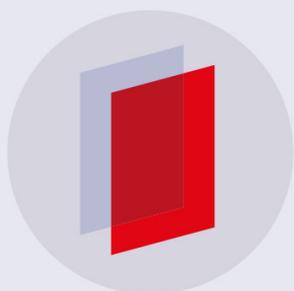


PAPER

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To cite this article: V G Hadjiev *et al* 2018 *J. Phys.: Condens. Matter* **30** 405703

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Phonon fingerprints of CsPb₂Br₅

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Received 18 June 2018, revised 21 August 2018

Accepted for publication 4 September 2018

Published 17 September 2018



CrossMark

Abstract

CsPb₂Br₅ is a stable, water-resistant, material derived from CsPbBr₃ perovskite and featuring two-dimensional Pb–Br framework separated by Cs layers. Both compounds can coexist at nanolength scale, which often produces conflicting optical spectroscopy results. We present a complete set of polarized Raman spectra of nonluminescent CsPb₂Br₅ single crystals that reveals the symmetry and frequency of nondegenerate Raman active phonons accessible from the basal (001) plane. The experimental results are in good agreement with density functional perturbation theory simulations, which suggests that the calculated frequencies of yet unobserved double degenerate Raman and infrared phonons are also reliable. Unlike CsPbBr₃, the lattice dynamics of CsPb₂Br₅ is stable as evidenced by the calculated phonon dispersion. The sharp Raman lines and lack of a dynamic-disorder-induced central peak in the spectra at room temperature indicate that the coupling of Cs anharmonic motion to Br atoms, known to cause the dynamic disorder in CsPbBr₃, is absent in CsPb₂Br₅.

Keywords: lead halides, Raman spectroscopy, lattice dynamics

(Some figures may appear in colour only in the online journal)

1. Introduction

Cs-based lead halide perovskites have emerged as more temperature stable optoelectronic materials than the hybrid organic–inorganic perovskite counterparts [1]. The latter are notable for their impressive power photoconversion efficiency of >20% [2], and potential applications as light emitting diodes [3] and thermoelectrics [4]. Hybrid organic–inorganic and all-inorganic perovskites have comparable photovoltaic performance

[5]. On the downside, both types of materials are water sensitive. In the presence of water, CH₃NH₃PbI₃ degrades or forms hydrites [6] and CsPbBr₃ turns into CsPb₂Br₅ [7]. CsPb₂Br₅ is a water-resistant material [7, 8] akin to the brightly photoluminescent (PL) CsPbBr₃ [9] but differing from the perovskites with its two-dimensional (2D) Pb–Br framework separated by Cs layers [10]. Both compounds are found or intentionally prepared to coexist at nanolength scale [8, 11]. The corresponding nanocomposites [11] and CsPbBr₃/CsPb₂Br₅ core/

shell nanostructures [8] show stable PL and structural integrity. As to the PL properties of CsPb_2Br_5 , reports are controversial: from emitting strong visible PL and even lasing capabilities [12] to inherent PL inactivity [13, 14]. Visible PL was observed in nanocrystalline CsPb_2Br_5 [15] and in nanoplatelets [16]. On the other hand [13], and [17] report lack of PL in CsPb_2Br_5 nanocubes and single crystals, respectively. The PL controversy stems from the fact that CsPb_2Br_5 is an indirect band gap ($E_g \approx 3$ eV) semiconductor [13, 14, 17] that is not supposed to emit PL in the range of 2.35–2.40 eV [12, 15, 16]. A common trend in these experimental observations is that the forbidden PL in CsPb_2Br_5 is seen in nanostructures with complex morphology. The reasons for that could be remnant CsPbBr_3 embedded in CsPb_2Br_5 , defects, crystal edge states or an interphase between the two materials. In most cases, attempts were made to resolve the controversy using x-ray diffraction (XRD) and differences in PL emissions of CsPb_2Br_5 and CsPbBr_3 , but ambiguity remains.

