Azetidinium lead halide Ruddlesden-Popper phases

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Abstract: A family of Ruddlesden-Popper (n = 1) layered perovskite-related phases, \(\text{Az}_2\text{Pb}\text{Cl}_{x}\text{Br}_{4-x}\) with composition \(0 \leq x \leq 4\) were obtained using mechanosynthesis. A linear variation in unit cell volume as a function of anion average radius is observed. A tunable bandgap is achieved, ranging from 2.81 to 3.43 eV, and the bandgap varies in a second order polynomial relationship with the halide composition.

Keywords: layered perovskite, bandgap tuning, azetidinium, Ruddlesden-Popper, structure-property relations

1. Introduction

Ruddlesden-Popper (R-P) phases are composed of layered perovskite structures with alternating layers of AMX\(_3\) perovskite and AX rock salt along the c-axis. They are described by the general formula \(\text{A}_n\text{M}_n\text{X}_{3n+1}\) (or \(\text{A'}\text{A''}_n\text{M}_n\text{X}_{3n+1}\) in the case of two distinct A-cations), where \(n\) is a positive integer representing the number of perovskite layers which are separated by additional ‘A-cation excess’ rock-salt layers.[1,2]

Importantly, the intergrowth rock salt layer means that the octahedra in the perovskite layers are aligned in the successive layers. In 1955, Balz and Plieth reported the first R-P phase layered structure \(\text{K}_2\text{NiF}_4\) (\(n = 1\)).[3] In 1957-58, Ruddlesden and Popper reported a series of layered structures in oxides, such as \(\text{Sr}_2\text{TiO}_4\) and \(\text{Ca}_2\text{TiO}_4\).[4] Nowadays, the R-P phase is more commonly used to represent this type of layered perovskite structure and increasingly in organic-inorganic hybrid perovskites (OIHPs). Several families of layered OIHPs containing alternating layers of AMX\(_3\) perovskite and organic cations with structures similar to R-P phases have been reported. Such examples of layered OIHPs include \(\text{BA}_2\text{PbI}_4\) (BA = C\(_4\)H\(_9\)NH\(_3\)+)[5] and \(\text{PEA}_2\text{PbX}_4\) (PEA = C\(_8\)H\(_{12}\)N\(_3\)\(^+\)), \(X = \text{Cl, Br, I}\).[6,7] in which the organic cations are too big to be accommodated in the cuboctahedral cavities of the 3D MX\(_6\) framework. Without the constraint of the size of the cuboctahedral cavities, a wider range of organic A-cations would be available for layered phases. In addition, by mixing large (\(A'\)) organic cations, such as those mentioned above, and small organic cations such as methylammonium (\(A'' = \text{MA}\)), organic-inorganic hybrid materials with the general formuarl \(\text{A'}\text{A''}_n\text{M}_n\text{X}_{3n+1}\) can be prepared.[5,8] They show good bandgap tunability by modifying the number of layers \((n)\) of \(\text{A''}\text{PbX}_3\). Stoumpos et al.[5] reported orthorhombic crystal structures of \(\text{BA}_2\text{MA}_n\text{Pb}_n\text{X}_{3n+1}\) (X =
Br, I) with bandgaps changing progressively from 2.43 eV \((n = 1)\) to 1.50 eV \((n = \infty)\), with intermediate values of 2.17 eV \((n = 2)\), 2.03 eV \((n = 3)\) and 1.91 eV \((n = 4)\). The thickness of the perovskite layer, \(n\), in \((BA)_{n-1}(MA)_{n+1}PbI_3\) can be reasonably controlled by modifying the ratio of BA/MA cations in the precursor solutions. However, many so-called R-P phase reported in such compounds often do not have the required rock salt-structured interlayer between the 2D perovskite layers, resulting in an offset in the alignment of the perovskite blocks in successive layers. Such examples, therefore, do not conform to the definition of a R-P phase and are more correctly termed R-P-like OIHPs. Such R-P-like layered OIHPs have demonstrated higher stability when exposed to light, humidity and heat stress compared to 3D perovskite analogues, which are prone to unwanted phase transition under these test conditions.[9,10]

