Phonon fingerprints of CsPb$_2$Br$_5$

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Abstract

CsPb$_2$Br$_5$ is a stable, water-resistant, material derived from CsPbBr$_3$ 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 CsPb$_2$Br$_5$ single crystals that reveals the symmetry and frequency of nondegenerate Raman active phonons accessible from the basal (0 0 1) 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 CsPbBr$_3$, the lattice dynamics of CsPb$_2$Br$_5$ 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 CsPbBr$_3$, is absent in CsPb$_2$Br$_5$.

Keywords: lead halides, Raman spectroscopy, lattice dynamics

(Some figures may appear in colour only in the online journal)
shell nanostructures [8] show stable PL and structural integrity. As to the PL properties of CsPbBr3, reports are controversial: from emitting strong visible PL and even losing capabilities [12] to inherent PL activity [13, 14]. Visible PL was observed in nanocrystalline CsPb2Br5 [15] and in nanoplatelets [16]. On the other hand [13], and [17] report lack of PL in CsPbBr3 nanocubes and single crystals, respectively. The PL controversy stems from the fact that CsPbBr3 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 CsPb2Br5 is seen in nanostructures with complex morphology. The reasons for that could be remnant CsPbBr3 embedded in CsPb2Br5, 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 CsPb2Br5 and CsPbBr3, 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 CsPbBr3. The potential of Raman spectroscopy to resolve this problem has not been fully explored yet as only the Raman spectra of CsPbBr3 are known [18] but not those of CsPb2Br3. CsPbBr3 undergoes two structural phase transitions with temperature: from cubic $Pm\overline{3}m$ to tetragonal $P4/mnm$ at 403 K, and further to orthorhombic $Pnmn$ at 361 K [19]. Although at room temperature CsPbBr3 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 CsPb2Br5 consists of apex-to-apex connected PbBr6 octahedra in a 3D framework. A combined Raman and molecular dynamics (MD) simulation study [18] of CsPbBr3 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 PbBr6 octahedra. The 2D Pb–Br framework in CsPb2Br5 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 CsPb2Br5 lack bridging Br atoms.

In this work, we present an original Raman study of CsPb2Br5 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 CsPb2Br5 and thereby to confirm the reliability of Raman experiment and structural purity of CsPb2Br5 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

CsPb2Br5 microplatelets were grown by conversion of CsPbBr3 in pure water [7]. CsPbBr3 powders (micro-cubes) were first synthesized using a modified method by mixing 0.5 M Pb(CH3COO)2 · 3H2O and 1 M CsBr in 48% HBr solution at room temperature [7, 20]. CsPb2Br5 was then synthesized by simply dropping CsPbBr3 micro-cubes in large quantity of water in a flask at room temperature. Orange CsPbBr3 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 CsPbBr3 and precipitated CsPb2Br5 materials [7, 20].

The Raman scattering spectra of CsPb2Br5 were measured with a Horiba JY T64000 triple spectrometer on samples placed in an Oxford Instruments MicrostatHe optical cryostat. All spectra were recorded in backscattering configurations with the laser beam propagation direction along [001]. The crystal thickness is 0.5 µm. The incident ($\varepsilon_i$) and scattered ($\varepsilon_s$) light polarization directions select $A_{2g}$ ($\varepsilon_i$) ($\varepsilon_i$ || [100]; $\varepsilon_s$ || [010]), $A_{1g} + B_{2g}$ ($\varepsilon_i$ || [110]; $\varepsilon_s$ || [110]), $B_{1g}$ ($\varepsilon_i$ || [110]; $\varepsilon_s$ || [110]), and $A_{1g} + B_{1g}$ ($\varepsilon_i$ || [100]; $\varepsilon_s$ || [000]).

Figure 1. Raman spectra of the CsPb2Br5 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 µm. The incident ($\varepsilon_i$) and scattered ($\varepsilon_s$) light polarization directions select $B_{2g}$ ($\varepsilon_i$) ($\varepsilon_i$ || [100]; $\varepsilon_s$ || [010]), $A_{1g} + B_{2g}$ ($\varepsilon_i$ || [110]; $\varepsilon_s$ || [110]), $B_{1g}$ ($\varepsilon_i$ || [110]; $\varepsilon_s$ || [110]), and $A_{1g} + B_{1g}$ ($\varepsilon_i$ || [100]; $\varepsilon_s$ || [000]).

