Effects on the emission discrepancy between two-dimensional Sn-based and Pb-based perovskites

Tianju Zhang (张天举)1,2, Chaocheng Zhou (周超成)3, Jia Lin (林 佳)3,*, and Jun Wang (王 俊)1,2,5**

1 Laboratory of Micro-Nano Optoelectronic Materials and Devices, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China
2 Center of Materials Science and Optoelectronic Engineering, University of Chinese Academy of Sciences, Beijing 100049, China
3 Department of Physics, Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai Jiao Tong University, Shanghai 200240, China
4 State Key Laboratory of Advanced Optical Communication Systems and Networks, School of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, China
5 CAS Center for Excellence in Ultra-Intense Laser Science, Shanghai 201800, China

*Corresponding author: jwang@siom.ac.cn
**Corresponding author: jlin@shiep.edu.cn
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Two-dimensional (2D) Sn-based perovskites are a kind of non-toxic environment-friendly emission material with low photoluminescence quantum yields (PLQYs) and enhanced emission linewidths compared to that of 2D Pb-based perovskites. However, there is no work systematically elucidating the reasons for the differences in the emission properties. We fabricate (BA)2SnI4 and (BA)2PbI4 having different defect densities and different exciton-phonon scattering intensities. We also reveal that 2D Sn-based perovskites have stronger exciton-phonon scattering intensity and higher defect density, significantly broadening the emission linewidth and accelerating the exciton relaxation process, which significantly reduces the PLQY of 2D Sn-based perovskites.

Keywords: temperature-dependent photoluminescence spectra; transient absorption spectra; defect state; exciton-phonon scattering; two-dimensional perovskites.
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1. Introduction

Self-assembled two-dimensional (2D) Ruddlesden–Popper phase organic–inorganic halide perovskites with quantum-well structures have attracted much research attention in optoelectronic devices, lasers, and light-emitting diodes (LEDs) by virtue of their superior features such as enhanced stability, high absorption coefficient, tunable light-emitting wavelength, high color purity, and high exciton binding energy11-10. Its chemical structure formula is (RNH3)2(A)n−1BnC3n+1, where R is an alkylor aromatic group, A is an organic cation, B is Pb2+, Sn2+, Ge2+, or other elements, and C is a halogen element11. For the 2D perovskites system with n = 1, the organic cation layer’s dielectric constant is smaller than that of the inorganic octahedral layer in combination with the inorganic layer’s thickness of about 0.7 nm12-14, which causes the weakened dielectric screening effect and the enhanced spatial confinement effect. These effects greatly weaken the dielectric screening between electron-hole pairs to enhance the Coulomb interaction force between them within the inorganic layer, and thus the exciton dominates the optical transitions in materials12,15-17. Although 2D Pb-based perovskites are favored in the field of LEDs for display applications and lasers, the element Pb2+ is extremely toxic to the environment, limiting its further development. Compared to Pb2+, Sn2+ is non-toxic and has the most similar ionic radius18, so the lattice parameters obtained by Sn2+ replacement are, in principle, not severely modified19,20, which makes Sn-based perovskites expected to replace Pb-based perovskites in the future. At the same time, compared with the 2D Pb-based perovskites LEDs for display applications, the 2D Sn-based perovskites LEDs suffer from the disadvantages of low photoluminescence quantum yields (PLQYs) and enhanced emission linewidths [full width at half-maximum (FWHM) > 40 nm]21,22. Although much research points out that Sn-based perovskites are more likely to have a higher density of defect states, due to the oxidation potential of Sn2+/Sn4+ (~0.15 eV) being much lower than that of Pb2+/Pb4+ (~1.8 eV)23, and numerous optimization strategies
proposed to improve their PLQY\textsuperscript{[20-22,24–26]}, it is still difficult to improve their emission linewidths comparable to that of Pb-based perovskites (FWHM < 20 nm)\textsuperscript{[3,5,20,27,28]}. There are a variety of factors affecting the emission linewidth of the material, mainly the inhomogeneous broadening caused by the disordered nature of the crystal structure and exciton-defect scattering effect, as well as the homogeneous broadening caused by the electron-phonon scattering effect\textsuperscript{[29–31]}. However, no research work exists so far to systematically study these effects affecting emission properties between 2D Pb-based perovskites and 2D Sn-based perovskites under the same experimental conditions and further reveal the differences between them.

