Exploring Structural Nuances in Germanium Halide Perovskites using Solid-state ^{73}Ge and ^{133}Cs NMR Spectroscopy

Riley W. Hooper^{1†}, Chuyi Ni^{1†}, Dylan G. Tkachuk¹, Yingjie He¹, Victor V. Terskikh², Jonathan G.C. Veinot¹, and Vladimir K. Michaelis^{1,*}

¹Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

²Metrology, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

[†]These authors contributed equally

*Corresponding Author: Vladimir K. Michaelis, vladimir.michaelis@ualberta.ca

ABSTRACT. Metal-halide perovskites remain top candidates for better-performing photovoltaic devices but concerns with leading lead-based materials continue. Ge perovskites remain understudied for use in solar cells compared to their Sn-based counterparts. In this work, we undertake a combined ^{133}Cs and ^{73}Ge solid-state NMR and DFT study of the bulk CsGeX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) series. We show how seemingly small structural variations within germanium halide perovskites have major consequences on their ^{73}Ge and ^{133}Cs NMR signatures and reveal a near cubic-like phase at room temperature for CsGeCl_3 with severe local Ge polyhedral distortion. Quantum chemical computations are effective at predicting the structural impact on NMR parameters for ^{73}Ge and ^{133}Cs . This study demonstrates the value of a combined experimental and theoretical approach for investigating attractive materials for energy applications – providing information that is out of reach with conventional characterization methods – and adds the challenging ^{73}Ge nucleus to the toolkit.

Metal halide ABX_3 perovskites have seen an explosion in popularity over the past decade, with lead-halide perovskites (LHPs) dominating application development in new-age photovoltaics (PVs).^{1–6} With tailorable optoelectronic properties, LHPs have been a focus of interest for not only energy generation materials used in solar cells, but also for applications including radiation detection, lasing, thermoelectrics, and spintronics.^{7–11} Though LHPs have shown promise for these uses, their potential in solar applications remains the driving factor for their popularity. In fact, a recent tandem perovskite/c-Si solar cell was certified to exhibit greater than 29% photoconversion efficiency (PCE),^{12–15} with the best performing perovskite solar cells (PSCs) recently surpassing 25% PCE.^{12,15–19} Despite these impressive metrics, LHPs still raise toxicity concerns stemming from the presence of Pb in these materials and their by-products.²⁰ These worries are highlighted in a recent study demonstrating the negative impacts that LHP-contaminated soils pose.²¹ As such, the search for alternative materials with comparable performance is essential.

Tin-based perovskites are compelling alternatives to traditional LHPs, but are plagued by stability and oxidation issues and suffer from lower PCEs.^{22–28} The best performing Sn candidates have recently surpassed 10% PCE, and are steadily improving.^{29–32} Their germanium-based counterparts are also well-known in the literature,^{33–44} and have typically garnered attention for their non-linear optical (NLO) properties.^{35,39,40,42} Germanium-based perovskites could prove promising as candidates for sustainable energy applications as well.^{45,46} In particular, the optical bandgap of $CsGeI_3$ (1.6 eV) is well-suited for absorbing in the visible region of the solar spectrum.^{42,46}

Compared with other perovskites, development of germanium halide-based PV applications thus far has been muted, only seeing modest PCEs to date. In 2015, measured efficiencies for $CsGeI_3$ and $MAGeI_3$ PSCs were only 0.11 and 0.20%, respectively.⁴⁶ Some improvement upon this figure was reported in 2018 for devices based on mixed I/Br methylammonium germanium perovskites (0.57% PCE).⁴⁵ Newer developments in the field of lead-free perovskite solar cells have emerged in the form of mixed Sn and Ge perovskite materials, which appear to have improved stability compared to an all-Sn or Ge PSC.^{47–50} Although still in their infancy, Sn-Ge perovskite materials have already achieved PCEs as high as 7.9%.⁵⁰ Further development of germanium and Sn-Ge alloyed materials may finally yield performances on par with or exceeding the best performing LHP devices of today. This goal can only be realized with a deep understanding of the roles atomic structure, defects, and dynamics have on the bulk properties of these materials.

Nuclear magnetic resonance (NMR) spectroscopy is a robust analytical characterization method for studying molecular- and atomic-level structure and dynamics in solids, and its utility extends to these new and emerging perovskite materials. NMR, has been used extensively in the characterization of LHPs, their Sn-based alternatives, and other extensions of these systems.^{51–71} This important tool has largely been overlooked for studying germanium-containing perovskites. This is likely due, in part, to germanium being a challenging nucleus to study using NMR techniques. ^{73}Ge possesses a low gyromagnetic ratio, γ , ($-0.9357 \times 10^7 \text{ rad/T}\cdot\text{s}$), has low natural abundance (7.76%), and is quadrupolar ($I = 9/2$, $Q_m = -19.6 \text{ fm}^2$). Still, probing this nucleus has proven useful in studies at high magnetic fields ($>18 \text{ T}$).^{72–77} Additionally, ^{133}Cs NMR – though itself a quadrupolar nucleus ($I = 7/2$, 100% abundant, $\gamma = 3.5277 \times 10^7 \text{ rad/T}\cdot\text{s}$, $Q_m = -0.34 \text{ fm}^2$), is much less laborious to study than ^{73}Ge , offering a rapid and extremely informative screening

tool.^{54,58,62,67,71,78,79} Therefore, the NMR study of these nuclei when investigating the inorganic germanium halide perovskites (GHPs) and their derivatives will provide invaluable structural and dynamic information that will facilitate further material design and development in this class of materials.

To demonstrate the necessity of complementing “standard” characterization techniques with NMR and quantum chemical computations to better assess their potential for photovoltaic applications, we present a detailed NMR and density functional theory (DFT) investigation on three bulk inorganic parent GHPs: CsGeCl₃, CsGeBr₃, and CsGeI₃. A facile and scalable solution-based synthesis is discussed, developed from previous reports.^{39,40,42,46} This synthesis approach is generally applicable to the halide series (CsGeX₃; X = Cl, Br, I). The GHPs in this study crystallize in the distorted rhombohedral structure (*R3m*), are phase-pure and impurity free. The identity and structure of the parent species was confirmed through NMR spectroscopy, powder X-ray diffraction (PXRD), Raman spectroscopy, diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). This study represents the first ⁷³Ge and ¹³³Cs NMR data reported for these compounds and demonstrates the power of experimental measurements and theoretical computations in unravelling the detailed structure of the inorganic GHPs.

The modified one-pot reaction used for the present study is inexpensive, efficient, and generally applicable to the entire CsGeX₃ (X = Cl, Br, I) series. Detailed preparation conditions are provided in the ESI. In brief, GeO₂, H₃PO₂, and HX are heated under inert atmosphere, followed by precipitation upon addition of the corresponding CsX salt. By substituting the halide source in the acid and cesium salt, large quantities of all three parent perovskites can be synthesized. PXRD, DRS and Raman spectroscopy data for the materials are summarized in **Fig. 1**.

Figure 1. PXRD diffractogram (a), and DRS (b) and Raman (c) spectra for CsGeX₃ (X = Cl, Br, I).

PXRD patterns obtained for the parent perovskites (**Fig. 1a**) agree well with calculated diffractograms for each (Rhombohedral, *R3m*; **Figs. S1-3**). Extracted lattice parameters for each material from PXRD refinement (see **Table S1**) are summarized in **Table 1**. DRS analysis provides optical bandgaps of 3.4, 2.3, and 1.6 eV for CsGeCl₃, CsGeBr₃, and CsGeI₃, respectively (**Fig. 1b**). These results are in good agreement with previous reports.^{35,41,42} It is clear that by defining the halide, the material bandgap can be manipulated over a range spanning nearly 2 eV. Raman spectra (**Fig. 1c**) provide further insight into the structure of CsGeX₃; two strong features at 127 and 293 cm⁻¹ for CsGeI₃ are attributed to the anti-symmetric stretching mode of -GeI₃ clusters and corresponding overtone band, respectively. CsGeBr₃ exhibits an anti-symmetric stretching mode at 139 cm⁻¹ and a symmetric stretching mode at 210 cm⁻¹.

Three strong Raman peaks at 200, 237 and 290 cm^{-1} are observed in the spectrum of CsGeCl_3 that arise from the anti-symmetric stretching, bending and symmetric stretching modes of $-\text{GeCl}_3$ clusters, respectively. Consistent with literature reports, weak features also appear at 91 cm^{-1} for CsGeBr_3 and 120 and 145 cm^{-1} for CsGeI_3 .^{38,42,80} EDX elemental mapping was performed for the CsGeX_3 parent phases with nominal elemental distributions for each material. SEM and EDX data are provided in the ESI (**Figs. S4-6**).

Table 1. Lattice parameters for CsGeX_3 (X = Cl, Br, I).

Lattice parameters	Cell length ($\text{\AA}$)	Cell angles ($^\circ$)	Cell volume ($\text{\AA}^3$)
CsGeCl_3	5.4451(7)	89.72(3)	161.44
CsGeBr_3	5.6471(4)	88.73(6)	179.96
CsGeI_3	5.9959(3)	88.62(1)	215.37

Scheme 1. Structures for CsGeCl_3 (a), CsGeBr_3 (b), and CsGeI_3 (c) derived from PXRD refinement.

Data from PXRD refinement (**Table S1**) was used to build structures for each compound (**Scheme 1**). Each material occupies a slightly distorted perovskite structure (Rhombohedral, space group $R3m$, BaTiO_3 -like).

^{133}Cs magic-angle spinning (MAS) NMR spectra (**Fig. 2a**) for the CsGeX_3 perovskite parent phases indicate a single Cs environment with a unique chemical shift for each of the GHPs, consistent with their crystal structure. The isotropic chemical shift (δ_{iso}) for CsGeCl_3 appears at 34 ppm and has the smallest full-width-at-half-max (FWHM) of 85 Hz. CsGeI_3 has a $\delta_{\text{iso}} = 39$ ppm and has an intermediate FWHM of 107 Hz. CsGeBr_3 has the broadest resonance (FWHM = 154 Hz), appearing at $\delta_{\text{iso}} = 47$ ppm.

Non-spinning ^{133}Cs NMR spectra (**Fig. 2b**) were acquired at 9.4 and 21.1 T, to determine the quadrupole coupling constant (C_Q), asymmetry parameter (η) and whether any measurable chemical shift anisotropy (CSA); span (Ω) and skew (κ) information was present (**Figs. S9-S11** and **Table S2**). For the Br and I parent phases we observe both the central and satellite transitions for this $I=7/2$ nuclear spin. Definitions of NMR parameters can be found in the ESI. For CsGeI_3 at 21.1 T, a large peak at high frequency attributed to CsI can be seen (**Figs. S11, S12**). Experimentally determined ^{133}Cs NMR parameters for the CsGeX_3 series are summarized in **Table 2**. CsGeCl_3 has a small C_Q (12 kHz) compared to CsGeBr_3 and CsGeI_3 (> 50 kHz), with

all having near-zero η values. The 21.1 T data support a small ~ 10 ppm contribution of CSA to both CsGeCl_3 and CsGeBr_3 phases (**Figs. S9 and S10**). ^{133}Cs δ_{iso} values for CsGeX_3 do not appear to follow an obvious halide trend (*vide infra*), with CsGeCl_3 appearing at 36.9 ppm, CsGeBr_3 at 48.2 ppm, and CsGeI_3 at 41.8 ppm.