Azetidinium \((\text{Az}^+,(\text{CH}_2)_3\text{NH}_3^+)\) is a four-membered ring ammonium cation. In our previous study on mixed halide azetidinium lead perovskites, \(\text{AzPbBr}_3\cdot X_\ell (X = \text{Cl or I})\), the structure progresses from 6H to 4H to 9R perovskite polytypes with varying halide composition from Cl\(^-\) to Br\(^-\) to I.[11] The fact that \(\text{AzPbX}_3\) \((X = \text{Cl or Br})\) forms a hexagonal perovskite rather than a cubic (3C) perovskite led to our study on mix-cation solid solutions of the form \(\text{AzA'}^\prime\text{PbBr}_3\), \(A'^\prime = \text{MA}^+\) or \(\text{FA}^+\) \((\text{FA}^+ = \text{formamidinium})\). Such systems show only partial solid solutions and phase separation of the hexagonal and cubic forms; the extent of solid solution formation also depends on the synthesis route.[12] These studies also suggest that the cation radius of \(\text{Az}^+\) is \(~310\) pm, which is larger than the calculated cation radius of \(\text{Az}\), \(r_{\text{Az}} = 250\) pm (for comparison the reported radii for \(\text{FA}^+\) and \(\text{MA}^+\) are \(r_{\text{FA}} = 253\) pm, \(r_{\text{MA}} = 217\) pm,[13] respectively). \(\text{MA}^+\) and \(\text{FA}^+\) are commonly used as A-site cations in OIHPs, and that adopt (pseudo-) cubic perovskite structures.[14,15] With our cation radius estimation that \(\text{Az}^+\) is larger than \(\text{MA}^+\) and \(\text{FA}^+\), \(\text{Az}_2\text{PbX}_4\) \((X = \text{Cl, Br})\) are found to adopt a \(n = 1\) R-P phase structure. The fact that \(\text{Az}^+\) can form layered structure indicate that our estimation of its cation radius is more accurate than that from computational calculation.[12,13] Furthermore, a family of mixed halide R-P phases, \(\text{Az}_2\text{PbCl}_x\text{Br}_{1-x}\) with composition \(0 \leq x \leq 4\) were prepared by mechanosynthesis and their structures and optical properties were analysed by powder X-ray diffraction (PXRD) and absorption spectroscopy, respectively. A linear variation in unit cell volume as a function of anion average radius is observed. The bandgap was found to range from 2.81 to 3.43 eV, which varies as a second order polynomial relationship with the halide composition.

2. Methods
PbBr\(_2\) (98%) and PbCl\(_2\) (98%) were purchased from Alfa Aesar. Hydrobromic acid in water (48%) and AzCl (95%) were purchased from Fluorochem. All other reagents and solvents were obtained from commercial sources and used as received. AzBr were synthesised according to our previous study.[16] Preparation of Az\(_2\)PbCl\(_x\)Br\(_{4-x}\) solid solutions with 0 \(\leq x \leq 4\) (in \(x = 0.67\) increments) was carried out by mechanosynthesis. Appropriate molar ratios of dry AzX and PbX\(_2\) (AzX:PbX\(_2\) = 2:1, X = Cl or Br) were ground together in a Fritsch Pulverisette planetary ball mill at 600 rpm for 1 hour using 60 cm\(^3\) Teflon pots and high-wear-resistant zirconia media (nine 10 mm diameter spheres). Az\(_2\)PbBr\(_4\) samples could also be obtained by hand grinding AzBr and PbBr\(_2\) in an agate mortar and pestle for 25 minutes.

PXRD was carried out using a PANalytical Empyrean diffractometer with Cu K\(\alpha_1\) (\(\lambda = 1.5406\) Å). Rietveld refinements of PXRD data using GSAS[17] were used to confirm phase formation and for determination of lattice parameters.

Optical properties were determined from solid-state absorption spectra recorded using a Shimadzu UV-2600 spectrophotometer and bandgaps were calculated by plotting \((\alpha h\nu)^2(eV*cm^{-1})^2\) with \(h\nu(eV)\) according to the Tauc method, in which \(\alpha\), \(h\) and \(\nu\) stand for absorbance, Planck’s constant and incident light frequency.