One of the pressing issues is to reconcile the results of DFT modeling, that is, the wide band gap and lack of reasons for emitting PL, with a particular crystal state of CsPb_2Br_5 . The potential of Raman spectroscopy to resolve this problem has not been fully explored yet as only the Raman spectra of CsPbBr_3 are known [18] but not those of CsPb_2Br_5 . CsPbBr_3 undergoes two structural phase transitions with temperature: from cubic $Pm\bar{3}m$ to tetragonal $P4/mbm$ at 403 K, and further to orthorhombic $Pbnm$ at 361 K [19]. Although at room temperature CsPbBr_3 is already in the lowest temperature phase, its Raman spectra show broad smeared phonon peaks and scattering background in a shape of a central peak (centered at zero cm^{-1} Raman shift) [18]. The perovskite structure of CsPbBr_3 consists of apex-to-apex connected PbBr_6 octahedra in a 3D framework. A combined Raman and molecular dynamics (MD) simulation study [18] of CsPbBr_3 show that the central peak is due to dynamic-disorder scattering from a head-to-head Cs anharmonic motion coupled to Br face expansion of PbBr_6 octahedra. The 2D Pb–Br framework in CsPb_2Br_5 is not connected along the c -axis but separated by Cs layers. Thus if the dynamic-disorder scattering mechanism proposed in [18] is viable then we should not expect a central peak because Pb–Br layers in CsPb_2Br_5 lack bridging Br atoms.

In this work, we present an original Raman study of CsPb_2Br_5 aimed to reveal the intrinsic vibrational properties of PL inactive single crystals. A complementary density-functional perturbation theory (DFPT) simulation was carried out for calculating the lattice dynamics in CsPb_2Br_5 and thereby to confirm the reliability of Raman experiment and structural purity of CsPb_2Br_5 crystals. We also predict the phonon frequencies of Raman active modes not seen yet experimentally because of crystal morphology constraints.

2. Material preparation, characterization, and Raman experiment

CsPb_2Br_5 microplatelets were grown by conversion of CsPbBr_3 in pure water [7]. CsPbBr_3 powders (micro-cubes) were

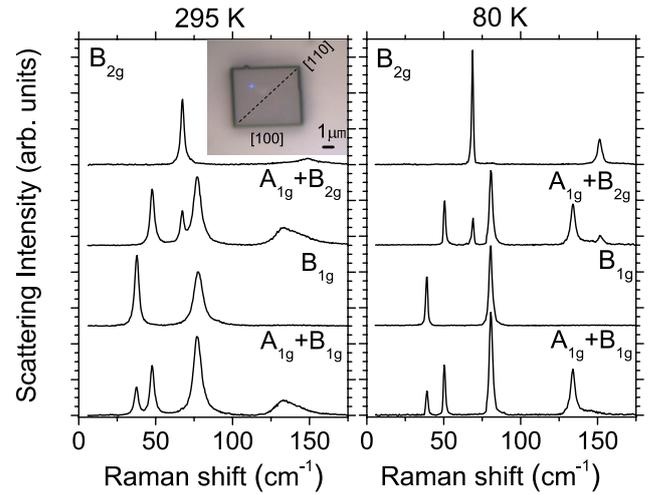


Figure 1. Raman spectra of the CsPb_2Br_5 single crystal shown in the inset, excited with 632.8 nm laser line and measured in backscattering configurations with the laser beam propagation direction along $[001]$. The crystal thickness is $0.5 \mu\text{m}$. The incident (\vec{e}_i) and scattered (\vec{e}_s) light polarization directions select B_{2g} ($\vec{e}_i \parallel [100]$; $\vec{e}_s \parallel [010]$), $A_{1g} + B_{2g}$ ($\vec{e}_i \parallel [110]$; $\vec{e}_s \parallel [110]$), B_{1g} ($\vec{e}_i \parallel [110]$; $\vec{e}_s \parallel [1\bar{1}0]$), and $A_{1g} + B_{1g}$ ($\vec{e}_i \parallel [100]$; $\vec{e}_s \parallel [100]$).

first synthesized using a modified method by mixing 0.5M $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and 1M CsBr in 48% HBr solution at room temperature [7, 20]. CsPb_2Br_5 was then synthesized by simply dropping CsPbBr_3 micro-cubes in large quantity of water in a flask at room temperature. Orange CsPbBr_3 quickly turned into white and precipitates at the bottom of the flask. The white precipitates, consisting of mainly platelet crystals, were taken out and dried for further study. XRD measurements revealed very pure phases of initial CsPbBr_3 and precipitated CsPb_2Br_5 materials [7, 20].