Figure 2. ^{133}Cs (a) MAS ($\nu_r = 10$ kHz) and (b) non-spinning Hahn echo NMR data for CsGeX_3 ($B_0 = 9.4$ T). CsI impurity indicated with (*). The non-spinning NMR data show both central and satellite transitions in the Br and I phases (CT = Central transition, ST = Satellite transition).

Table 2. Experimental & GIPAW DFT ^{133}Cs NMR parameters for CsGeX_3 (X = Cl, Br, I).

^{133}Cs	C_Q (kHz)		η		δ_{iso} (ppm)		Ω (ppm)		κ	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
CsGeCl_3	12(1)	-19	<0.1	0.00	36.9(4)	29.2	10(1)	11	-1	1
CsGeBr_3	52(1)	-61	0.00(1)	0.00	48.2(8)	52.6	12(4)	21	$-1 \leq \kappa \leq 0$	1
CsGeI_3	55(1)	-64	0.05(4)	0.00	41.8(3)	40.5	n.d.	9	n.d.	1

Detailed DFT computed information for each compound can be found in the ESI and **Table S3**. Overall, the GIPAW based DFT computations agree well with the experimentally determined NMR parameters as shown in **Table 2**. Briefly, the computed isotropic chemical shifts reflect the experimentally observed parabolic shift trend (where $\delta(\text{Br}) > \delta(\text{I}) > \delta(\text{Cl})$). The magnitude of the calculated C_Q increasing from $\text{CsGeCl}_3 < \text{CsGeBr}_3 < \text{CsGeI}_3$ also agrees well with the fitted experimental ^{133}Cs data, and a small CSA is predicted.

To explore the B-site of the GHPs, non-spinning ^{73}Ge NMR spectra were acquired at 21.1 T (**Fig. 3**) and fit to determine their unique NMR parameters including δ_{iso} , C_Q , η , Ω , and κ . **Tables 3 and S3** summarize the experimentally and theoretically determined NMR parameters. A sizeable decrease in C_Q is readily apparent (**Fig. 3**) when the halide is substituted through the series $\text{Cl} \rightarrow \text{I}$ across the CsGeX_3 parent phases, decreasing from 33.7 to 8.4 MHz. Likewise, a clear inverse halide trend is seen with experimental ^{73}Ge δ_{iso} values of -50, 25, and 145 ppm for CsGeCl_3 , CsGeBr_3 , and CsGeI_3 , respectively. Computed C_Q values were predicted well when compared to simulated values from the experimental data, with the trend of C_Q being accurately predicted across the $\text{CsGeCl}_3 > \text{CsGeBr}_3 > \text{CsGeI}_3$ series.

Figure 3. Simulated (blue) and experimental (black) non-spinning ^{73}Ge NMR spectra for (a) CsGeCl_3 , (b) CsGeBr_3 , and (c) CsGeI_3 ($B_0 = 21.1$ T). NMR parameters are summarized in **Table 3**. Simulated NMR spectra were processed with 1500 Hz of Lorentzian broadening with all Euler angles equal to 0° .

Table 3. Experimental & GIPAW DFT ^{73}Ge NMR parameters for CsGeX_3 (X = Cl, Br, I).

^{73}Ge	C_Q (MHz)		η		δ_{iso}		Ω (ppm) [†]		κ	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
CsGeCl_3	33.7(1)	29.4	0.03(1)	0.00	-50(25)	-160	n.d.	218	n.d.	-1
CsGeBr_3	18.3(2)	14.3	0.00(1)	0.00	25(5)	-91	n.d.	135	n.d.	-1
CsGeI_3	8.4(1)	6.0	0.00(2)	0.00	145(5)	-121	n.d.	76	n.d.	-1

[†] CSA was not determined (n.d.) for ^{73}Ge NMR data as the sizable C_Q hampered further assessment at 21.1 T. Although, CSA is suspected from the DFT computations, higher magnetic field strengths are needed to further assess this parameter.

NMR investigations of the A-site for traditional ABX_3 perovskites are routine in the field, accessible through $^{13}\text{C}/^{1}\text{H}/^{14}\text{N}$ for hybrid (A site = methylammonium/formamidinium) perovskites^{53,55,60,61} and ^{133}Cs for non-hybrid perovskites.^{54–56,68,70,71} Other indirect probes of the A-site exist in the form of dopants at the A-site.^{62,63} ^{207}Pb and ^{119}Sn are popular nuclei to access the B-site of Pb- and Sn-based ABX_3 perovskites.^{20,55,59,68–71} Recently, the re-emergence of nuclear quadrupolar resonance (NQR) spectroscopy^{57,67,84} has provided an ability to reach challenging quadrupolar nuclei including $^{79/81}\text{Br}$ and ^{127}I . Interestingly, ^{73}Ge remains absent from this body of work until now. NMR spectroscopy is sensitive to local chemical environment – influenced by changes to the electronic structure and coordination environment of the nucleus of interest. For example, in the A-site NMR spectra for inorganic LHPs, ^{133}Cs chemical shifts exhibit an inverse halide trend (increasing frequency when substituting $\text{Cl} \rightarrow \text{I}$).^{54,56} In CsSnX_3 perovskites, this shift trend follows a normal halide dependency (δ_{iso} decreases as Z increases) as shown in Fig. 4.^{55,71}

Figure 4. General chemical shift trends for the A-site (top) and B-site (bottom) for inorganic Sn- (left, green) and Pb-halide (right, red) perovskites. Here, a decreasing shift with increasing Z represents a normal halide dependency, while increasing shift with Z depicts an inverse halide dependency.^{81–83}

The ^{133}Cs chemical shift in the CsGeX_3 series exhibits a parabolic-like trend in its chemical shift, with quantum chemical calculations accurately reproducing this parabolic-like behavior. Although sample heating by MAS has been shown to influence the ^{133}Cs chemical shift,⁶⁴ we only observed minor changes between the non-spinning and MAS data across two magnetic field strengths. As such, we have attributed this observation to a pseudo-cubic CsGeCl_3 structure (vs. the deviated trigonal CsGeBr_3 and CsGeI_3 parent phases, also supported by the contrast in CsGeCl_3 C_Q with C_Q values for CsGeBr_3 and CsGeI_3). The presence of a semi-symmetric, pseudo-cubic perovskite phase has been reported previously for tetragonal MASnI_3 according to single crystal XRD studies in 2013⁸⁵, and again *via* ^{119}Sn NMR on MASnI_3 in 2020.⁶⁹ Our data indicate that CsGeCl_3 is similar in this regard to MASnI_3 , in which the most accurate XRD refinement ascribes a lower symmetry space group to the material (trigonal $R\bar{3}m$ in this case), while appearing cubic-like through NMR. It has also been noted previously that increasing CsBX_3 lattice symmetry results in a shift to lower frequency ^{133}Cs δ_{iso} , consistent with the lower frequency position of CsGeCl_3 compared to the less symmetric trigonal CsGeBr_3 and CsGeI_3 signals.⁵⁵ The parabolic trend in the ^{133}Cs ssNMR is thus the result of having a Sn-like normal halide dependency for CsGeBr_3 and CsGeI_3 , and a cubic-like signal for CsGeCl_3 .

Unlike the A-site, previous studies on the B-site of bulk inorganic ABX_3 perovskites tends to reveal a common inverse halide dependency for both ^{207}Pb and ^{119}Sn isotropic chemical shifts (δ_{iso} increases as Z increases), as shown in **Fig. 4**.^{54,55,65,69} These halide dependencies have been attributed to the interplay of the paramagnetic and spin-orbit contributions to the total shielding, where one will dominate over the other, causing a push-pull effect between normal or inverse halide dependence.⁸⁶ Examining the ^{73}Ge δ_{iso} values, they follow the same inverse halide dependency as seen for the Pb- and Sn-halide perovskite series. This suggests that this series has a sizeable paramagnetic shielding contribution leading to the observed trends.

To investigate GHP structure further, Cs-X and Ge-X bond angles and distances have been extracted (**Table 4**). Note, there are two sets of A-X and B-X distances (denoted as **X** and **X'**) in each structure (See **Scheme 1** for designation). The shorter A/B-halide distances are designated as **X**, while **X'** indicates the longer A/B-halide set.

Table 4. Cs- and Ge-X bond lengths and angles for CsGeX_3 (X = Cl, Br, I) from PXRD analysis.

	Cs-X (Å)	Ge-X (Å)	Cs-X' (Å)	Ge-X' (Å)	X-Cs-X (°)	X-Ge-X (°)	X'-Cs-X' (°)	X'-Ge-X' (°)	X-Cs-X' (°)	X-Ge-X' (°)
CsGeCl_3	3.8520	2.3528	3.8912	3.0986	53.14	94.16	66.71	86.23	60.14	89.67
CsGeBr_3	3.9516	2.5392	4.0592	3.1230	56.63	95.15	63.32	83.24	60.59	90.50
CsGeI_3	4.1891	2.7533	4.3184	3.2688	58.80	96.65	61.18	81.41	60.56	90.47

In the idealized cubic ABX_3 perovskite structure (with unit cell $\alpha = \beta = \gamma = 90^\circ$), the A-site forms a 12-coordinate cuboctahedron. In the GHP materials, which occupy a trigonal space group, Cs atoms form an imperfect cuboctahedron (slightly distorted from a right-angle unit cell). By analyzing the lattice parameters for each material (**Table 1**), CsGeCl_3 can be seen to be near-cubic, with $\alpha = \beta = \gamma = 89.72^\circ$ ($\sim 90^\circ$). CsGeBr_3 and CsGeI_3 deviate further from 90° but vary only slightly from each other (0.11° difference in lattice angles between CsGeBr_3 and CsGeI_3 , with both having $\sim 1^\circ$ difference from CsGeCl_3). Although

each material crystallizes in a trigonal space group, CsGeCl₃ can be described as pseudo-cubic. These structural differences become more apparent when looking at variations in longest and shortest bond lengths for Cs-X. In particular, the Cs-Cl cuboctahedron has the smallest difference in Cs-X/X' bond lengths (~0.04 Å), leading to a near perfect Cs-X cuboctahedron (the Cs-X/X' bond lengths would be identical – equidistant from all nearby halide atoms).