3. Results
The PXRD data for Az\(_2\)PbCl\(_x\)Br\(_{4-x}\) with compositions ranging from 0 \(\leq x \leq 4\) were prepared by mechanosynthesis and are shown in Figure 1b. The structures of these samples were determined to be R-P \(n = 1\) phase in the \(I4/mmm\) space group (Figure 1a). The Az\(^+\) cations, which are represented as solid spheres situated at the centre of electron density, form rock salt layers with the X-anions. Synthesis from solution is preferred when manufacturing devices because solutions can be easily processed into thin films by spin-coating and blade-coating methods compared to bulk powder.[18] Thus, precipitation synthesis of Az\(_2\)PbX\(_4\) (X = Cl, Br) were also attempted (synthetic details included in the supporting information) and their PXRD data are shown in Figure S1. Although the precipitated samples contain additional phase(s) associated with additional peaks (e.g., at 6° and 11°) and have yet to be assigned to a structure. Ganguli[19] reported an empirical prediction that possible R-P phase structures are associated with a ratio of A-site and metal cation radii \((r_A/r_M)\) in the range of 1.7 to 2.4. As discussed in our previous study,[11] our estimation of the cation radius of Az\(^+\) (~310 pm) differs from that calculated (250 pm).[13] The \(r_A/r_M\) calculated using our estimated radius is 2.60, while that using the literature value[13] is 2.10.
Figure 1. a) $n = 1$ Ruddlesden-Popper (R-P) phase of Az$\text{PbX}_4$ ($X = \text{Cl, Br}$) showing alternating Az$\text{PbX}_3$ perovskite and Az$X$ rock salt layers along the $c$-axis, b) PXRD data of mix-halide layered R-P phases: Az$\text{PbCl}_x\text{Br}_{4-x}$ with composition $0 \leq x \leq 4$ prepared by mechanosynthesis.

Unfortunately, our attempts to synthesise single phase Az$\text{PbI}_4$ were unsuccessful. The PXRD of mechanosynthesised Az$\text{PbI}_4$ is shown in Figure S2. In addition to the R-P phase, there are evident amounts of 9R Az$\text{PbI}_3$ phase [11,20] and the relative intensity of this phase increased with increased ball mill grinding time (1 to 3 hours). PXRD of the Az$\text{PbI}_4$ sample obtained from a hand grinding synthesis showed that this method can increase the proportion of R-P phase in the samples, evidenced by the increased relative intensity of peaks associated with the R-P phase, but the presence of the 9R phase persisted across all samples. These results indicate that the 9R phase is the more stable phase compared to the R-P phase for the iodide analogue. It is likely that the activation energy for the transformation of azetidinium lead iodide from a layered phase to the 9R phase is low.

For simplicity, Rietveld refinements were carried out by replacing the organic Az$^+$ cations with Mn$^{2+}$, as they have similar electron densities. Figure 2 shows an example of the PXRD data refinement of Az$\text{PbX}_4$ ($X = \text{Cl, Br}$) samples obtained from the ball mill mechanosynthesis. The refined lattice parameters of Az$\text{PbBr}_4$ are $a = 5.993(6)$ Å and $c = 21.501(1)$ Å, with goodness-of-fit parameters $\chi^2 = 10.21$ and $wR_e = 0.115$, while those of Az$\text{PbCl}_4$ are $a = 5.765(0)$ Å and $c = 21.027(2)$ Å, with goodness-of-fit parameters $\chi^2 = 7.20$ and $wR_e = 0.102$. The difference between the organic moieties and Mn$^{2+}$, which is associated with their actual
atomic position and thermal motion, is one possible reason for such high $\chi^2$ values for both refinements and may be responsible for the differences in the peak shape and intensities shown. However, it is clear that all peaks are accounted for and that the PXRD are consistent with formations of single phase $n = 1$ R-P materials.

![Rietveld refinement of PXRD data](image)

**Figure 2.** Rietveld refinement of PXRD data in $I4/mmm$ space group of $A_{2}PbX_4$, $X = Br$ (top) and $Cl$ (bottom) obtained from mechanosynthesis with observed data (open circles), calculated data (red line for Br and magenta line for Cl), background (green lines), reflection positions (black bars) and difference plots (blue lines).