In this work, we have fabricated (A)\textsubscript{2}SnI\textsubscript{4} and (A)\textsubscript{2}PbI\textsubscript{4} [A: n-butylammonium (CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{3}NH\textsuperscript{+} (BA\textsuperscript{+})] using the same method, which has different defect densities and different exciton-phonon scattering intensities. Taking advantage of the temperature-dependent photoluminescence (PL) spectra, transient absorption (TA) spectra, time-dependent PL relaxation kinetics, and PLQY experiments, we also revealed that 2D Sn-based perovskites have stronger exciton-phonon scattering intensity and higher defect-state density relative to 2D Pb-based perovskites, which lead to a significant broadening of the emission linewidth and accelerate the exciton relaxation process of 2D Sn-based perovskites, and these effects reduce the PLQY of 2D Sn-based perovskites. These results can guide further improvement in the emission performance of 2D Sn-based perovskites, in which we should select new structures for organic cation layers with relatively high rigidity to reduce the exciton-phonon scattering intensity and use antioxidants to reduce the defect-state density and thus the energy non-radiative loss.

2. Results and Discussion

To explain the physical mechanism affecting the optical properties of 2D Sn-based perovskites, we prepared (BA)\textsubscript{2}SnI\textsubscript{4} and (BA)\textsubscript{2}PbI\textsubscript{4} films by the spin-coating method. The schematic of the hybrid quantum-well structure of (BA)\textsubscript{2}SnI\textsubscript{4} and (BA)\textsubscript{2}PbI\textsubscript{4} crystal structures [Fig. 1(a)] shows the perovskite octahedra sandwiched between organic spacer molecules (BA\textsuperscript{+}). Figure 1 shows the ultraviolet-visible (UV-Vis) absorption, steady-state PL spectroscopy, and PLQY of (BA)\textsubscript{2}SnI\textsubscript{4} and (BA)\textsubscript{2}PbI\textsubscript{4}. The inset shows that the optical bandgap of (BA)\textsubscript{2}SnI\textsubscript{4} and (BA)\textsubscript{2}PbI\textsubscript{4} was obtained as 1.97 eV and 2.37 eV by the Tauc-plot method, respectively. The PLQY of (BA)\textsubscript{2}SnI\textsubscript{4} is lower than that of (BA)\textsubscript{2}PbI\textsubscript{4}, indicating that the defect density of (BA)\textsubscript{2}SnI\textsubscript{4} is higher than that of (BA)\textsubscript{2}PbI\textsubscript{4}. Such defect states might arise from undesirable and uncontrollable conversion of Sn\textsuperscript{2+} to Sn\textsuperscript{4+}, as the oxidation potential of Sn\textsuperscript{2+}/Sn\textsuperscript{4+} (−0.15 eV), during the process of sample preparation in a glove box with almost the nitrogen environment, in which there is still a trace amount of oxygen that allows the Sn\textsuperscript{2+} to oxidize to Sn\textsuperscript{4+}\textsuperscript{[22,23]}. Besides, the oxidation potential of Pb\textsuperscript{2+}/Pb\textsuperscript{4+} is 1.8 eV, which is more negative than that of Sn\textsuperscript{2+}/Sn\textsuperscript{4+}, making Pb\textsuperscript{2+} a stable state in (BA)\textsubscript{2}PbI\textsubscript{4}. In addition, the FWHM of the normalized PL peak of (BA)\textsubscript{2}PbI\textsubscript{4} is 18.5 nm smaller than that of (BA)\textsubscript{2}SnI\textsubscript{4} (39.2 nm), as shown in Fig. 2. For 2D hybrid organic–inorganic perovskites, there is a trapping-state PL phenomenon due to its lattice being relatively soft. For the existence of two types of trap states, one is the intrinsic self-trapped exciton (STE) state caused by the exciton-phonon coupling, and the other trap state is the extrinsic STE state; the STE state is influenced by the local heterogeneity of the permanent defects lattice, which will sink to a different trapping depth\textsuperscript{[32–34]}. These trap states can make the PL peaks deviate from the Gaussian line shape with PL tails in the broad spectral range at the low energy edge. To better fit the PL spectral

![Fig. 1](image1.png) Spectral characteristics of (BA)\textsubscript{2}SnI\textsubscript{4} (B: Sn/Pb) perovskites. (a) Schematic of the hybrid quantum-well structure of the crystal structure, showing the perovskite octahedra sandwiched between organic spacer molecules (BA\textsuperscript{+}). The UV-visible (UV-Vis) absorption, steady-state photoluminescence (PL) spectra of (b) (BA)\textsubscript{2}SnI\textsubscript{4} and (c) (BA)\textsubscript{2}PbI\textsubscript{4}. (d) PLQY of (BA)\textsubscript{2}SnI\textsubscript{4} and (BA)\textsubscript{2}PbI\textsubscript{4}.