The B-site for an idealized ABX₃ perovskite structure forms a perfect six-coordinate octahedron. The Ge-X polyhedra seen in this study, however, occupy heavily distorted six-coordinate octahedra-like geometries. The trend in symmetry seen for the Cs-X cuboctahedra is reversed at the B-site for these materials. The difference in shortest and longest Ge-X bond lengths for CsGeCl₃ are noticeably larger than for CsGeBr₃ and CsGeI₃. In an ideal octahedron, these bond length differences are zero. CsGeCl₃ possesses the most distorted Ge-X octahedron in the series, while still being the closest to a cubic lattice. The dramatic impact of these distortions is explored further below.

Previous attempts have been made to correlate structural parameters indicative of tetrahedral and octahedral distortion such as angular variance and mean quadratic elongation to observed NMR parameters such as C_Q, with some success.^{73,74,87,88} While studying the influence of structure on ⁷³Ge NMR,^{73,74} the authors found a more useful and simplified assessment of structural variance by using differences in Ge-O or Ge-X bond lengths and O-Ge-O or X-Ge-X bond angles to correlate to experimentally measured C_Q values. Assessing the differences in longest and shortest bond lengths have been shown to be a strong gauge of distortion in symmetric polyhedra.^{73,74} To explore these structural nuances further we turn our attention to the ⁷³Ge and ¹³³Cs quadrupole coupling constants and investigate how they are influenced by A- and B-site geometry for the GHPs. Evaluation of the Cs cuboctahedron and Ge octahedron, respectively, along with the quadrupolar coupling allows a comparison of how the distances and angles influence the electric field gradient of Cs and Ge. Bond length/angle differences (from **Table 4**) are presented with extracted C_Q values for Cs and Ge (**Table 5**) and plotted in **Fig. 5**.

Table 5. Differences in shortest and longest experimental Cs/Ge-X bond lengths and angles determined from PXRD (see Table 4).

	Bond length difference (Å)		Bond angle difference (°)		C _Q (^a kHz/ ^b MHz)	
	Cs-X	Ge-X	Cs-X	Ge-X	Cs-X ^a	Ge-X ^b
CsGeCl ₃	0.0392	0.7458	13.57	7.93	12(1)	33.7(1)
CsGeBr ₃	0.1076	0.5838	6.69	11.91	52(1)	18.3(1)
CsGeI ₃	0.1293	0.5155	2.38	15.24	55(1)	8.4(1)

Figure 5. C_Q as a function of Cs- and Ge-X (a) bond angle difference, and (b) bond length difference. (a) Equations of fit: $y = -4.0251x + 70.0426$ (black), $y = -3.4742x + 60.7578$ (blue). (b) Equations of fit: $y = 503.1408x - 6.6391$ (black), $y = 107.1815x - 45.7868$ (blue).

Fig. 5 shows bond length and angle differences for GHPs trend with C_Q . There are clear linear relationships between $^{133}\text{Cs}/^{73}\text{Ge } C_Q$ and Cs/Ge-halide bond and angle differences in their respective polyhedra. Increasing the difference between longest and shortest bond lengths in the Cs cuboctahedron or Ge-X octahedron results in a measurable increase in C_Q for each nucleus. Related to this, an increase in bond angle differences for Cs/Ge-X results in a reduction in measured C_Q . This seems to be a sensitive analytical method for evaluating the degree of distortion not only for germanium halide polyhedra, but also cesium cuboctahedra. This reinforces the structural sensitivity of the EFG and its ability to be further applied to metal halide materials using magnetic resonance-based methods.

This study demonstrates that the ^{133}Cs nucleus may be used as a probe of the medium-range order of the perovskite crystal structure. Cesium-133 NMR reflects the symmetry of the neighboring chemical environment (essentially, how symmetric the cuboctahedron is). Larger variations in Cs-X distances and deviations of lattice angles from 90° act as a measure of distortion in the Cs-X cuboctahedra. This is information that remains inaccessible *via* routine diffraction methods or other characterization that preceded this study.

The B-site can act as a gauge for octahedral distortion. Our ^{73}Ge NMR data is impacted by the local octahedral-like halide environment around the nucleus. In this way, parameters such as C_Q and trends in δ_{iso} give us insight into the local Ge environment, with more distortion and less symmetry in the polyhedron resulting in larger C_Q values. From this data, CsGeI_3 has the nearest-to-ideal octahedron out of the three perovskites. As the Ge-X/X' bond length differences become more pronounced, the $^{73}\text{Ge } C_Q$ increases. These differences in Ge-X symmetry result in drastic changes to C_Q , with CsGeCl_3 having a large C_Q of 33.7 MHz. The trend towards the “ideal” Ge-X octahedron as you progress from CsGeCl_3 to CsGeI_3 results in CsGeI_3 having the smallest C_Q of 8.4 MHz. This finding reinforces that the EFG is sensitive to the distortion within the GeX_6 polyhedron whereby the C_Q drastically shrinks as the distortion between X and X' diminish and should be considered more often within materials analysis in semiconducting materials containing quadrupolar nuclei.

To gauge the predictability of quantum chemical computations for GHPs using GIPAW DFT, a series of calculations were performed on the parent phases. Calculated vs. experimental comparison plots for ^{73}Ge and ^{133}Cs are shown in **Fig. 6**. Overall, the GIPAW DFT calculations support the experimental data well. ^{133}Cs C_Q values were well predicted and aided in our understanding of the experimental ^{133}Cs data. The slight changes in lattice parameters that significantly impacted the NMR data were reflected through computation, providing more evidence of the pseudo-cubic nature of CsGeCl_3 and the observed experimental trends. The computed δ_{iso} values for ^{133}Cs are accurate and agree qualitatively with the experimental trends. The calculated ^{73}Ge C_Q values also agree well with experimentally calculated C_Q values. At the same time, the trend for the computed ^{73}Ge δ_{iso} values do not agree well with the experimental results (i.e., a reverse halide dependency), and the halide trend was not reflected in the DFT data. We have witnessed similar discrepancies when computing the heavier Sn and Pb halide perovskites where we attribute this to sizeable spin-orbit effects.^{58,59,69,86,89} Although Ge is lighter, these factors can still influence the nuclear magnetic shielding.⁹⁰ Simulating shielding information for six-coordinate germanium halide centers may prove difficult, with the presence of multiple quadrupolar nuclei in the Ge local environment and extremely broad spectra over a narrow chemical shift range complicating calculations and subsequent analysis. Nevertheless, ^{73}Ge C_Q values were instructive, and the computed parameters were impressively accurate, enabling one to predict the influences on polyhedral distortions on quadrupole coupling as seen earlier in oxides and halides.^{72–74}

Figure 6. Calculated vs. Experimental ^{73}Ge (a) and ^{133}Cs C_Q (c), and ^{73}Ge (b) and ^{133}Cs δ_{iso} (d). Equations of fit: $y = 0.9297x - 2.1519$ (a), $y = 0.1602x - 130.4990$ (b), $y = -1.0480x - 6.4292$ (c), $y = 2.0618x - 46.4483$ (d).

CONCLUSION. In this work, three parent inorganic ABX₃ germanium halide perovskites were synthesized using a facile and scalable method and to assess their optical properties. Solid-state ⁷³Ge and ¹³³Cs NMR spectroscopy was used in concert with DFT calculations to probe the detailed microscopic structure of these GHPs. DFT computations were used to further complement the ¹³³Cs and ⁷³Ge NMR results.

¹³³Cs NMR spectroscopy was demonstrated as a probe of medium-range crystal structure symmetry in these inorganic GHPs, while ⁷³Ge NMR was used to assess the degree of octahedral distortion around germanium. ¹³³Cs NMR and DFT computations, along with existing literature lend support for the higher-symmetry CsGeCl₃ as pseudo-cubic, while still occupying the trigonal space group *R3m* at room temperature. Cubic-like lead-free perovskite phases that belong to lower symmetry space groups (such as trigonal CsGeCl₃ and tetragonal MASnI₃) are an interesting class of structure that is made accessible through NMR spectroscopy. What influence these types of semisymmetric phases have on the properties of these materials necessitates further investigation.

This study further builds on expanding the realm of ⁷³Ge NMR in materials science. The marriage of computation and ⁷³Ge NMR opens the door to studies of other germanium-containing perovskite materials. As Sn/Ge-alloyed perovskites continue to grow in popularity, ⁷³Ge may be able to provide vital insight into the balance between structure and optoelectronic properties of this new class of materials. It is clear a truly comprehensive NMR study requires a combination of experimental and theoretical data to realize the potential of new materials in solar applications and pushing PCEs ever higher. Growing our understanding in the synthesis, structure, and optoelectronic properties and how they interact will be paramount for these lead-free photovoltaic materials to reach their potential.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgements

The Natural Science and Engineering Research Council (NSERC Discovery Grant program; RGPIN-2021-02540, RGPIN-2015-03896 and RGPIN-2020-04045), the ATUMS training program supported by NSERC CREATE (CREATE-463990-2015) as well as the University of Alberta Faculties of Science and Graduate Studies, and Alberta Innovates Strategic Projects Program are recognized for their generous support of this project. RWH is supported by an NSERC CGSD3, and Alberta Innovates Graduate Fellowship. CN is supported by an Alberta Innovates Graduate Fellowship. VKM acknowledges CFI, Canada Research Chairs and Government of Alberta for research support. Access to the 21.1 T NMR spectrometer was provided by the National Ultrahigh-Field NMR Facility for Solids (Ottawa, Canada), a national research facility funded by a consortium of Canadian Universities and managed by the National Research Council Canada (<http://nmr900.ca>).

Supporting Information. Supporting Information is available free of charge at: Materials & methods, definitions of NMR parameters, PXRD data, SEM/EDX data, supplemental NMR figures and fits, and DFT outputs.