To study the mixed-halide solid solutions $A_{2}PbCl_xBr_{4-x}$, the lattice parameters of each mechanosynthesised composition were determined by Rietveld refinement of PXRD data. The cell volume of these R-P phases varies linearly as a function of average anion radius, Figure 3a (the average anion radius was calculated using $r_{Br} = 196$ pm and $r_{Cl} = 181$ pm according to Shannon [21]). This linear variation is expected in accordance with Vegard’s law. The lattice parameters $a$ and $c$, on the other hand, show a nonlinear
relationship with the average anion radius (Figure 3b), which suggests anisotropic expansion/contraction along \(a\)- and \(c\)-axis. The larger expansion in \(a\) is consistent with the increase \(X\) anion radius which affords a larger void for the \(Az^+\) cation, resulting in less required expansion in the interlayer spacing. Based on the analysis using \(Mn^{2+}\) as a proxy for \(Az^+\) we have no information regarding any orientation or dynamics of the \(Az^+\) cation.

The optical properties of \(Az_2\text{PbCl}_x\text{Br}_{4-x}\) \((0 \leq x \leq 4)\) solid solutions were studied by absorption spectroscopy (Figure 4a). The absorption onsets are systematically red-shifted from ca. 386 nm (\(Az_2\text{PbCl}_4\)) to ca. 457 nm (\(Az_2\text{PbBr}_4\)) with increasing average anion size (from Cl\(^-\) to Br\(^-\)). The bandgaps of \(Az_2\text{PbCl}_4\) and \(Az_2\text{PbBr}_4\) are calculated to be 3.43 and 2.81 eV, which are the same (within error) to the bandgap of the 6H hexagonal perovskite \(Az\text{PbCl}_3\) (3.43 eV) and \(Az\text{PbBr}_3\) (2.81 eV).[11] However, unlike the linear variation in the 6H \(Az\text{PbX}_3\) \((X^\text{-} = \text{Cl}^-, \text{Br}^-)\), the bandgap of layered R-P \(Az\text{PbX}_4\) \((X = \text{Cl}, \text{Br})\) shows a bowing with the average anion radius (Figure 4b). The bowing effect[22,23] simply describes deviation of measured band gap in continuous solid solutions from the values expected by linear interpolation of the end member values. Bandgap bowing is often fitted to a second order polynomial to account for the divergence from linearity, with a bowing parameter \(b\) as the binomial coefficient of the fitting equation 1:[23]

![Figure 3. a) Cell volume b) lattice parameters as a function of average halide anion radius for \(n = 1\) R-P phases \(Az_2\text{PbCl}_x\text{Br}_{4-x}\) \((0 \leq x \leq 4)\) as determined from Rietveld refinement of PXRD data.](image)
\[ E_g(x) = (1 - x)E_g(x=0) + xE_g(x=1) - bx(1 - x) \] (1)

The bowing parameter, \( b \), of the mechanosynthesised mixed halide layered \( \text{Az}_2\text{PbCl}_{x}\text{Br}_{4-x} \) \((0 \leq x \leq 4)\) is 0.47 with a goodness-of-fit R\(^2\) value of 0.995. The bowing parameter of mixed halide OIHPs are usually smaller, variously reported as \(7 \times 10^{-4}\) to 0.33 for MAPbBr\(_{3-x}\)X\(_{x}\) \((X = \text{Cl or I})\)\([24,25]\) compared to the bowing parameters (0.4 to 1.33) found for other mixed metal perovskite systems such as MA\(_x\)(Sb\(_{1-x}\)Bi\(_x\))I\(_9\) \((0.4\) for Bi rich region and 1.3 for Sb rich region) and 1.06 for MA(Pb\(_{1-x}\)Sn\(_x\))I\(_3\)\([22,23,26]\)

![Figure 4](image_url)

Figure 4. a) Absorption spectra; b) bandgap determination from the absorption spectra of samples \( \text{Az}_2\text{PbCl}_{x}\text{Br}_{4-x} \) with composition \(0 \leq x \leq 4\) plotted as a function of average halide anion radius.