![Fig. 2](image2.png) Analysis of PL characteristics. (a) Multi-peak fit analysis of (BA)\textsubscript{2}PbI\textsubscript{4}, (b) multi-peak fit analysis of (BA)\textsubscript{2}SnI\textsubscript{4}, (c) percentage of subpeaks of (BA)\textsubscript{2}PbI\textsubscript{4} and (BA)\textsubscript{2}SnI\textsubscript{4}, (d) normalized PL decay kinetics.
The valence band maximum (VBM) consists of an antibonding hybridization between I\(^{-}\)\(5p\) states and Pb\(^{2+}\)\(6p\) states\[^{[23,35]}\]. For the \((BA)\(_2\)Sn\(_4\)I\(_4\) sample, the VBM consists of an antibonding hybridization between Pb\(^{2+}\)\(6p\) states and Sn\(^{2+}\)\(5s\) states, and the CBM comprises a bonding hybridization between Sn\(^{2+}\)\(5s\) states and Pb\(^{2+}\)\(5p\) states\[^{[23]}\]. The spin-orbit coupling of the Sn\(^{2+}\)\(5p\) state is lower than that of the Pb\(^{2+}\)\(6p\) state\[^{[36]}\], so this lowering of spin-orbit coupling increases the probability of defect states in \((BA)\(_2\)Sn\(_4\)I\(_4\)\). In summary, we proved that \((BA)\(_2\)Sn\(_4\)I\(_4\) has a higher defect density relative to \((BA)\(_2\)Pb\(_4\)I\(_4\)\). For the \((BA)\(_2\)Sn\(_4\)I\(_4\) sample, the CBM consists of a bonding hybridization between I\(^{-}\)\(5p\) states and Sn\(^{2+}\)\(5s\) states, and the CBM comprises a bonding hybridization between Sn\(^{2+}\)\(5s\) states and Sn\(^{2+}\)\(5s\) states\[^{[23]}\]. The spin-orbit coupling of the Sn\(^{2+}\)\(5p\) state is lower than that of the Pb\(^{2+}\)\(6p\) state\[^{[36]}\], so this lowering of spin-orbit coupling increases the probability of defect states in \((BA)\(_2\)Sn\(_4\)I\(_4\)\). In order to further analyze the factors affecting the FWHM, we conducted the temperature-dependent PL spectra to analyze the different physical processes of scattering (Fig. 3).

The variation of PL FWHM with temperature involves different physical processes of scattering, and the analysis of temperature-dependent PL FWHM is the main means to evaluate the electron-phonon coupling mechanism in various semiconductors\[^{[29,30]}\]. Using first-order perturbation theory, the temperature-dependent FWHM can be approximately simplified to a model that contains four scattering mechanisms, as shown in Eq. (1)^{[37,38]}.

\[
\Gamma(T) = \Gamma_0 + \gamma_{ac} T + \frac{\Gamma_{LO}}{e^{E_{LO}/kBT}-1} + \Gamma_{imp} e^{-E_{imp}/kBT},
\]

where the first term \(\Gamma_0\) on the right-hand side of Eq. (1) is the temperature-independent inhomogeneous broadening, which originates from the disordered nature of the crystal structure\[^{[29,30]}\]. The second and third terms are temperature-dependent homogeneous broadening due to exciton-acoustic phonon scattering interactions and exciton-longitudinal optical (LO) phonon scattering interactions, where \(\gamma_{ac}\) is the coupling strength of the exciton-acoustic phonon scattering. \(\Gamma_{LO}\) is the Fröhlich coupling strength of the exciton scattering with LO phonons, and \(E_{LO}\) is the energy of the LO phonon. The last term describes the inhomogeneous broadening caused by ionized impurities (coupling \(\Gamma_{imp}\)), where the impurities with the binding energy, \(E_{imp}\), are completely ionized. Since the FWHM gradient of increase is close to zero for both samples at low temperatures\[^{[38]}\], the exciton-acoustic phonon scattering effect can be excluded because its contribution can cause a linear growth characteristic of the FWHM at low temperatures, so \(\gamma_{ac}\) is equal to zero. This judgment is consistent with the results of polar inorganic semiconductors, i.e., acoustic phonon scattering is relatively negligible compared with the optical phonon scattering at room temperature\[^{[37–40]}\].