REFERENCES

- (1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131* (17), 6050–6051. <https://doi.org/10.1021/ja809598r>.
- (2) Im, J.-H.; Lee, C.-R.; Lee, J.-W.; Park, S.-W.; Park, N.-G. 6.5% Efficient Perovskite Quantum-Dot-Sensitized Solar Cell. *Nanoscale* **2011**, *3* (10), 4088–4093. <https://doi.org/10.1039/C1NR10867K>.
- (3) Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; et al. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Sci. Rep.* **2012**, *2* (1), 591. <https://doi.org/10.1038/srep00591>.
- (4) Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science* (80-.). **2012**, *338* (6107), 643 LP – 647. <https://doi.org/10.1126/science.1228604>.
- (5) Liu, M.; Johnston, M. B.; Snaith, H. J. Efficient Planar Heterojunction Perovskite Solar Cells by Vapour Deposition. *Nature* **2013**, *501* (7467), 395–398. <https://doi.org/10.1038/nature12509>.
- (6) Eperon, G. E.; Stranks, S. D.; Menelaou, C.; Johnston, M. B.; Herz, L. M.; Snaith, H. J. Formamidinium Lead Trihalide: A Broadly Tunable Perovskite for Efficient Planar Heterojunction Solar Cells. *Energy Environ. Sci.* **2014**, *7* (3), 982–988. <https://doi.org/10.1039/C3EE43822H>.
- (7) Stoumpos, C. C.; Malliakas, C. D.; Peters, J. A.; Liu, Z.; Sebastian, M.; Im, J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; et al. Crystal Growth of the Perovskite Semiconductor CsPbBr₃: A New Material for High-Energy Radiation Detection. *Cryst. Growth Des.* **2013**, *13* (7), 2722–2727. <https://doi.org/10.1021/cg400645t>.
- (8) Xing, G.; Mathews, N.; Lim, S. S.; Yantara, N.; Liu, X.; Sabba, D.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. Low-Temperature Solution-Processed Wavelength-Tunable Perovskites for Lasing. *Nat. Mater.* **2014**, *13* (5), 476–480. <https://doi.org/10.1038/nmat3911>.
- (9) He, Y.; Galli, G. Perovskites for Solar Thermoelectric Applications: A First Principle Study of CH₃NH₃Al₃ (A = Pb and Sn). *Chem. Mater.* **2014**, *26* (18), 5394–5400. <https://doi.org/10.1021/cm5026766>.
- (10) Kim, M.; Im, J.; Freeman, A. J.; Ihm, J.; Jin, H. Switchable $S = 1/2$ and $J = 1/2$ Rashba Bands in Ferroelectric Halide Perovskites. *Proc. Natl. Acad. Sci.* **2014**, *111* (19), 6900 LP – 6904. <https://doi.org/10.1073/pnas.1405780111>.
- (11) Jin, H.; Im, J.; Freeman, A. J. Topological Insulator Phase in Halide Perovskite Structures. *Phys. Rev. B* **2012**, *86* (12), 121102. <https://doi.org/10.1103/PhysRevB.86.121102>.
- (12) Green, M. A.; Dunlop, E. D.; Hohl-Ebinger, J.; Yoshita, M.; Kopidakis, N.; Hao, X. Solar Cell Efficiency Tables (Version 58). *Prog. Photovoltaics Res. Appl.* **2021**, *29* (7), 657–667. <https://doi.org/https://doi.org/10.1002/pip.3444>.
- (13) Hutchins, M. Tandem Cells Approaching 30% Efficiency. *PV Mag. January* **2020**, *30*.
- (14) Al-Ashouri, A.; Köhnen, E.; Li, B.; Magomedov, A.; Hempel, H.; Caprioglio, P.; Márquez, J. A.; Vilches, A. B. M.; Kasparavicius, E.; Smith, J. A.; et al. Monolithic Perovskite/Silicon Tandem Solar

- Cell with >29% Efficiency by Enhanced Hole Extraction. *Science* (80-.). **2020**, *370* (6522), 1300–1309. <https://doi.org/10.1126/science.abd4016>.
- (15) Best Research-Cell Efficiency Chart <https://www.nrel.gov/pv/cell-efficiency.html> (accessed Sep 16, 2021).
 - (16) Jung, E. H.; Jeon, N. J.; Park, E. Y.; Moon, C. S.; Shin, T. J.; Yang, T.-Y.; Noh, J. H.; Seo, J. Efficient, Stable and Scalable Perovskite Solar Cells Using Poly(3-Hexylthiophene). *Nature* **2019**, *567* (7749), 511–515. <https://doi.org/10.1038/s41586-019-1036-3>.
 - (17) Jeong, J.; Kim, M.; Seo, J.; Lu, H.; Ahlawat, P.; Mishra, A.; Yang, Y.; Hope, M. A.; Eickemeyer, F. T.; Kim, M.; et al. Pseudo-Halide Anion Engineering for α -FAPbI₃ Perovskite Solar Cells. *Nature* **2021**, *592* (7854), 381–385. <https://doi.org/10.1038/s41586-021-03406-5>.
 - (18) Yoo, J. J.; Seo, G.; Chua, M. R.; Park, T. G.; Lu, Y.; Rotermund, F.; Kim, Y.-K.; Moon, C. S.; Jeon, N. J.; Correa-Baena, J.-P.; et al. Efficient Perovskite Solar Cells via Improved Carrier Management. *Nature* **2021**, *590* (7847), 587–593. <https://doi.org/10.1038/s41586-021-03285-w>.
 - (19) Gwisu, K.; Hanul, M.; Su, L. K.; Yoon, L. Do; Me, Y. S.; Il, S. S. Impact of Strain Relaxation on Performance of α -Formamidinium Lead Iodide Perovskite Solar Cells. *Science* (80-.). **2020**, *370* (6512), 108–112. <https://doi.org/10.1126/science.abc4417>.
 - (20) Askar, A. M.; Bernard, G. M.; Wiltshire, B.; Shankar, K.; Michaelis, V. K. Multinuclear Magnetic Resonance Tracking of Hydro, Thermal, and Hydrothermal Decomposition of CH₃NH₃PbI₃. *J. Phys. Chem. C* **2017**, *121* (2), 1013–1024. <https://doi.org/10.1021/acs.jpcc.6b10865>.
 - (21) Li, J.; Cao, H.-L.; Jiao, W.-B.; Wang, Q.; Wei, M.; Cantone, I.; Lü, J.; Abate, A. Biological Impact of Lead from Halide Perovskites Reveals the Risk of Introducing a Safe Threshold. *Nat. Commun.* **2020**, *11* (1), 310. <https://doi.org/10.1038/s41467-019-13910-y>.
 - (22) Ke, W.; Stoumpos, C. C.; Kanatzidis, M. G. “Unleaded” Perovskites: Status Quo and Future Prospects of Tin-Based Perovskite Solar Cells. *Adv. Mater.* **2019**, *31* (47), 1803230. <https://doi.org/https://doi.org/10.1002/adma.201803230>.
 - (23) Xiao, Z.; Song, Z.; Yan, Y. From Lead Halide Perovskites to Lead-Free Metal Halide Perovskites and Perovskite Derivatives. *Adv. Mater.* **2019**, *31* (47), 1803792. <https://doi.org/https://doi.org/10.1002/adma.201803792>.
 - (24) Schileo, G.; Grancini, G. Lead or No Lead? Availability, Toxicity, Sustainability and Environmental Impact of Lead-Free Perovskite Solar Cells. *J. Mater. Chem. C* **2021**, *9* (1), 67–76. <https://doi.org/10.1039/D0TC04552G>.
 - (25) Yao, H.; Zhou, F.; Li, Z.; Ci, Z.; Ding, L.; Jin, Z. Strategies for Improving the Stability of Tin-Based Perovskite (ASnX₃) Solar Cells. *Adv. Sci.* **2020**, *7* (10), 1903540. <https://doi.org/https://doi.org/10.1002/advs.201903540>.
 - (26) Jokar, E.; Chien, C.-H.; Tsai, C.-M.; Fathi, A.; Diau, E. W.-G. Robust Tin-Based Perovskite Solar Cells with Hybrid Organic Cations to Attain Efficiency Approaching 10%. *Adv. Mater.* **2019**, *31* (2), 1804835. <https://doi.org/https://doi.org/10.1002/adma.201804835>.
 - (27) Ke, W.; Kanatzidis, M. G. Prospects for Low-Toxicity Lead-Free Perovskite Solar Cells. *Nat. Commun.* **2019**, *10* (1), 965. <https://doi.org/10.1038/s41467-019-08918-3>.

- (28) Hao, F.; Stoumpos, C. C.; Cao, D. H.; Chang, R. P. H.; Kanatzidis, M. G. Lead-Free Solid-State Organic–Inorganic Halide Perovskite Solar Cells. *Nat. Photonics* **2014**, *8* (6), 489–494. <https://doi.org/10.1038/nphoton.2014.82>.
- (29) Liu, X.; Wang, Y.; Wu, T.; He, X.; Meng, X.; Barbaud, J.; Chen, H.; Segawa, H.; Yang, X.; Han, L. Efficient and Stable Tin Perovskite Solar Cells Enabled by Amorphous-Polycrystalline Structure. *Nat. Commun.* **2020**, *11* (1), 2678. <https://doi.org/10.1038/s41467-020-16561-6>.
- (30) Nakamura, T.; Yakumaru, S.; Truong, M. A.; Kim, K.; Liu, J.; Hu, S.; Otsuka, K.; Hashimoto, R.; Murdey, R.; Sasamori, T.; et al. Sn(IV)-Free Tin Perovskite Films Realized by in Situ Sn(0) Nanoparticle Treatment of the Precursor Solution. *Nat. Commun.* **2020**, *11* (1), 3008. <https://doi.org/10.1038/s41467-020-16726-3>.
- (31) Wang, C.; Zhang, Y.; Gu, F.; Zhao, Z.; Li, H.; Jiang, H.; Bian, Z.; Liu, Z. Illumination Durability and High-Efficiency Sn-Based Perovskite Solar Cell under Coordinated Control of Phenylhydrazine and Halogen Ions. *Matter* **2021**, *4* (2), 709–721. <https://doi.org/10.1016/j.matt.2020.11.012>.
- (32) Meng, X.; Wang, Y.; Lin, J.; Liu, X.; He, X.; Barbaud, J.; Wu, T.; Noda, T.; Yang, X.; Han, L. Surface-Controlled Oriented Growth of FASnI₃ Crystals for Efficient Lead-Free Perovskite Solar Cells. *Joule* **2020**, *4* (4), 902–912. <https://doi.org/https://doi.org/10.1016/j.joule.2020.03.007>.
- (33) Laubengayer, A. W.; Billings, O. B.; Newkirk, A. E. Chlorogermanic Acid and the Chlorogermanates. Properties and Crystal Structure of Cesium Hexachlorogermanate. *J. Am. Chem. Soc.* **1940**, *62* (3), 546–548. <https://doi.org/10.1021/ja01860a027>.
- (34) Christensen, A. N.; Rasmussen, S. E. A Ferroelectric Chloride of Perovskite Type. *Acta Chem. Scand* **1965**, *19*, 421–428.
- (35) Walters, G.; Sargent, E. H. Electro-Optic Response in Germanium Halide Perovskites. *J. Phys. Chem. Lett.* **2018**, *9* (5), 1018–1027. <https://doi.org/10.1021/acs.jpclett.7b03353>.
- (36) Men, L.; Rosales, B. A.; Gentry, N. E.; Cady, S. D.; Vela, J. Lead-Free Semiconductors: Soft Chemistry, Dimensionality Control, and Manganese-Doping of Germanium Halide Perovskites. *ChemNanoMat* **2019**, *5* (3), 334–339. <https://doi.org/https://doi.org/10.1002/cnma.201800497>.
- (37) Thiele, G.; Rotter, H. W.; Schmidt, K. D. Kristallstrukturen Und Phasentransformationen von Caesiumtrihalogenogermanaten(II) CsGeX₃ (X = Cl, Br, I). *Zeitschrift für Anorg. und Allg. Chemie* **1987**, *545* (2), 148–156. <https://doi.org/https://doi.org/10.1002/zaac.19875450217>.
- (38) Tang, L.-C.; Chang, C.-S.; Tang, L.-C.; Huang, J. Y. Electronic Structure and Optical Properties of Rhombohedral CsGeI₃ crystal. *J. Phys. Condens. Matter* **2000**, *12* (43), 9129–9143. <https://doi.org/10.1088/0953-8984/12/43/303>.
- (39) QingTian, G.; QiWei, P.; Wei, S.; Xun, S.; ChangShui, F. CsGeCl₃: A New IR Nonlinear Material. *Prog. Cryst. Growth Charact. Mater.* **2000**, *40* (1), 89–95. [https://doi.org/https://doi.org/10.1016/S0960-8974\(00\)00009-7](https://doi.org/https://doi.org/10.1016/S0960-8974(00)00009-7).
- (40) Tang, L. C.; Huang, J. Y.; Chang, C. S.; Lee, M. H.; Liu, L. Q. New Infrared Nonlinear Optical Crystal CsGeBr₃: Synthesis, Structure and Powder Second-Harmonic Generation Properties. *J. Phys. Condens. Matter* **2005**, *17* (46), 7275–7286. <https://doi.org/10.1088/0953-8984/17/46/011>.
- (41) Lin, Z.-G.; Tang, L.-C.; Chou, C.-P. Study on Mid-IR NLO Crystals CsGe(Br_xCl_{1-x})₃. *Opt. Mater. (Amst)*. **2008**, *31* (1), 28–34. <https://doi.org/https://doi.org/10.1016/j.optmat.2008.01.004>.