4. Conclusions

\( n = 1 \) Ruddlesden-Popper (R-P) layered perovskite phases were successfully obtained by mechanosynthesis in the mixed halide solid solution \( \text{Az}_2\text{PbCl}_{x}\text{Br}_{4-x} \) with composition \(0 \leq x \leq 4\). \( \text{Az}_2\text{PbX}_4(X = \text{Cl, Br}) \) was determined to be the conventional R-P \( n = 1 \) \((\text{K}_2\text{NiF}_4)\) structure with a space group of \( I4/mmm \). A linear variation in unit cell volume as a function of anion average radius is observed. The bandgap of the R-P phases \( \text{Az}_2\text{PbCl}_4 \) and \( \text{Az}_2\text{PbBr}_4 \) are determined to be 3.43 and 2.81 eV, which are the same (within error) to the bandgap of 6H hexagonal perovskite \( \text{AzPbCl}_3 \) (3.43 eV) and \( \text{AzPbBr}_3 \) (2.81 eV)\([11]\) A bowing effect with a bowing parameter of 0.47 is observed in the bandgap-composition relationship of R-P layered mixed halide solid solutions, compared to the linear relationship observed in the 6H hexagonal perovskite.
Supplementary Materials: The Supporting Information contains additional experimental information including synthetic details of precipitation synthesis of Az₂PbXₓ (X = Cl, Br) and synthesis of Az₂PbI₄.

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Sample Availability: Samples of the Az₂PbCl₁₋ₓBrₓ with composition 0 ≤ x ≤ 4 are available from the authors.
References

1. Lichtenberg, F.; Herrnberger, A.; Wiedenmann, K. Synthesis, structural, magnetic and transport properties of layered perovskite-related titanates, niobates and tantalates of the type AmBnO3n+2, A’AkBkO3k+1 and AmBm-I03m. Prog. Solid State Chem. 2008, 36, 253–387, doi:10.1016/j.progsolidstchem.2008.10.001.

2. Aleksandrov, K.S.; Beznosikov, V. V. Hierarchies of perovskite-like crystals (Review). Phys. Solid State 1997, 39, 695–715, doi:10.1134/1.1130120.

3. Balz, D.; Pliboth, K. Die Struktur des Kaliumnickelfluorids, K2NiF. Zeitschrift für Elektrochemie, Berichte der Bunsengesellschaft für Phys. Chemie 1955, 59, 545–551, doi:10.1002/bbpc.19550590613.

4. Ruddlesden, S.N.; Popper, P. New compounds of the K 2 NIF 4 type. Acta Crystallogr. 1957, 10, 538–539, doi:10.1107/S0001888557001929.

5. Stoumpos, C.C.; Cao, D.H.; Clark, D.J.; Young, J.; Rondinelli, J.M.; Jang, J.I.; Hupp, J.T.; Kanatzidis, M.G. Ruddlesden-Popper Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors. Chem. Mater. 2016, 28, 2852–2867, doi:10.1021/acs.chemmater.6b00847.

6. Du, K.Z.; Tu, Q.; Zhang, X.; Han, Q.; Liu, J.; Zauscher, S.; Mitzi, D.B. Two-Dimensional Lead(II) Halide-Based Hybrid Perovskites Templated by Acene Halides: Crystal Structures, Optical Properties, and Piezoelectricity. Inorg. Chem. 2017, 56, 9291–9302, doi:10.1021/acs.inorgchem.7b01094.

7. Mitzi, D.B. A Layered Solution Crystal Growth Technique and the Crystal Structure of (C 6 H 5 C 2 H 4 NH 3 ) 3659, doi:10.1021/acs.chemmater.1c00470.

8. Bandgap Tuning in Azetidinium Lead Halide Perovskites. Tian, J.; Cordes, D.B.; Slawin, A.M.Z.; Zysman-Colman, E.; Morrison, F.D. Progressive Polytypism and Bandgap Tuning in Azetidinium Lead Halide Perovskites. Inorg. Chem. 2021, 60, 12247–12254, doi:10.1021/acs.inorgchem.1c01425.

9. Tian, J.; Cordes, D.B.; Slawin, A.M.Z.; Zysman-Colman, E.; Morrison, F.D. Progressive Polytypism and Bandgap Tuning in Azetidinium Lead Halide Perovskites. Inorg. Chem. 2021, 60, 12247–12254, doi:10.1021/acs.inorgchem.1c01425.

