frequency response of the complex permittivity ϵ^* using the Cole–Cole formalism (see Figure S6 and SI for details),⁶² which allowed us to extract the mean relaxation time τ of the dominant relaxation process. Figure 5 shows the temperature dependence of τ , plotted in an inverse-temperature representation, for the nonmixed $\text{BA}_2\text{MAPb}_2\text{Br}_7$ ($n = 2$, $x = 0$) and mixed $\text{BA}_2(\text{MA}_{0.86}\text{DMA}_{0.14})_4\text{Pb}_5\text{Br}_{16}$ ($n = 5$, $x = 0.14$) compounds. To access relaxation processes on the nanosecond time scale, the measurement frequency range for these samples was extended into the more challenging GHz regime. A linear dependence is observed for $\text{BA}_2\text{MAPb}_2\text{Br}_7$, indicating that the mean relaxation time follows the Arrhenius behavior, $\tau = \tau_0 \exp(E_a/kT)$, where E_a and τ_0 denote the activation energy and attempt time, respectively, and k is the Boltzmann constant.⁶² The obtained activation energy is $E_a = 143(1)$ meV, which is comparable to values reported for molecular cation dynamics in other hybrid perovskites.¹²

In contrast, for a mixed $n = 5$ $\text{BA}_2(\text{MA}_{0.86}\text{DMA}_{0.14})_4\text{Pb}_5\text{Br}_{16}$ compound, the temperature dependence of the relaxation time deviates from the Arrhenius behavior, indicating the freezing of dipolar dynamics at a finite temperature. The experimental

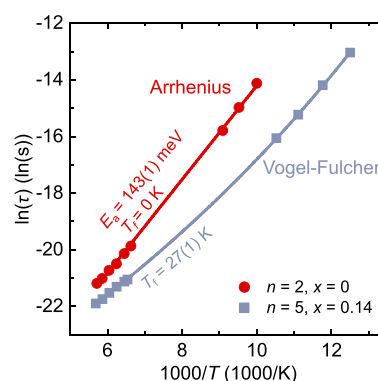


Figure 5. Relaxation behavior of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$. Inverse temperature dependence of the mean relaxation time τ of nonmixed $\text{BA}_2\text{MAPb}_2\text{Br}_7$ and mixed $\text{BA}_2(\text{MA}_{0.86}\text{DMA}_{0.14})_4\text{Pb}_5\text{Br}_{16}$ compounds obtained from broadband dielectric spectroscopy. Solid curves represent fits using the Arrhenius and Vogel–Fulcher relations.

data can be described using the Vogel–Fulcher relation, $\tau = \tau_0 \exp[E_a/k(T - T_f)]$, where T_f denotes the freezing temperature at which τ diverges.^{45,46,63} Fitting the data yields $E_a = 63(1)$ meV and a finite freezing temperature of $T_f = 27(1)$ K. The emergence of Vogel–Fulcher freezing instead of the Arrhenius behavior is a signature of relaxor systems, further indicating relaxor-like properties of the mixed $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ compounds.

DISCUSSION

We summarize our main findings by mapping the phase diagrams of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$. Figure 6a shows a phase diagram in the x vs n representation highlighting the stability limits of the mixed compositions. The inability to obtain nonmixed MA- and DMA-based compounds at high n values arises from the high stability of the 3D MAPbBr_3 and hexagonal DMAPbBr_3 ⁶⁴ phases, which crystallize preferentially under these conditions. Consequently, for mixed MA/DMA compositions at high n values, only a limited range of compositions can be stabilized. Overall, these results indicate that cation mixing offers an effective strategy to tune the dimensionality of hybrid perovskites, enabling access to the highest slab thicknesses ($n = 5$) achieved to date in single-crystal samples.

Figure 6b shows the temperature–composition phase diagram indicating that the phase transitions in $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ are comparatively less affected by DMA substitution than in the 3D compounds, where DMA strongly suppresses phase transitions due to its larger size.^{41,54} On the other hand, our experiments show that the 2D perovskite can tolerate a higher degree of structural variability while maintaining long-range order, likely aided by the BA cations, which are known to contribute to the ordering in these systems.¹⁹

In addition, since nonmixed $\text{BA}_2\text{DMAPb}_2\text{Br}_7$ exhibits no SHG response and is therefore nonferroelectric, the incorporation of DMA induces a crossover from ferroelectric to nonferroelectric behavior in $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$. This crossover also depends on the slab thickness, as for $n = 5$ compounds, no SHG was detected even at low DMA concentrations. This observation is consistent with the system starting to approach the 3D limit where proper ferroelectric properties are absent. In general, it is instructive to consider how the layered perovskite system evolves toward the 3D limit.