- (42) Stoumpos, C. C.; Frazer, L.; Clark, D. J.; Kim, Y. S.; Rhim, S. H.; Freeman, A. J.; Ketterson, J. B.; Jang, J. I.; Kanatzidis, M. G. Hybrid Germanium Iodide Perovskite Semiconductors: Active Lone Pairs, Structural Distortions, Direct and Indirect Energy Gaps, and Strong Nonlinear Optical Properties. *J. Am. Chem. Soc.* **2015**, *137* (21), 6804–6819. <https://doi.org/10.1021/jacs.5b01025>.
- (43) Wu, X.; Song, W.; Li, Q.; Zhao, X.; He, D.; Quan, Z. Synthesis of Lead-Free CsGeI₃ Perovskite Colloidal Nanocrystals and Electron Beam-Induced Transformations. *Chem. – An Asian J.* **2018**, *13* (13), 1654–1659. <https://doi.org/10.1002/asia.201800573>.
- (44) Chen, L.-J. Synthesis and Optical Properties of Lead-Free Cesium Germanium Halide Perovskite Quantum Rods. *RSC Adv.* **2018**, *8* (33), 18396–18399. <https://doi.org/10.1039/C8RA01150H>.
- (45) Kopacic, I.; Friesenbichler, B.; Hoeffler, S. F.; Kunert, B.; Plank, H.; Rath, T.; Trimmel, G. Enhanced Performance of Germanium Halide Perovskite Solar Cells through Compositional Engineering. *ACS Appl. Energy Mater.* **2018**, *1* (2), 343–347. <https://doi.org/10.1021/acsaem.8b00007>.
- (46) Krishnamoorthy, T.; Ding, H.; Yan, C.; Leong, W. L.; Baikie, T.; Zhang, Z.; Sherburne, M.; Li, S.; Asta, M.; Mathews, N.; et al. Lead-Free Germanium Iodide Perovskite Materials for Photovoltaic Applications. *J. Mater. Chem. A* **2015**, *3* (47), 23829–23832. <https://doi.org/10.1039/C5TA05741H>.
- (47) Ito, N.; Kamarudin, M. A.; Hirotani, D.; Zhang, Y.; Shen, Q.; Ogomi, Y.; Iikubo, S.; Minemoto, T.; Yoshino, K.; Hayase, S. Mixed Sn–Ge Perovskite for Enhanced Perovskite Solar Cell Performance in Air. *J. Phys. Chem. Lett.* **2018**, *9* (7), 1682–1688. <https://doi.org/10.1021/acs.jpclett.8b00275>.
- (48) Nagane, S.; Ghosh, D.; Hoyer, R. L. Z.; Zhao, B.; Ahmad, S.; Walker, A. B.; Islam, M. S.; Ogale, S.; Sadhanala, A. Lead-Free Perovskite Semiconductors Based on Germanium–Tin Solid Solutions: Structural and Optoelectronic Properties. *J. Phys. Chem. C* **2018**, *122* (11), 5940–5947. <https://doi.org/10.1021/acs.jpcc.8b00480>.
- (49) Chen, M.; Ju, M.-G.; Garces, H. F.; Carl, A. D.; Ono, L. K.; Hawash, Z.; Zhang, Y.; Shen, T.; Qi, Y.; Grimm, R. L.; et al. Highly Stable and Efficient All-Inorganic Lead-Free Perovskite Solar Cells with Native-Oxide Passivation. *Nat. Commun.* **2019**, *10* (1), 16. <https://doi.org/10.1038/s41467-018-07951-y>.
- (50) Ng, C. H.; Nishimura, K.; Ito, N.; Hamada, K.; Hirotani, D.; Wang, Z.; Yang, F.; Iikubo, S.; Shen, Q.; Yoshino, K.; et al. Role of GeI₂ and SnF₂ Additives for SnGe Perovskite Solar Cells. *Nano Energy* **2019**, *58*, 130–137. <https://doi.org/10.1016/j.nanoen.2019.01.026>.
- (51) Hooper, R. W.; Klein, B. A.; Michaelis, V. K. Dynamic Nuclear Polarization (DNP) 101: A New Era for Materials. *Chem. Mater.* **2020**, *32* (11), 4425–4430. <https://doi.org/10.1021/acs.chemmater.0c01801>.
- (52) Piveteau, L.; Ong, T.-C.; Rossini, A. J.; Emsley, L.; Copéret, C.; Kovalenko, M. V. Structure of Colloidal Quantum Dots from Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy. *J. Am. Chem. Soc.* **2015**, *137* (43), 13964–13971. <https://doi.org/10.1021/jacs.5b09248>.
- (53) Kubicki, D. J.; Prochowicz, D.; Hofstetter, A.; Péchy, P.; Zakeeruddin, S. M.; Grätzel, M.; Emsley, L. Cation Dynamics in Mixed-Cation (MA)_x(FA)_{1-x}PbI₃ Hybrid Perovskites from Solid-State NMR. *J. Am. Chem. Soc.* **2017**, *139* (29), 10055–10061. <https://doi.org/10.1021/jacs.7b04930>.
- (54) Karmakar, A.; Dodd, M. S.; Zhang, X.; Oakley, M. S.; Klobukowski, M.; Michaelis, V. K.

- Mechanochemical Synthesis of 0D and 3D Cesium Lead Mixed Halide Perovskites. *Chem. Commun.* **2019**, 55 (35), 5079–5082. <https://doi.org/10.1039/C8CC09622H>.
- (55) Kubicki, D. J.; Prochowicz, D.; Salager, E.; Rakhmatullin, A.; Grey, C. P.; Emsley, L.; Stranks, S. D. Local Structure and Dynamics in Methylammonium, Formamidinium, and Cesium Tin(II) Mixed-Halide Perovskites from ^{119}Sn Solid-State NMR. *J. Am. Chem. Soc.* **2020**, 142 (17), 7813–7826. <https://doi.org/10.1021/jacs.0c00647>.
 - (56) Prochowicz, D.; Yadav, P.; Saliba, M.; Kubicki, D. J.; Tavakoli, M. M.; Zakeeruddin, S. M.; Lewiński, J.; Emsley, L.; Grätzel, M. One-Step Mechanochemical Incorporation of an Insoluble Cesium Additive for High Performance Planar Heterojunction Solar Cells. *Nano Energy* **2018**, 49, 523–528. <https://doi.org/10.1016/j.nanoen.2018.05.010>.
 - (57) Piveteau, L.; Aebli, M.; Yazdani, N.; Millen, M.; Korosec, L.; Krieg, F.; Benin, B. M.; Morad, V.; Piveteau, C.; Shiroka, T.; et al. Bulk and Nanocrystalline Cesium Lead-Halide Perovskites as Seen by Halide Magnetic Resonance. *ACS Cent. Sci.* **2020**, 6 (7), 1138–1149. <https://doi.org/10.1021/acscentsci.0c00587>.
 - (58) Karmakar, A.; Mukhopadhyay, S.; Gachod, P. G. B.; Mora-Gomez, V. A.; Bernard, G. M.; Brown, A.; Michaelis, V. K. Uncovering Halogen Mixing and Octahedral Dynamics in Cs_2SnX_6 by Multinuclear Magnetic Resonance Spectroscopy. *Chem. Mater.* **2021**. <https://doi.org/10.1021/acs.chemmater.1c01561>.
 - (59) Karmakar, A.; Askar, A. M.; Bernard, G. M.; Terskikh, V. V.; Ha, M.; Patel, S.; Shankar, K.; Michaelis, V. K. Mechanochemical Synthesis of Methylammonium Lead Mixed-Halide Perovskites: Unraveling the Solid-Solution Behavior Using Solid-State NMR. *Chem. Mater.* **2018**, 30 (7), 2309–2321. <https://doi.org/10.1021/acs.chemmater.7b05209>.
 - (60) Van Gompel, W. T. M.; Herckens, R.; Reekmans, G.; Ruttens, B.; D'Haen, J.; Adriaenssens, P.; Lutsen, L.; Vanderzande, D. Degradation of the Formamidinium Cation and the Quantification of the Formamidinium–Methylammonium Ratio in Lead Iodide Hybrid Perovskites by Nuclear Magnetic Resonance Spectroscopy. *J. Phys. Chem. C* **2018**, 122 (8), 4117–4124. <https://doi.org/10.1021/acs.jpcc.7b09805>.
 - (61) Kubicki, D. J.; Prochowicz, D.; Hofstetter, A.; Saski, M.; Yadav, P.; Bi, D.; Pellet, N.; Lewiński, J.; Zakeeruddin, S. M.; Grätzel, M.; et al. Formation of Stable Mixed Guanidinium–Methylammonium Phases with Exceptionally Long Carrier Lifetimes for High-Efficiency Lead Iodide-Based Perovskite Photovoltaics. *J. Am. Chem. Soc.* **2018**, 140 (9), 3345–3351. <https://doi.org/10.1021/jacs.7b12860>.
 - (62) Kubicki, D. J.; Prochowicz, D.; Hofstetter, A.; Zakeeruddin, S. M.; Grätzel, M.; Emsley, L. Phase Segregation in Cs-, Rb- and K-Doped Mixed-Cation $(\text{MA})_x(\text{FA})_{1-x}\text{PbI}_3$ Hybrid Perovskites from Solid-State NMR. *J. Am. Chem. Soc.* **2017**, 139 (40), 14173–14180. <https://doi.org/10.1021/jacs.7b07223>.
 - (63) Kubicki, D. J.; Prochowicz, D.; Hofstetter, A.; Zakeeruddin, S. M.; Grätzel, M.; Emsley, L. Phase Segregation in Potassium-Doped Lead Halide Perovskites from ^{39}K Solid-State NMR at 21.1 T. *J. Am. Chem. Soc.* **2018**, 140 (23), 7232–7238. <https://doi.org/10.1021/jacs.8b03191>.
 - (64) Karmakar, A.; Dodd, M. S.; Agnihotri, S.; Ravera, E.; Michaelis, V. K. Cu(II)-Doped $\text{Cs}_2\text{SbAgCl}_6$ Double Perovskite: A Lead-Free, Low-Bandgap Material. *Chem. Mater.* **2018**, 30 (22), 8280–8290. <https://doi.org/10.1021/acs.chemmater.8b03755>.