The fitting parameters obtained by using the global fit optimization algorithm based on simulated annealing are shown in Table 1. We can obtain from the fitting results that for \((BA)\(_2\)Pb\(_4\)I\(_4\), the optical phonon energy \(E_{LO}\) is 20.85 ± 1 meV, and the exciton-optical phonon scattering intensity \(\Gamma_{LO}\) is 14.5 ± 2 meV, which is in agreement with the results reported in the literature to indicate the rationality of the fitting results\[^{[38,39]}\]. We found that the \(\Gamma_0\) of \((BA)\(_2\)Sn\(_4\)I\(_4\) is almost twice as large as that of \((BA)\(_2\)Pb\(_4\)I\(_4\), demonstrating that the crystal structure of \((BA)\(_2\)Sn\(_4\)I\(_4\) is more disordered. Second, the exciton-optical phonon scattering intensity of \((BA)\(_2\)Sn\(_4\)I\(_4\) is much larger than that of \((BA)\(_2\)Pb\(_4\)I\(_4\), which greatly enlarges the PL FWHM of \((BA)\(_2\)Sn\(_4\)I\(_4\). Therefore, compared to 2D Pb-based perovskites, 2D Sn-based perovskites have higher crystal structure disorder and stronger exciton-optical phonon scattering intensities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\Gamma_0) (meV)</th>
<th>(\Gamma_{LO}) (meV)</th>
<th>(E_{LO}) (meV)</th>
<th>(E_{imp}) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((BA)(_2)Sn(_4)I(_4)</td>
<td>63.1 ± 2</td>
<td>192.8 ± 4</td>
<td>56.5 ± 2</td>
<td>94.9 ± 2</td>
</tr>
<tr>
<td>((BA)(_2)Pb(_4)I(_4)</td>
<td>37.7 ± 1</td>
<td>14.5 ± 2</td>
<td>20.85 ± 1</td>
<td>188.3 ± 2</td>
</tr>
</tbody>
</table>
Femtosecond TA spectroscopy was utilized to further investigate the photophysical processes of the nonequilibrium interactions of photogenerated carriers. The recombination characteristics of the photogenerated carriers in a material determine the emission properties of the material. TA spectroscopy measurements of polycrystalline thin films prepared on quartz substrates were performed using our custom-built TA spectroscopy setup. The light pulse generated by the Spectra-Physics Spirit laser (350 fs, 1 kHz, 40 μJ/pulse) is split into two parts by an ultraviolet beam splitter with a reflection to transmission energy ratio of 1:4. A frequency-doubled 520 nm output from the transmitted light was used as the pump beam, whereas the reflected laser pulse was used to excite a sapphire crystal for generating a white light continuous spectrum, whose chirp is corrected. The pump beam was chopped at 500 Hz, and the probe beam transmitting the sample is collected by an ultraviolet fiber optic spectrometer after passing through a short pass filter with a cutoff wavelength of 950 nm. The time window of the TA measurement was 1.6 ns. The spot radii of the pump light and probe light are determined to be 320 ± 0.5 and 10 ± 0.5 μm, respectively, by the knife-cut method, and the pump light and probe light overlap at the same point of the sample in a noncollinear manner.

Figure 4 shows the false-color 2D TA mappings of the (BA)$_2$SnI$_4$ and (BA)$_2$PbI$_4$ thin films. For the TA spectra of (BA)$_2$SnI$_4$, there are photoinduced ground-state bleaching signals approximately at 610 nm and 518 nm, which are caused by the band filling effect induced by pump light. Within the first picosecond (ps), the interaction of hot excitons leads to the bandgap renormalization process, which in turn results in the signal of photoinduced absorption. The photoinduced bleaching signals also exist in the broad spectral range (650–750 nm) below the bandgap, mainly caused by the filling of defect states with carriers excited by pump light. For the TA spectra of (BA)$_2$PbI$_4$, there is a photoinduced bleaching signal at about 518 nm caused by the band filling effect, while there is still a photoinduced bleaching signal in the wide range below the bandgap.