The Raman scattering spectra of CsPb_2Br_5 were measured with a Horiba JY T64000 triple spectrometer on samples placed in an Oxford Instruments Microstat^{He} optical cryostat. All spectra were recorded in backscattering configurations with incident and scattered light propagating normal to the CsPb_2Br_5 crystal platelet surfaces. The backscattering configurations are given in Porto's notation: $A(BC)\bar{A}$, where A and \bar{A} are the propagation directions of incident and scattered light, respectively, and B and C are the corresponding light polarizations \vec{e}_i and \vec{e}_s .

3. Experimental results

CsPb_2Br_5 crystallizes in a body-centered tetragonal structure [10], space group $I4/mcm$ (No. 140), with lattice parameters typically close to those originally reported in [21]. The CsPb_2Br_5 crystals adopt a platelet morphology with large faces parallel to the crystallographic (001) plane [10]. The primitive unit cell (PC) contains two formula units of CsPb_2Br_5 , $N_{\text{cell}} = 16$ atoms per PC with $3N_{\text{cell}} = 48$ degrees of vibrational freedom. The irreducible representations of the Γ -point phonon modes are $3A_{1g} + 2B_{1g} + 3B_{2g} + 5E_g + 2A_{1u} + 5A_{2u} + 3B_{1u} + B_{2u} + 8E_u$, and only the A_{1g} , B_{1g} , B_{2g} , and E_g phonons are Raman active [22]. The acoustic modes have A_{2u} and E_u symmetry, whereas

Table 1. Experimental and DFPT Raman (R) and infrared (IR) phonon frequencies in CsPb₂Br₅ calculated using PAW and NC pseudopotentials. The corresponding lattice constants are $a = b = 8.38$ Å and $c = 15.27$ Å (PAW) and $a = b = 8.31$ Å and $c = 15.26$ Å (NC). TO/LO splitting of E_u modes is given for a phonon wavevector $\mathbf{q} \rightarrow 0$ along Γ -M in the Brillouin zone.

Mode sym. (R)	Exp. 80 K (cm ⁻¹)	PAW Γ -point (cm ⁻¹)	NC Γ -point (cm ⁻¹)	Mode sym. (IR)	PAW Γ -point (cm ⁻¹)	PAW $\mathbf{q} \rightarrow 0$ along Γ -M TO/LO (cm ⁻¹)
A_{1g}	51	54	55	A_{2u}	58	59
A_{1g}	81	82	83	A_{2u}	73	73
A_{1g}	134	132	132	A_{2u}	91	94
B_{1g}	39	41	42	A_{2u}	141	153
B_{1g}	80	77	77	E_u	18	18/38
B_{2g}	69	69	71	E_u	46	46/53
B_{2g}		95	92	E_u	60	60/64
B_{2g}	152	148	147	E_u	73	73/84
E_g		36	31	E_u	95	95/106
E_g		56	52	E_u	112	112/116
E_g		70	64	E_u	131	131/135
E_g		78	76			
E_g		114	113			

A_{1u} , B_{1u} , and B_{2u} are neither IR nor Raman active. The remaining $4A_{2u}$ and $7E_u$ modes can be observed in far-IR spectroscopy experiments. The Raman tensor, $\mathfrak{R}_S = |\alpha_{ij}|$ with $i, j = x, y, z$, of active modes $S = A_{1g}, B_{1g}, B_{2g}, E_g$, has the following non-zero components: $\mathfrak{R}_{A_{1g}}(\alpha_{xx} = \alpha_{yy} = a, \alpha_{zz} = b)$, $\mathfrak{R}_{B_{1g}}(\alpha_{xx} = -\alpha_{yy} = c)$, $\mathfrak{R}_{B_{2g}}(\alpha_{xy} = \alpha_{yx} = d)$, $\mathfrak{R}_{E_{g,1}}(\alpha_{yz} = \alpha_{zy} = e)$, and $\mathfrak{R}_{E_{g,2}}(\alpha_{xz} = \alpha_{zx} = -e)$ [22]. The analysis of Raman scattering activity $I_S = [\vec{e}_s \cdot \mathfrak{R}_S \cdot \vec{e}_i]^2$ suggests that measurements in four back scattering configurations from the surface of a CsPb₂Br₅ platelet are enough to determine the symmetry of nondegenerate phonons. These are $Z(XY)\bar{Z}$ with $I_{B_{2g}} \neq 0$, $Z(X'X')\bar{Z}$ with $I_{A_{1g}} \neq 0$ and $I_{B_{2g}} \neq 0$, $Z(X'Y')\bar{Z}$ with $I_{B_{1g}} \neq 0$, and $Z(XX)\bar{Z}$ with $I_{A_{1g}} \neq 0$ and $I_{B_{1g}} \neq 0$, where Z and Z' are parallel to $[001]$ crystallographic direction, X is along $[100]$ and orthogonal to Y , X' and Y' denote $[110]$ and $[1\bar{1}0]$ directions, respectively. Note that in these scattering configurations the Raman intensity of the E_g modes is vanishing, $I_{E_g} = 0$.