- (65) Askar, A. M.; Karmakar, A.; Bernard, G. M.; Ha, M.; Terskikh, V. V.; Wiltshire, B. D.; Patel, S.; Fleet, J.; Shankar, K.; Michaelis, V. K. Composition-Tunable Formamidinium Lead Mixed Halide Perovskites via Solvent-Free Mechanochemical Synthesis: Decoding the Pb Environments Using Solid-State NMR Spectroscopy. *J. Phys. Chem. Lett.* **2018**, *9* (10), 2671–2677. <https://doi.org/10.1021/acs.jpcllett.8b01084>.
- (66) Franssen, W. M. J.; Kentgens, A. P. M. Solid-State NMR of Hybrid Halide Perovskites. *Solid State Nucl. Magn. Reson.* **2019**, *100*, 36–44. <https://doi.org/https://doi.org/10.1016/j.ssnmr.2019.03.005>.
- (67) Piveteau, L.; Morad, V.; Kovalenko, M. V. Solid-State NMR and NQR Spectroscopy of Lead-Halide Perovskite Materials. *J. Am. Chem. Soc.* **2020**, *142* (46), 19413–19437. <https://doi.org/10.1021/jacs.0c07338>.
- (68) Chen, Y.; Smock, S. R.; Flintgruber, A. H.; Perras, F. A.; Brutchey, R. L.; Rossini, A. J. Surface Termination of CsPbBr₃ Perovskite Quantum Dots Determined by Solid-State NMR Spectroscopy. *J. Am. Chem. Soc.* **2020**, *142* (13), 6117–6127. <https://doi.org/10.1021/jacs.9b13396>.
- (69) Ha, M.; Karmakar, A.; Bernard, G. M.; Basilio, E.; Krishnamurthy, A.; Askar, A. M.; Shankar, K.; Kroeker, S.; Michaelis, V. K. Phase Evolution in Methylammonium Tin Halide Perovskites with Variable Temperature Solid-State ¹¹⁹Sn NMR Spectroscopy. *J. Phys. Chem. C* **2020**, *124* (28), 15015–15027. <https://doi.org/10.1021/acs.jpcc.0c03589>.
- (70) Karmakar, A.; Bhattacharya, A.; Bernard, G. M.; Mar, A.; Michaelis, V. K. Revealing the Local Sn and Pb Arrangements in CsSn_xPb_{1-x}Br₃ Perovskites with Solid-State NMR Spectroscopy. *ACS Mater. Lett.* **2021**, *3* (3), 261–267. <https://doi.org/10.1021/acsmaterialslett.0c00596>.
- (71) Karmakar, A.; Bhattacharya, A.; Sarkar, D.; Bernard, G. M.; Mar, A.; Michaelis, V. K. Influence of Hidden Halogen Mobility on Local Structure of CsSn(Cl_{1-x}Br_x)₃ Mixed-Halide Perovskites by Solid-State NMR. *Chem. Sci.* **2021**, *12* (9), 3253–3263. <https://doi.org/10.1039/D0SC05614F>.
- (72) Michaelis, V. K.; Aguiar, P. M.; Terskikh, V. V.; Kroeker, S. Germanium-73 NMR of Amorphous and Crystalline GeO₂. *Chem. Commun.* **2009**, No. 31, 4660–4662. <https://doi.org/10.1039/B906642J>.
- (73) Michaelis, V. K.; Kroeker, S. ⁷³Ge Solid-State NMR of Germanium Oxide Materials: Experimental and Theoretical Studies. *J. Phys. Chem. C* **2010**, *114* (49), 21736–21744. <https://doi.org/10.1021/jp1071082>.
- (74) Greer, B. J.; Michaelis, V. K.; Terskikh, V. V.; Kroeker, S. Reconnaissance of Diverse Structural and Electronic Environments in Germanium Halides by Solid-State ⁷³Ge NMR and Quantum Chemical Calculations. *Can. J. Chem.* **2011**, *89* (9), 1118–1129. <https://doi.org/10.1139/v11-052>.
- (75) Sutrisno, A.; Hanson, M. A.; Rupar, P. A.; Terskikh, V. V.; Baines, K. M.; Huang, Y. Exploring the Limits of ⁷³Ge Solid-State NMR Spectroscopy at Ultrahigh Magnetic Field. *Chem. Commun.* **2010**, *46* (16), 2817–2819. <https://doi.org/10.1039/B926071D>.
- (76) Hanson, M. A.; Sutrisno, A.; Terskikh, V. V.; Baines, K. M.; Huang, Y. Solid-State ⁷³Ge NMR Spectroscopy of Simple Organogermanes. *Chem. – A Eur. J.* **2012**, *18* (43), 13770–13779. <https://doi.org/https://doi.org/10.1002/chem.201201944>.
- (77) Javadi, M.; Michaelis, V. K.; Veinot, J. G. C. Thermally Induced Evolution of “Ge(OH)₂”: Controlling the Formation of Oxide-Embedded Ge Nanocrystals. *J. Phys. Chem. C* **2018**, *122* (30), 17518–17525. <https://doi.org/10.1021/acs.jpcc.8b04640>.

- (78) Bernard, G. M.; Karmakar, A.; Michaelis Molecular Sciences and Chemical Engineering, V. K. B. T.-R. M. in C. Solid-State NMR Studies of Halide Perovskite Materials with Photoconversion Potential; Elsevier, 2021. <https://doi.org/https://doi.org/10.1016/B978-0-12-823144-9.00018-2>.
- (79) Kubicki, D. J.; Stranks, S. D.; Grey, C. P.; Emsley, L. NMR Spectroscopy Probes Microstructure, Dynamics and Doping of Metal Halide Perovskites. *Nat. Rev. Chem.* **2021**, 5 (9), 624–645. <https://doi.org/10.1038/s41570-021-00309-x>.
- (80) Applications in Inorganic Chemistry. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. December 31, 2008, pp 149–354. <https://doi.org/https://doi.org/10.1002/9780470405840.ch2>.
- (81) Kantola, A. M.; Lantto, P.; Vaara, J.; Jokisaari, J. Carbon and Proton Shielding Tensors in Methyl Halides. *Phys. Chem. Chem. Phys.* **2010**, 12 (11), 2679–2692. <https://doi.org/10.1039/B923506J>.
- (82) Jameson, C. J.; Mason, J. The Chemical Shift. In *Multinuclear NMR*; Mason, J., Ed.; Springer US: Boston, MA, 1987; pp 51–88. https://doi.org/10.1007/978-1-4613-1783-8_3.
- (83) Kidd, R. G. Nuclear Shielding of the Transition Metals; Webb, G. A., Ed.; Annual Reports on NMR Spectroscopy; Academic Press, 1980; Vol. 10, pp 1–79. [https://doi.org/https://doi.org/10.1016/S0066-4103\(08\)60392-0](https://doi.org/https://doi.org/10.1016/S0066-4103(08)60392-0).
- (84) Szell, P. M. J.; Bryce, D. L. Solid-State Nuclear Magnetic Resonance and Nuclear Quadrupole Resonance as Complementary Tools to Study Quadrupolar Nuclei in Solids. *Concepts Magn. Reson. Part A* **2016**, 45A (6), e21412. <https://doi.org/https://doi.org/10.1002/cmr.a.21412>.
- (85) Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties. *Inorg. Chem.* **2013**, 52 (15), 9019–9038. <https://doi.org/10.1021/ic401215x>.
- (86) Dmitrenko, O.; Bai, S.; Dybowski, C. Prediction of ^{207}Pb NMR Parameters for the Solid Ionic Lead(II) Halides Using the Relativistic ZORA-DFT Formalism: Comparison with the Lead-Containing Molecular Systems. *Solid State Nucl. Magn. Reson.* **2008**, 34 (3), 186–190. <https://doi.org/https://doi.org/10.1016/j.ssnmr.2008.08.003>.
- (87) Keith, R.; V., G. G.; H., R. P. Quadratic Elongation: A Quantitative Measure of Distortion in Coordination Polyhedra. *Science*. **1971**, 172 (3983), 567–570. <https://doi.org/10.1126/science.172.3983.567>.
- (88) Fleet, M. E. Distortion Parameters for Coordination Polyhedra. *Mineral. Mag.* **1976**, 40 (313), 531–533. <https://doi.org/DOL: 10.1180/minmag.1976.040.313.18>.
- (89) Bernard, G. M.; Wasylshen, R. E.; Ratcliffe, C. I.; Tersikh, V.; Wu, Q.; Buriak, J. M.; Hauger, T. Methylammonium Cation Dynamics in Methylammonium Lead Halide Perovskites: A Solid-State NMR Perspective. *J. Phys. Chem. A* **2018**, 122 (6), 1560–1573. <https://doi.org/10.1021/acs.jpca.7b11558>.
- (90) Quarti, C.; Furet, E.; Katan, C. DFT Simulations as Valuable Tool to Support NMR Characterization of Halide Perovskites: The Case of Pure and Mixed Halide Perovskites. *Helv. Chim. Acta* **2021**, 104 (5), e2000231. <https://doi.org/https://doi.org/10.1002/hlca.202000231>.

Exploring Structural Nuances in Germanium Halide Perovskites using Solid-state ^{73}Ge and ^{133}Cs NMR Spectroscopy

Riley W. Hooper¹, Chuyi Ni¹, Dylan G. Tkachuk¹, Yingjie He¹, Victor V. Terskikh², Jonathan G.C. Veinot¹, and Vladimir K. Michaelis^{1,*}

¹Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

²Metrology, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

Table of Contents

Materials and Methods	2
Experimental	2
Synthesis.....	2
Powder X-Ray Diffraction	2
Diffuse Reflectance Spectroscopy Measurements	2
Raman Spectroscopy	2
Scanning Electron Microscopy/Energy-dispersive X-ray Analysis	2
Quantum Chemical Computations	2
NMR Processing and Analysis.....	3
Solid-state NMR Spectroscopy	3
Definitions	3
PXRD Data	5
SEM/EDX Data	7
Supplemental NMR Figures	9
DFT Calculations	12
References	14

Materials and Methods

Experimental

GeO₂ (99.99+%), CsCl (99.9%), CsBr (99.999%), CsI (99.999%), 57% aqueous HI, and 50% aqueous H₃PO₂ were purchased from Sigma Aldrich and used as-is.