3. Experimental results

CsPb2Br5 crystalizes 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 CsPb2Br5 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 CsPb2Br5, $N_{cell} = 16$ atoms per PC with 3$N_{cell} = 48$ degrees of vibrational freedom. The irreducible representations of the $\Gamma$-point phonon modes are $A_{1g} + 2B_{1g} + 2B_{2g} + 5E_{g} + 2A_{1u} + 5A_{2u} + 3B_{1u} + B_{2u} + 8E_{u}$, 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
$A_{1g}$, $B_{1g}$, and $B_{2v}$ are neither IR nor Raman active. The remaining $A_{2u}$ and $E_u$ modes can be observed in far-IR spectroscopy experiments. The Raman tensor, $\mathbf{R}_S = |\alpha ij\rangle$ with $i, j = x, y, z$, of active modes $S = A_{1g}, B_{1g}, B_{2g}, E_g$, has the following non-zero components: $\mathbf{R}_{S_{A_{1g}}}(\alpha_{xx} = \alpha_{yy} = \alpha_{zz})$, $\mathbf{R}_{S_{B_{1g}}}(\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = c)$, $\mathbf{R}_{S_{B_{2g}}}(\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = d)$, $\mathbf{R}_{S_{E_g}}(\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = e)$, and $\mathbf{R}_{S_{E_g}}(\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = -e)$ [22]. The analysis of Raman scattering activity $I_S = |\mathbf{S} \cdot \mathbf{R}_S |^2$ suggests that measurements in four backscattering configurations from the surface of a CsPb$_2$Br$_5$ platelet are enough to determine the symmetry of nondegenerate phonons. These are $Z(XY)Z$ with $I_{B_{2g}} \neq 0$, $Z(X'X')Z$ with $I_{A_{1g}} \neq 0$ and $I_{B_{2g}} \neq 0$, $Z(X'Y')Z$ with $I_{B_{1g}} \neq 0$, and $Z(XX)Z$ 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 [110] 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 CsPb$_2$Br$_5$ 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 CsPb$_2$Br$_5$ different crystals including those immersed in water. For CsPb$_2$Br$_5$ crystals in water we believe they are completely free of CsPbBr$_3$. 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 $E_u$ modes were observed in the measured crystal due to the platelet crystal morphology.

The measured CsPb$_2$Br$_5$ 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 $\approx 3$ eV [13, 14, 17]. Thus we correlate the lack of PL emission to the single crystal nature of CsPb$_2$Br$_5$ sample. Similar conclusions are also found in [17].

4. DFPT calculation details

The DFPT lattice dynamics calculations of CsPb$_2$Br$_5$ 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 $5.10^{-6}$ 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 CsPb$_2$Br$_5$ at lower density $k$- and $q$-point grids produced phonon dispersions with imaginary frequencies thus implying possible inherent lattice instabilities as those seen in CsPbBr$_3$. However, increasing the density of both grids, although becoming quite computational demanding, resulted in a stable lattice dynamics with calculated $\Gamma$-phonon frequencies in a very good agreement with the low temperature experiment. The lattice constants calculated for the fully relaxed structure of CsPb$_2$Br$_5$ 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 CsPb$_2$Br$_5$ but none gave results as close to the experiment.
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, \( a = b = 8.31 \, \text{Å} \) and \( c = 15.26 \, \text{Å} \), and \( \Gamma \)-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 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\(_2\)Br\(_5\) calculated using GGA-PBEsol-PAW. The TO/LO splitting of \( E_u \) modes at \( \Gamma \)-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 \( P(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \) 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\(_2\)Br\(_5\) difficult and unstable. In addition, the out-of-plane acoustic modes in 2D materials have quadratic dispersion and tend to produce negative frequencies around \( \Gamma \)-point if the fast Fourier transformation grid is not dense enough as shown in [31] for CsPb\(_2\)Br\(_5\) slab calculations. The quadratic dispersion effect in figure 2 is seen in the flattening of one of the acoustic modes most pronounced at \( \Gamma \)-point along the \( \Gamma \)-P and \( \Gamma \)-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 \( I(\omega) = |\vec{e}_s \cdot (\partial \vec{q}/\partial Q_i) \cdot \vec{e}_i|^2 \), where \( \vec{e} \) 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\(_2\)Br\(_5\). 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 $B_{3g}$ mode at 95 cm$^{-1}$.

Figure 4 demonstrates the difference between the Raman spectra of CsPb$_2$Br$_5$ 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 CsPb$_2$Br$_5$ 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$_2$Br$_5$ 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$_2$Br$_5$ 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$_2$Br$_5$.

6. Conclusions

In summary, we have presented a comprehensive Raman scattering study of CsPb$_2$Br$_5$. 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$_2$Br$_5$ single crystals.

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