Figure 1 shows the polarized Raman spectra of the CsPb₂Br₅ crystal displayed in the inset, measured in backscattering configurations from (001) crystal face. As seen in figure 1, the symmetry of A_{1g} , B_{1g} , and B_{2g} phonons is experimentally well established. The high single crystal quality of the sample is evidenced by the strongly polarized Raman spectra. The presented in figure 1 polarized Raman spectra were also reproduced in the measurements of a number of CsPb₂Br₅ different crystals including those immersed in water. For CsPb₂Br₅ crystals in water we believe they are completely free of CsPbBr₃. The frequency of all Raman phonons measured at 80 K are listed in table 1. Notably, one B_{2g} mode is missing in the strongly polarized Raman data. Having detected only two B_{2g} phonons may confuse their symmetry assignment with that of the B_{1g} modes. The results of DFPT calculations given in table 1, however, are very helpful in this case and confirm the mode assignment in figure 1. As expected, none of the E_g modes were observed in the measured crystal due to the platelet crystal morphology.

The measured CsPb₂Br₅ crystal show no PL emission in the visible light range [7] in accordance with the calculated electronic band structure featuring a wide indirect band gap

of ≈ 3 eV [13, 14, 17]. Thus we correlate the lack of PL emission to the single crystal nature of CsPb₂Br₅ sample. Similar conclusions are also found in [17].

4. DFPT calculation details

The DFPT lattice dynamics calculations of CsPb₂Br₅ were performed within the generalized-gradient approximation (GGA) with PBEsol functional [23] using the DFPT code [24] as implemented in the Quantum Espresso (QE) suite [25]. In the calculations, we used the projector-augmented-wave (PAW) approach [26] with pseudopotentials generated [27] for use with QE. The geometry optimization of crystal structure, electronic band structure, and related properties were calculated self-consistently (SCF) with 75 Ry kinetic energy cutoff for the plane wave, 300 Ry charge density cut-off, SCF tolerance better than 10^{-11} , and $5 \cdot 10^{-6}$ Ry/au total residual force on atoms over $4 \times 4 \times 4$ Monkhorst-Pack (MP) k -point grid. The dynamical matrices were calculated over $4 \times 4 \times 4$ MP q -point grid and used after that for constructing the force constant matrix. Initial attempts to simulate the lattice dynamics of CsPb₂Br₅ at lower density k - and q -point grids produced phonon dispersions with imaginary frequencies thus implying possible inherent lattice instabilities as those seen in CsPbBr₃. However, increasing the density of both grids, although becoming quite computational demanding, resulted in a stable lattice dynamics with calculated Γ -phonon frequencies in a very good agreement with the low temperature experiment. The lattice constants calculated for the fully relaxed structure of CsPb₂Br₅ are $a = b = 8.38$ Å and $c = 15.27$ Å. The DFPT calculations relax the size and shape of crystallographic unit cell through minimization of all quantum mechanical forces in a static lattice, that is, at $T = 0$ K. The calculated lattice constants are in a good agreement with the experimental ones measured at room temperature: $a = b = 8.48$ Å and $c = 15.25$ Å [21]. We explored multiple combinations of functionals and pseudopotentials in the calculations of lattice dynamics of CsPb₂Br₅ but none gave results as close to the experiment

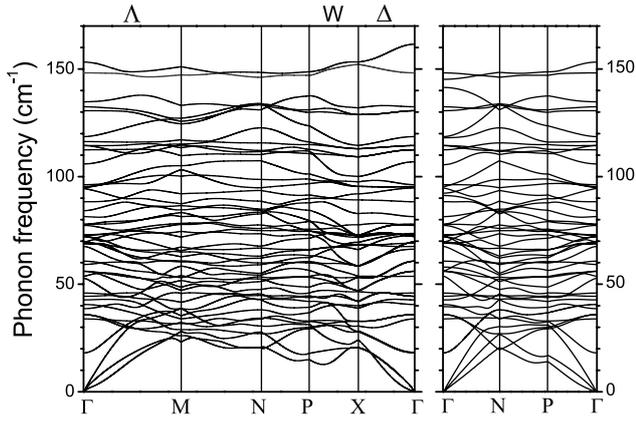


Figure 2. DFPT calculated phonon dispersion in CsPb_2Br_5 with TO/LO splitting included.