Synthesis

Three parent CsGeX₃ compounds were made by expanding on the syntheses of Tiang, Tang, Stoumpos, and Krishnamoorthy.^{1–4} GeO₂, 50% H₃PO₂ and aqueous HX (X = Cl, Br, I) were added to an evacuated three-neck round-bottom flask under inert atmosphere. The reaction mixture was maintained at 105 °C for three hours under vigorous stirring. Upon addition of a stoichiometric amount of cesium halide salt and removal from heat, the cesium germanium halide perovskite precipitates out of solution.

In a typical reaction, 1 mmol each of GeO₂ and CsX were used, with 7 mL each of H₃PO₂ and HX (1:1). The products were left overnight under inert atmosphere in the mother liquor and purified *via* filtration. The products were washed with a small amount of degassed EtOH and dried overnight in a vacuum chamber. It was found that to collect all product from the reaction vessel, small amounts of HX could be added to the flask to “wash” the remaining crystals off the flask for easier transfer to filter.

Powder X-Ray Diffraction

Powder X-ray diffraction (PXRD) measurements were carried out on a Bruker D8 Advance diffractometer (Cu-K_{α1} (λ = 1.5406 Å) and K_{α2} (λ = 1.5444 Å) radiation). PXRD spectra were scanned between 2θ ranges of 10–80° with a scanning steps of 0.06 °/s. PXRD refinement was performed using Jade 6.5 via WPF refinement to the corresponding PDF cards (CsGeCl₃; 85-1272, CsGeBr₃; 85-1273, CsGeI₃; 85-1274).

Diffuse Reflectance Spectroscopy Measurements

Diffuse reflectance spectroscopy (DRS) analysis was performed using a Cary 5000 UV-Vis-NIR, with a diffuse reflectance integrating sphere attachment. Samples were prepared by mounting the powder in the sample holder. The detector and grating filter were changed at 900 nm.

Raman Spectroscopy

Raman spectroscopy was performed using a Renishaw inVia Raman microscope equipped with a 532 nm diode laser operating at a power of 50 mW on the sample. Samples were prepared by mounting the powder on a glass slide. At least three spots were measured for each sample, with an integration of 10 scans on each spot with 10 % of laser power.

Scanning Electron Microscopy/Energy-dispersive X-ray Analysis

Scanning electron microscopy (SEM) was performed on a Zeiss Sigma 300 VP-FESEM (accelerating voltage of 5-20 kV) equipped with secondary and backscattered electron detectors, an in-lens detector, and an energy dispersive X-ray (EDX) spectrometer. SEM samples were prepared by applying powdered samples onto carbon tape on an aluminum stub in a N₂ filled glovebox.

Quantum Chemical Computations

Density functional theory (DFT) computations were performed using the CASTEP⁵ and NMR CASTEP^{6–8} software packages, which uses the gauge-including projector augmented waves (GIPAW) method for

computing magnetic resonance properties of periodic structures. Calculations were done using the Perdew-Burke-Ernzerhof (PBE)⁹ generalized gradient approximation (GGA) exchange-correlation functional, ultrasoft pseudopotentials and zeroth-order regular approximation (ZORA) relativistic effects. Spin-orbit effects were not considered. A Monkhorst-Pack grid of $n \times n \times n$ k -points ($n = 12$ for CsGeCl₃, CsGeBr₃; $n = 14$ for CsGeI₃; $n = 9$ for CsCl) and an extreme basis set precision (corresponding to a plane wave cutoff energy of 566 eV for CsGeX₃ and 305 eV for CsCl) was applied to all computations. Magnetic shielding values converged to $\Delta\sigma^{\text{calc}} \leq 1$ ppm between increases in the k -point grid dimension parameter, n . DFT-computed ¹³³Cs and ⁷³Ge magnetic shieldings were converted to chemical shifts using computed values for CsCl (Materials Project, mp-22865) and GeCl₄ (Materials Project, mp-30086) CIFs¹⁰ as reference samples with $\delta(\text{ppm}) = \sigma_{\text{ref}}^{\text{calc}} (\text{ppm}) - \sigma_{\text{model}}^{\text{calc}} (\text{ppm})$.

NMR Processing and Analysis

All NMR spectra were processed with Bruker TopSpin 3.6.2. ¹³³Cs and ⁷³Ge NMR spectra were fit using the WSolids1 NMR simulation program.¹¹ Euler angles were extracted from CIF files using EFGShield (Version 4.6) to aid in simulation.¹² Data were plotted using Origin 2020.

Solid-state NMR Spectroscopy

¹³³Cs NMR spectroscopy was carried out on a Bruker AVANCE III HD 400 NMR spectrometer ($B_0 = 9.4$ T) equipped with a 4 mm double-resonance (H/X) Bruker magic-angle spinning (MAS) probe. MAS NMR spectra were acquired at natural abundance using a Bloch-decay experiment with a $4.0 \mu\text{s}$ $\pi/2$ pulse ($\nu_{\text{rf}} = 62.5$ kHz), 16 co-added transients, recycle delay of 400 seconds, and a spinning frequency of 10 kHz. Non-spinning ¹³³Cs NMR spectra were acquired using a Hahn echo experiment using similar experimental parameters as noted above. The ¹³³Cs NMR spectra at 9.4 T were referenced to a secondary standard (solid CsCl to 223.2 ppm) with respect to 0.5 M CsCl ($\delta(^{133}\text{Cs}) = 0.00$ ppm).¹³ Cesium-133 NMR spectroscopy was also carried out on a Bruker AVANCE II 900 NMR spectrometer ($B_0 = 21.1$ T). Non-spinning NMR spectra were acquired on a home-built 7 mm X solenoid probe using a static quad-echo experiment ($\pi/2_x - \tau - \pi/2_y$), with a $2.0 \mu\text{s}$ $\pi/2$ pulse ($\nu_{\text{rf}} = 125$ kHz), $98 \mu\text{s}$ interpulse delay, 64 co-added transients and a recycle delay of 900 seconds. ¹³³Cs spectra at 21.1 T were referenced to 0.1 M CsCl (aq) ($\delta_{\text{iso}} = 0.00$ ppm).

⁷³Ge NMR spectra were acquired on a Bruker AVANCE II 900 NMR spectrometer ($B_0 = 21.1$ T). Non-spinning NMR spectra were acquired on a 7 mm single resonance MAS Bruker probe at natural abundance via Carr–Purcell Meiboom–Gill (CPMG) (32k (CsGeI₃), 64k (CsGeBr₃), or 96k (CsGeCl₃) co-added transients) and quad-echo ($\pi/2_x - \tau - \pi/2_y$), with a $4.0 \mu\text{s}$ $\pi/2$ pulse ($\nu_{\text{rf}} = 62.5$ kHz), $196 \mu\text{s}$ interpulse delay, 640k co-added transients and a recycle delay of 0.2 seconds. ⁷³Ge NMR spectra were referenced to a secondary standard (liquid GeCl₄ to 30.9 ppm) with respect to GeH₄ ($\delta(^{73}\text{Ge}) = 0.00$ ppm).¹⁴

Definitions

More extensive work describing interactions in solid-state NMR can be found elsewhere.^{15–18} Here, we will present some brief theory and important parameters of interest for this study. We are interested in describing the isotropic magnetic shielding (σ_{iso}) and chemical shift (δ_{iso}), chemical shift anisotropic information in the form of a span (Ω) and skew (κ), and the nuclear quadrupole coupling constant (C_Q) and its asymmetry parameter (η).

σ_{iso} : the isotropic magnetic shielding is the result of averaging the principal components of the anisotropic shielding tensor.

$$\sigma_{iso} = \frac{(\sigma_{11} + \sigma_{22} + \sigma_{33})}{3}$$

δ_{iso} : the isotropic chemical shift is the result of averaging the principal components of the anisotropic shift tensor.

$$\delta_{iso} = \frac{(\delta_{11} + \delta_{22} + \delta_{33})}{3}$$

Ω : The span represents the breadth of the chemical shift anisotropy (CSA).

$$\Omega = \sigma_{33} - \sigma_{11} = \delta_{11} - \delta_{33}$$

κ : The asymmetry of the CSA pattern ($-1 \leq \kappa \leq 1$).

$$\kappa = \frac{3(\sigma_{iso} - \sigma_{22})}{\Omega} = \frac{3(\delta_{22} - \delta_{iso})}{\Omega}$$

C_Q : The magnitude of the quadrupolar coupling interaction.

$$C_Q = \frac{eV_{33}Q}{h}$$

Where e is the elementary charge, V_{33} is the largest principal component of the electric field gradient (EFG) tensor, Q is the quadrupolar moment of the nucleus, and h is Planck's constant.

η : The quadrupolar asymmetry parameter ($0 \leq \eta \leq 1$) describes the asymmetry of the quadrupolar interaction.

$$\eta = \frac{V_{11} - V_{22}}{V_{33}}$$

PXRD Data

Figure S1. Calculated (black) and experimental (red) diffractogram for CsGeCl_3 .

Figure S2. Calculated (black) and experimental (red) diffractogram for CsGeBr_3 .

Figure S3. Calculated (black) and experimental (red) diffractogram for CsGeI_3 .

Table S1. PXRD cell refinement for synthesized perovskites.

Formula	CsGeCl_3	CsGeBr_3	CsGeI_3
Crystal system	Trigonal	Trigonal	Trigonal
Space group	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$
PDF card	85-1272	85-1273	85-1274
Cell parameters	$a = 5.4451 \text{ \AA}$	$a = 5.6471 \text{ \AA}$	$a = 5.9959 \text{ \AA}$
	$b = 5.4451 \text{ \AA}$	$b = 5.6471 \text{ \AA}$	$b = 5.9959 \text{ \AA}$
	$c = 5.4451 \text{ \AA}$	$c = 5.6471 \text{ \AA}$	$c = 5.9959 \text{ \AA}$
	$\alpha = \beta = \gamma = 89.72^\circ$	$\alpha = \beta = \gamma = 88.73^\circ$	$\alpha = \beta = \gamma = 88.62^\circ$
Volume ($\text{\AA}^3$)	161.44	179.96	215.37
Z	1	1	1
R	5.42%	7.12%	8.03%

SEM/EDX Data

Figure S4. Elemental mapping for CsGeCl_3 .

Figure S5. Elemental mapping for CsGeBr_3 .

Figure S6. Elemental mapping for CsGeI_3 .

Supplemental NMR Figures

Figure S7. ^{133}Cs MAS NMR ($\nu_{\text{rot}} = 10$ kHz, $B_0 = 9.4$ T). ‡ indicate spinning sidebands.