10. Kieslich, G.; Sun, S.; Cheetham, A.K.; Cheetham, T.; Gregor, K.; Shijing, S.; Anthony, K.C. Solid-State Principles Applied to Organic-Inorganic Perovskites: New Tricks for an Old Dog. Chem. Sci. 2014, 5, 4712–4715, doi:10.1039/C4SC02211D.

11. Levchuk, I.; Osvet, A.; Tang, X.; Brandl, M.; Perea, J.D.; Hoegl, F.; Matt, G.J.; Hock, R.; Batentschuk, M.; Brabec, C.J. Brightly Luminescent and Color-Tunable Formamidinium Lead Halide Perovskite FA3PbX 3 (X = Cl, Br, I) Colloidal Nanocrystals. Nano Lett. 2017, 17, 2765–2770, doi:10.1021/acs.nanolett.6b04781.

12. Cao, M.; Tian, J.; Cai, Z.; Peng, L.; Yang, L.; Wei, D. Perovskite heterojunction based on CH3NH3PbBr3 single crystal for high-sensitive self-powered photodetector. Appl. Phys. Lett. 2016, 109, 233303, doi:10.1063/1.4971772.

13. Tian, J.; Cordes, D.B.; Quart, C.; Beljonne, D.; Slawin, A.M.Z.; Zysman-Colman, E.; Morrison, F.D. Stable 6H Organic-Inorganic Hybrid Lead Perovskite and Competitive Formation of 6H and 3C Perovskite Structure with Mixed A Cations. ACS Appl. Energy Mater. 2019, 2, 5427–5437, doi:10.1021/acsaeem.9b00419.
17. A. C. Larson and R.B. V. Dreene Los Alamos National Laboratory Report LAUR; 2004;
18. Yu, J.C.; Kim, D. Bin; Jung, E.D.; Lee, B.R.; Song, M.H. High-performance perovskite light-emitting diodes via morphological control of perovskite films. *Nanoscale* 2016, 8, 7036–7042, doi:10.1039/c5nr05604g.
19. Ganguli, D. Cationic radius ratio and formation of K2NiF4-type compounds. *J. Solid State Chem.* 1979, 30, 353–356, doi:10.1016/0022-4596(79)90247-0.
20. Panetta, R.; Righini, G.; Colapietro, M.; Barba, L.; Tedeschi, D.; Polimeni, A.; Ciccioli, A.; Latini, A. Azetidinium lead iodide: Synthesis, structural and physico-chemical characterization. *J. Mater. Chem. A* 2018, 6, 10135–10148, doi:10.1039/c8ta02210k.
21. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A* 1976, 32, 751–767, doi:10.1107/S0567739476001551.
22. Lee, S.; Levi, R.D.; Qu, W.; Lee, S.C.; Randall, C.A. Band-gap nonlinearity in perovskite structured solid solutions. *J. Appl. Phys.* 2010, 107, 1–6, doi:10.1063/1.3291102.
23. Chatterjee, S.; Payne, J.; Irvine, J.T.S.; Pal, A.J. Bandgap bowing in a zero-dimensional hybrid halide perovskite derivative: Spin-orbit coupling: Versus lattice strain. *J. Mater. Chem. A* 2020, 8, 4416–4427, doi:10.1039/c9ta12263j.
24. Noh, J.H.; Im, S.H.; Heo, J.H.; Mandal, T.N.; Seok, S. Il Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. *Nano Lett.* 2013, 13, 1764–1769, doi:10.1021/nl400349b.
25. Wang, W.; Su, J.; Zhang, L.; Lei, Y.; Wang, D.; Lu, D.; Bai, Y. Growth of mixed-halide perovskite single crystals. *CrystEngComm* 2018, 20, 1635–1643, doi:10.1039/c7ce01691c.
26. Hu, Z.; Lin, Z.; Su, J.; Zhang, J.; Chang, J.; Hao, Y. A Review on Energy Band-Gap Engineering for Perovskite Photovoltaics. *Sol. RRL* 2019, 3, 1–9, doi:10.1002/solr.201900304.