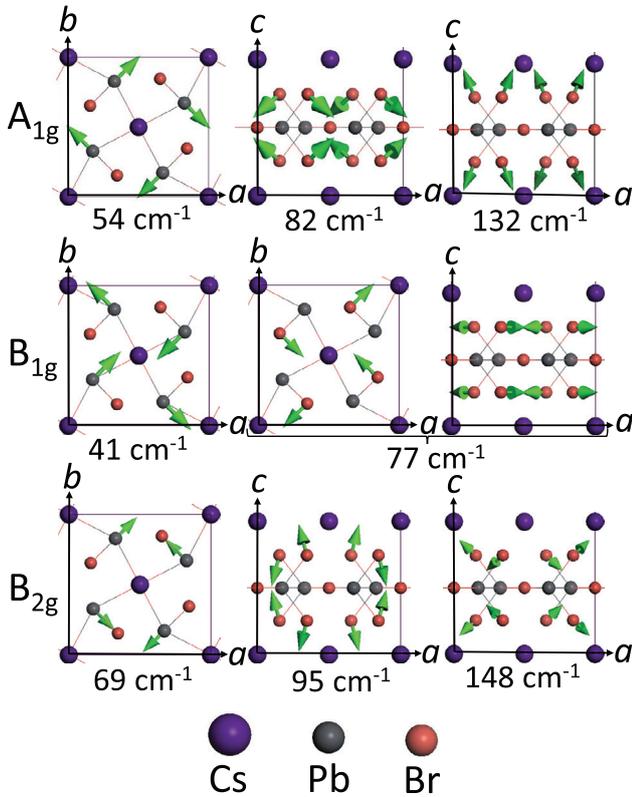


Figure 3. Calculated atomic displacements for the non-degenerate Raman modes in CsPb_2Br_5 . The axes a , b , and c are along the crystallographic directions $[100]$, $[010]$, and $[001]$, respectively. Note that the unit cell of CsPb_2Br_5 contains two Pb–Br layers. The atomic displacements of only one of them are shown for clarity. The displacements in the second layer are as those of the shown one but rotated at 180° around $[110]$.

as those produced by the GGA-PBESol-PAW scheme. Only the calculations using the norm-conserved (NC) PBESol pseudopotentials gave reasonable values for the lattice constants, $a = b = 8.31 \text{ \AA}$ and $c = 15.26 \text{ \AA}$, and Γ -point phonon frequencies (e.g. see table 1) but failed to produce a stable phonon dispersion. For the calculation of non-resonant Raman intensity [30] we used the DFPT code [28, 29] within the

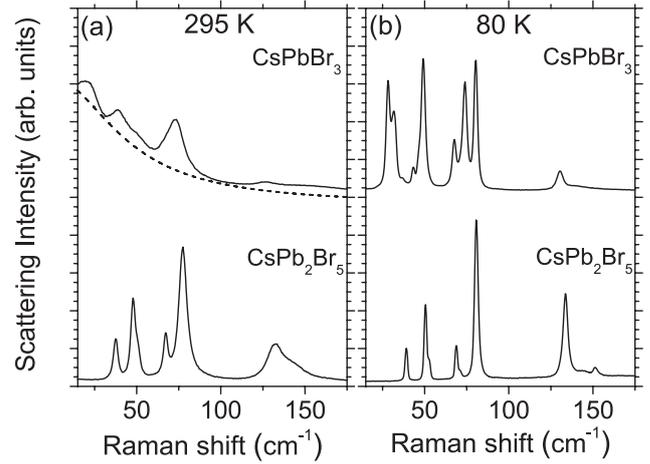


Figure 4. Comparison of non-polarised Raman spectra of CsPb_2Br_5 and CsPbBr_3 . The dash curve in (a) is a guide to the eye that depicts the dynamic-disorder-induced central peak in CsPbBr_3 [18].