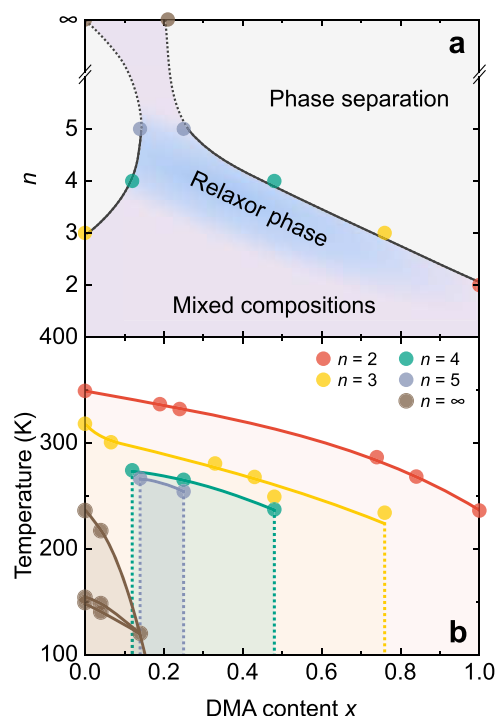


Figure 6. Phase diagrams of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$. (a) x - n phase diagram showing the stability region of the mixed phase of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$. Solid curves are guides to the eye, while dashed curves indicate a tentative interpolation between $n = 5$ and $n = \infty$ (3D MAPbBr₃) data points. The shaded blue region approximately highlights the relaxor-like behavior observed in the studied mixed compositions. (b) Temperature–composition phase diagram of $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$. Circles denote phase transition temperatures determined using various experimental techniques, where closely spaced doublet anomalies observed for some compositions were averaged into a single point.

For $n = 5$, the transition temperature is closer to, yet still substantially different from, the cubic–tetragonal transition temperature of 3D MAPbBr₃¹² (Figure 6b). Moreover, the number of observed phase transitions and the associated crystal symmetries differ from the 3D case, suggesting that BA cations still play a major role in the ordering process and that the correlation length during the phase transition extends well beyond five MA units.

Our broadband dielectric measurements at high DMA content and for large n values reveal dipolar relaxations typical for relaxors, providing evidence of this behavior in mixed 2D perovskites. Note that mixed 3D hybrid perovskites also often exhibit broad dipolar relaxations, but their response resembles a dipolar glass, with dynamics typically following the Arrhenius law, which indicates a very low glass freezing temperature.¹² In contrast, 2D perovskites such as $\text{BA}_2\text{MAPb}_2\text{Br}_7$ and $\text{BA}_2\text{MA}_2\text{Pb}_3\text{Br}_{10}$ exhibit ferroelectric hysteresis loops,^{17,20} and thus DMA incorporation induces the relaxor phase observed here. This suggests that relaxor behavior may be a general feature of ferroelectric low-dimensional perovskites, adding to the rich functional diversity of these materials. Further studies of the dipolar freezing could reveal the microscopic mechanisms governing electric dipole interactions.

We note that a complete mapping of the relaxor behavior across all DMA concentrations remains challenging as broadband dielectric measurements in the GHz frequency range are experimentally demanding. Moreover, overlapping

relaxations observed for some compositions further complicate the analysis. Consequently, the region of relaxor behavior indicated in Figure 6a should be regarded as approximate, reflecting the limitations of the current measurements. Future work on this and other cation systems, combined with high-frequency dielectric spectroscopy and complementary experiments, will be essential to clarify how relaxor properties, such as the freezing temperature, evolve with the degree of mixing.

CONCLUSIONS

In conclusion, we have demonstrated that molecular cation mixing provides an effective strategy for controlling both the dimensionality and functional properties of 2D hybrid perovskites. By systematically varying the MA/DMA ratio in $\text{BA}_2(\text{MA}_{1-x}\text{DMA}_x)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$, we accessed single crystals with unprecedented slab thicknesses up to $n = 5$ and mapped the stability regions of mixed compositions. Our experiments revealed that DMA incorporation partially suppresses phase transitions and induces relaxor behavior in mixed 2D perovskites, providing the first direct evidence of a crossover from ferroelectric to relaxor dynamics in hybrid perovskites. Although the full mapping of relaxor behavior is limited by experimental challenges, our results establish a framework for future studies exploring different cation systems and the microscopic mechanisms governing dipolar freezing. Collectively, these findings highlight the potential of cation engineering to tune the structural, polar, and dielectric properties in layered hybrid perovskites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.6c00851>.

Experimental section; additional NMR, Raman, heat capacity, light absorption, and dielectric data (PDF)

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Notes

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