The relaxation process of photogenerated carriers at low excitation fluence of 3 μJ/cm$^2$ is analyzed by global fitting based on three relaxation decay components with different lifetimes. Among them, the first ultrafast relaxation component has a lifetime of about the order of a hundred femtoseconds. In the recent study of TA kinetics, the first fast component was attributed to the surface defect trapping process (< 1 ps) in 2D (CH$_3$CH$_2$)$_2$NH$_3$)$_2$PbBr$_4$ perovskite, and the surface trap state captured the exciton process (600 fs) for monolayer MoS$_2$ materials. So, the process is assigned to a defect trapping excitons process and a bandgap renormalization process. The second relaxation component with a lifetime of about the order of a hundred picoseconds is attributed to an interband exciton recombination process. The recombination rate of this process is affected by the excitation fluence, exciton-defect scattering effect, and exciton-phonon scattering effect. The third process with the lifetime of a few nanoseconds is attributed to a defect-state-assisted recombination process. The band-side exciton radiative relaxation recombination rate of (BA)$_2$SnI$_4$ is faster compared with that of (BA)$_2$PbI$_4$. This is mainly due to the stronger exciton-phonon scattering intensity and exciton-defect scattering intensity, which both accelerate the exciton recombination rate and reduce the percentage of exciton radiative recombination processes. Tretiak et al. revealed that the more flexible geometry results in faster electron-hole recombination and shorter carrier lifetime, diminishing the PLQY for softer 2D perovskites by the density generalized function theory calculations. Therefore, the soft organic cations can be replaced by relatively rigid structural organic cations containing benzene rings to limit their thermal movement between the inorganic octahedron layers and further reduce the exciton-phonon scattering intensity. At the same time, PEA$^+$ has a greater ability to hinder the formation of tin oxidation, where BA$^+$ ions increased the defect formation energy of Sn$^{4+}$ by 0.33 eV, whereas PEA$^+$ could increase the defect formation energy of Sn$^{4+}$ by 0.6 eV. Therefore, there is a necessity to find organic cation layers with the appropriate structure to further improve the emission characteristics of 2D Sn-based perovskites.
3. Conclusion

In summary, we have fabricated samples (A)\textsubscript{2}SnI\textsubscript{4} and (A)\textsubscript{2}PbI\textsubscript{4} [A: n-butyrammonium (CH\textsubscript{3}CH\textsubscript{2}NH\textsuperscript{+})] using the same method and have revealed that 2D Sn-based perovskites have stronger exciton-phonon scattering intensity and higher defect density of states relative to 2D Pb-based perovskites by the temperature-dependent PL spectra, TA spectra, time-dependent PL relaxation kinetics, and PLQY experiments. These factors lead to a significant broadening of the emission linewidth and accelerate the exciton relaxation process, which reduces the PLQY of 2D Sn-based perovskites. Our results can be a guide for further improving the emission performance of 2D Sn-based perovskites by selecting new structures of organic cation layers with relatively high rigidity to reduce the exciton-phonon scattering intensity and by using antioxidants to reduce the defect-state density in the material and thus the energy loss of non-radiative transitions.

4. Experimental Section

4.1. Syntheses of the (BA)\textsubscript{2}SnI\textsubscript{4} and (BA)\textsubscript{2}PbI\textsubscript{4} perovskites polycrystalline thin films

The glass substrate was cleaned sequentially with detergent, deionized water, ethanol, and isopropanol. Then, the substrate was treated with oxygen plasma for 10 min and dried in an argon flow. For the synthesis of (BA)\textsubscript{2}SnI\textsubscript{4} perovskite film, 0.1 mmol SnI\textsubscript{2} and 0.2 mmol BAI were dissolved in 1 mL dimethyl formamide (DMF) : dimethyl sulfoxide (DMSO) (v : v = 4 : 1) to form the perovskite precursor solution, which was heated and stirred at 70°C for a few hours before use. Subsequently, the above-mentioned precursor solution was deposited on top of the glass substrate via a spin-coating process at 2500 r/min and accelerated the exciton relaxation process, which reduces the PLQY of 2D Sn-based perovskites.

4.2. Temperature-dependent PL measurement

For temperature-dependent PL measurement, polycrystalline thin films prepared on silica substrates were mounted in a cryostat (Janis ST-100) and cooled by liquid nitrogen. The samples were excited by the continuous wave (CW) laser excitation at a wavelength of 405 nm at 1 μJ/cm\textsuperscript{2}, and 25 K intervals. Fluorescence is separated by the 150 g/mm grating in the Monochromator SP2500 of Princeton Instruments. Then, the spectral information was collected by the PIXIS-100BX CCD at −75°C.

4.3. Photoluminescence quantum yield

PLQY of polycrystalline thin films prepared on silica substrates was measured using the Edinburgh FLS1000 instrument with an excitation wavelength of 520 nm.

4.4. UV/visible absorption

UV-Vis absorption spectra of polycrystalline thin films prepared on glass substrates were collected by a Lambda 950 UV-Vis spectrometer.

4.5. Time-resolved PL

The TRPL kinetics was detected by a HORIBA DeltaFlex ultra-fast time-resolved fluorescence spectrometer, where the excitation wavelength is 405 nm at 1 μJ/cm\textsuperscript{2}.

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