GGA-PBESol-NC computational scheme. Table 1 shows that the Raman phonon frequencies calculated by using both codes [25], and [28, 29], are very close thus lending credibility to the Raman intensity calculations.

5. Discussion

Figure 2 displays the phonon dispersion of CsPb_2Br_5 calculated using GGA-PBESol-PAW. The TO/LO splitting of E_u modes at Γ -point is also accounted for phonon propagation towards the Brillouin zone boundaries points $M(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$, $X(0, 0, \frac{1}{2})$, $N(0, \frac{1}{2}, 0)$, and $P(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ given in the primitive basis. The phonon dispersion in figure 2 displays phonon bands that are closely spaced in frequency and have to be resolved by their eigenvectors. This is one of the reasons for making the lattice dynamics calculations of CsPb_2Br_5 difficult and unstable. In addition, the out-of-plane acoustic modes in 2D materials have quadratic dispersion and tend to produce negative frequencies around Γ -point if the fast Fourier transformation grid is not dense enough as shown in [31] for CsPb_2Br_5 slab calculations. The quadratic dispersion effect in figure 2 is seen in the flattening of one of the acoustic modes most pronounced at Γ -point along the Γ -P and Γ -X directions.

As seen in figure 1 the predicted B_{2g} mode at 95 cm^{-1} lacks measurable Raman intensity. The calculations of Raman activity $I_S(\omega) = [\vec{e}_s \cdot (\partial \tilde{\alpha} / \partial Q_i) \cdot \vec{e}_i]^2$, where $\tilde{\alpha}$ is the polarizability tensor and Q_i the normal mode coordinates, yielded $I_{B_{2g}}(95 \text{ cm}^{-1}) / I_{B_{2g}}(69 \text{ cm}^{-1}) = 1.3 \times 10^{-3}$ and $I_{B_{2g}}(95 \text{ cm}^{-1}) / I_{B_{2g}}(148 \text{ cm}^{-1}) = 8 \times 10^{-4}$ for the scattering configuration with $\vec{e}_i \parallel [100]$ and $\vec{e}_s \parallel [010]$. Therefore, the eigenvector of the 95 cm^{-1} mode produces vanishing modulation of the crystal polarizability.

In figure 3, we show the calculated atomic displacements for all non-degenerate Raman modes in CsPb_2Br_5 . Comparing

the experimental Raman intensities in figure 1 with the vibrational patterns in figure 3 we conclude that the intensity is strong for all modes in which Br atoms move in-phase and predominantly in-plane in the Pb–Br layer. Apparently, this does not apply to the B_{2g} mode at 95 cm^{-1} .

Figure 4 demonstrates the difference between the Raman spectra of CsPb_2Br_5 and CsPbBr_3 at room and low temperatures. The assignment of Raman phonons in CsPbBr_3 is given in [18]. We note, however, that the Raman spectrum of CsPbBr_3 shown in figure 4(b) was measured at a higher spectral resolution than that in [18] and exhibits more spectral lines although not all of the expected by symmetry considerations. The presence of small amount of CsPbBr_3 as an impurity in CsPb_2Br_5 might be challenging to detect at room temperature because of the smeared Raman features of CsPbBr_3 . At low temperatures, however, the spectral range below 40 cm^{-1} is free of CsPb_2Br_5 Raman lines and the presence of CsPbBr_3 as an impurity can be monitored through the Raman peaks at 28 cm^{-1} and 32 cm^{-1} . We believe that figure 4 serves as a useful reference for the material characterization of both compounds and will be helpful in detecting traces of CsPbBr_3 in CsPb_2Br_5 .

6. Conclusions

In summary, we have presented a comprehensive Raman scattering study of CsPb_2Br_5 . The DFPT calculation results are in very good agreement with experimental phonon frequencies and symmetry. The latter gives us confidence that the calculated phonon dispersion and phonon related, yet unmeasured, properties are also accessed properly. The present Raman study provides evidence that the lack of visible PL emission is an intrinsic property of CsPb_2Br_5 single crystals.

Acknowledgments

VGH work was supported by the State of Texas through the Texas Center for Superconductivity at the University of Houston (UH) and in part with resources provided by the Center for Advanced Computing and Data Science (CACDS) at UH. JMB acknowledges support from the Robert A Welch Foundation (E-1728). HAC acknowledges support from IPN (SIP, COFAA) for a sabbatical stay at the Molecular Foundry-LBNL. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under Contract No. DE-AC02-05CH1123.

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