Figure S8. Non-spinning ^{73}Ge CPMG NMR spectra for CsGeX_3 ($X = \text{Cl}, \text{Br}, \text{I}$; $B_0 = 21.1$ T).

Figure S9. Non-spinning ^{133}Cs Hahn Echo (black) and simulated (blue) NMR spectra for CsGeCl_3 at 9.4 T (left) and 21.1 T (right). Fitting parameters can be found in Table S7.

Figure S10. Non-spinning ^{133}Cs Hahn Echo (black) and simulated (blue) NMR spectra for CsGeBr_3 at 9.4 T (left) and 21.1 T (right). Fitting parameters can be found in Table S2. CT = Central transition, ST = Satellite transition.

Figure S11. Non-spinning ^{133}Cs Hahn Echo (black) and simulated (blue) NMR spectra for CsGeI_3 at 9.4 T (left) and 21.1 T (right). (*) indicates CsI impurity. Fitting parameters can be found in Table S7. CT = Central transition, ST = Satellite transition.

Table S2. ^{133}Cs fitting parameters for CsGeX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) data at 9.4 and 21.1 T. Euler angles used are $\alpha = \gamma = 0^\circ$, $\beta = 90^\circ$.

^{133}Cs	C_Q (kHz)		η		δ_{iso} (ppm)		Ω (ppm)		κ		Gaussian broadening (Hz)	
	9.4 T	21.1 T	9.4 T	21.1 T	9.4 T	21.1 T	9.4 T	21.1 T	9.4 T	21.1 T	9.4 T	21.1 T
CsGeCl_3	12(1)	12(1)	<0.10	<0.10	36.9(4)	33.7(2)	10(1)	10(1)	-1	-1	450	750
CsGeBr_3	52(1)	50(1)	0.00(1)	0.00(3)	48.2(8)	47.5(3)	12(2)	16(1)	0	-1	450	400
CsGeI_3	55(1)	52(1)	0.05(4)	0.05(5)	41.8(3)	39.2(7)	n.d.	n.d.	n.d.	n.d.	350	700

Figure S12. ^{133}Cs MAS NMR for CsX salts ($\nu_{\text{rot}} = 10$ kHz, $B_0 = 9.4$ T). $\dagger$ indicate spinning sidebands.

DFT Computations

Table S3. Summary of NMR parameters obtained from CASTEP DFT calculations.

CsGeCl₃

Nucleus		Shielding Tensor			EFG Tensor	
Species	No.	σ_{calc} (ppm)	Ω (ppm)	κ	C_Q (MHz)	η
Cl	1	708.17	254.07	-0.67	-25.30	0.02
Cl	2	708.17	254.07	-0.67	-25.30	0.02
Cl	3	708.17	254.07	-0.67	-25.30	0.02
Ge	1	1355.71	218.25	-1.00	29.38	0.00
Cs	1	5837.13	10.80	1.00	-18.70E-03	0.00

CsGeBr₃

Nucleus		Shielding Tensor			EFG Tensor	
Species	No.	σ_{calc} (ppm)	Ω (ppm)	κ	C_Q (MHz)	η
Ge	1	1286.39	134.85	-1	14.25	0.00
Br	1	2188.46	510.03	-0.81	173.3	0.00
Br	2	2188.46	510.03	-0.81	173.3	0.00
Br	3	2188.46	510.03	-0.81	173.3	0.00
Cs	1	5813.67	20.86	1.00	-61.43E-03	0.00

CsGeI₃

Nucleus		Shielding Tensor			EFG Tensor	
Species	No.	σ_{calc} (ppm)	Ω (ppm)	κ	C_Q (MHz)	η
Ge	1	1316.28	76.19	-1.00	5.980	0.00
I	1	4125.87	746.59	-0.96	-797.6	0.01
I	2	4125.87	746.59	-0.96	-797.6	0.01
I	3	4125.87	746.59	-0.96	-797.6	0.01
Cs	1	5825.81	8.39	1.00	-62.91E-03	0.00

CsCl (mp-22865)

Nucleus		Shielding Tensor			EFG Tensor	
Species	No.	σ_{calc} (ppm)	Ω (ppm)	κ	C_Q (MHz)	η
Cl	1	829.45	0.00	0.00	0.00	0.00
Cs	1	5643.09	0.00	0.00	0.00	0.00

GeCl₄ (mp-30086)

Nucleus		Shielding Tensor			EFG Tensor	
Species	No.	σ_{calc} (ppm)	Ω (ppm)	κ	C_Q (MHz)	η
Cl	1	586.38	535.97	-0.99	-52.66	0.00
Cl	2	586.38	535.97	-0.99	-52.66	0.00
Cl	3	586.38	535.97	-0.99	-52.66	0.00
Cl	4	586.38	535.97	-0.99	-52.66	0.00
Cl	5	584.14	533.59	-1.00	-52.72	0.01
Cl	6	584.14	533.59	-1.00	-52.72	0.01
Cl	7	584.14	533.59	-1.00	-52.72	0.01
Cl	8	584.14	533.59	-1.00	-52.72	0.01
Cl	9	583.99	530.57	-1.00	-52.79	0.01
Cl	10	583.99	530.57	-1.00	-52.79	0.01
Cl	11	583.99	530.57	-1.00	-52.79	0.01
Cl	12	583.99	530.57	-1.00	-52.79	0.01
Cl	13	585.03	536.14	-1.00	-52.48	0.00
Cl	14	585.03	536.14	-1.00	-52.48	0.00
Cl	15	585.03	536.14	-1.00	-52.48	0.00
Cl	16	585.03	536.14	-1.00	-52.48	0.00
Ge	1	1164.47	3.23	0.23	-0.4951	0.83
Ge	2	1164.47	3.23	0.23	-0.4951	0.83
Ge	3	1164.47	3.23	0.23	-0.4951	0.83
Ge	4	1164.47	3.23	0.23	-0.4951	0.83

References

- (1) QingTian, G.; QiWei, P.; Wei, S.; Xun, S.; ChangShui, F. CsGeCl₃: A New IR Nonlinear Material. *Prog. Cryst. Growth Charact. Mater.* **2000**, *40* (1), 89–95. [https://doi.org/https://doi.org/10.1016/S0960-8974\(00\)00009-7](https://doi.org/https://doi.org/10.1016/S0960-8974(00)00009-7).
- (2) Tang, L. C.; Huang, J. Y.; Chang, C. S.; Lee, M. H.; Liu, L. Q. New Infrared Nonlinear Optical Crystal CsGeBr₃: Synthesis, Structure and Powder Second-Harmonic Generation Properties. *J. Phys. Condens. Matter* **2005**, *17* (46), 7275–7286. <https://doi.org/10.1088/0953-8984/17/46/011>.
- (3) Stoumpos, C. C.; Frazer, L.; Clark, D. J.; Kim, Y. S.; Rhim, S. H.; Freeman, A. J.; Ketterson, J. B.; Jang, J. I.; Kanatzidis, M. G. Hybrid Germanium Iodide Perovskite Semiconductors: Active Lone Pairs, Structural Distortions, Direct and Indirect Energy Gaps, and Strong Nonlinear Optical Properties. *J. Am. Chem. Soc.* **2015**, *137* (21), 6804–6819. <https://doi.org/10.1021/jacs.5b01025>.
- (4) Krishnamoorthy, T.; Ding, H.; Yan, C.; Leong, W. L.; Baikie, T.; Zhang, Z.; Sherburne, M.; Li, S.; Asta, M.; Mathews, N.; et al. Lead-Free Germanium Iodide Perovskite Materials for Photovoltaic Applications. *J. Mater. Chem. A* **2015**, *3* (47), 23829–23832. <https://doi.org/10.1039/C5TA05741H>.
- (5) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I. J.; Refson, K.; Payne, M. C. First Principles Methods Using CASTEP. *Zeitschrift für Krist. - Cryst. Mater.* **2005**, *220* (5–6), 567–570. <https://doi.org/doi:10.1524/zkri.220.5.567.65075>.
- (6) Pickard, C. J.; Mauri, F. All-Electron Magnetic Response with Pseudopotentials: NMR Chemical Shifts. *Phys. Rev. B* **2001**, *63* (24), 245101. <https://doi.org/10.1103/PhysRevB.63.245101>.
- (7) Yates, J. R.; Pickard, C. J.; Mauri, F. Calculation of NMR Chemical Shifts for Extended Systems Using Ultrasoft Pseudopotentials. *Phys. Rev. B* **2007**, *76* (2), 24401. <https://doi.org/10.1103/PhysRevB.76.024401>.
- (8) Profeta, M.; Mauri, F.; Pickard, C. J. Accurate First Principles Prediction of ¹⁷O NMR Parameters in SiO₂: Assignment of the Zeolite Ferrierite Spectrum. *J. Am. Chem. Soc.* **2003**, *125* (2), 541–548. <https://doi.org/10.1021/ja027124r>.
- (9) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (10) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; et al. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater.* **2013**, *1* (1), 11002. <https://doi.org/10.1063/1.4812323>.
- (11) Eichele, K. WSolids1 Ver. 1.21. 3. *Univ. Tübingen* **2015**.
- (12) Adiga, S.; Aebi, D.; Bryce, D. L. EFGShield — A Program for Parsing and Summarizing the Results of Electric Field Gradient and Nuclear Magnetic Shielding Tensor Calculations. *Can. J. Chem.* **2007**, *85* (7–8), 496–505. <https://doi.org/10.1139/v07-069>.
- (13) Wong, A.; Sham, S.; Wang, S.; Wu, G. A Solid-State ¹³³Cs Nuclear Magnetic Resonance and X-Ray Crystallographic Study of Cesium Complexes with Macrocyclic Ligands. *Can. J. Chem.* **2000**, *78* (7), 975–985. <https://doi.org/10.1139/v00-097>.
- (14) Michaelis, V. K.; Kroeker, S. ⁷³Ge Solid-State NMR of Germanium Oxide Materials: Experimental and Theoretical Studies. *J. Phys. Chem. C* **2010**, *114* (49), 21736–21744. <https://doi.org/10.1021/jp1071082>.
- (15) Slichter, C. P. *Principles of Magnetic Resonance*; Springer Science & Business Media, 2013; Vol. 1.
- (16) Xu, J.; Wang, Q.; Li, S.; Deng, F. Solid-State NMR Principles and Techniques. In *Solid-State NMR in Zeolite Catalysis*; Springer Singapore: Singapore, 2019; pp 1–55. https://doi.org/10.1007/978-981-13-6967-4_1.
- (17) Taulelle, F. NMR of Quadrupolar Nuclei in the Solid State. In *Multinuclear Magnetic Resonance in Liquids and Solids—Chemical Applications*; Springer, 1990; pp 393–407.
- (18) MacKenzie, K. J. D.; Smith, M. E. *Multinuclear Solid State NMR of Inorganic Materials*, Pergamon Materials Series. Pergamon/Elsevier Oxford 2002.