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Point Defects and Green Emission in Zero-dimensional Perovskites

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ABSTRACT

Zero-dimensional (0D) perovskites have recently opened a new frontier in device engineering for light conversion technologies due to their unprecedented high photoluminescence quantum yield as solids. Although many experimental and theoretical efforts have been made to understand their optical behavior, the origin of their green emission is still opaque. Here, we develop a complete experimental and theoretical picture of point defects in Cs-Pb-Br perovskites and demonstrate that bromide vacancies (V_{Br}) in prototype 0D perovskite Cs_4PbBr_6 have low formation energy and a relevant defect level to contribute to the mid-gap radiative state. Moreover, the state-of-the-art characterizations including atomic-resolution electron imaging not only confirm the purity of 0D-phase of Br-deficient green-emissive Cs_4PbBr_6 nanocrystals (NCs), but also exclude the presence of CsPbBr_3 NCs impurities. Our findings provide robust evidence for defect-induced green luminescence in 0D perovskite nanocrystals, which helps extend the scope of the utility of these bulk 0D quantum materials in optoelectronic applications.

TOC Graphic

Zero-dimensional (0D) perovskites have recently received great attention¹⁻⁵ owing to their tunable emission wavelength, high photoluminescence quantum yield, and narrow emission line-width. These characteristics make them excellent candidates for optoelectronic applications such as light-emitting diodes⁶⁻⁷, lasers⁸, and photodetectors⁹⁻¹⁰. Unlike the well-studied three-dimensional (3D) perovskite structures (*e.g.*, CsPbBr₃)¹¹⁻¹⁵, 0D perovskites are bulk quantum materials without corner-sharing connectivity; and as a result, their optical and photo-physical properties, such as exciton localization and self-trapping¹⁶, intrinsic Pb²⁺ ion emissions¹⁷, and small-polaron generation¹⁸, are determined by the isolated [PbX₆]⁴⁻ octahedral units.

Despite the progress made in understanding the optical and photo-physical properties of Cs₄PbBr₆ materials in different forms (*i.e.*, powder, single crystal, nanocrystal, and nanosheet), the nature of the bright green emission, especially in Cs₄PbBr₆ nanocrystals (NCs), is still under debate. Two vastly different explanations of this issue have been given in the literature. Some authors have attributed the green fluorescence of Cs₄PbBr₆ NCs to embedded CsPbBr₃ NCs impurities.¹⁹⁻²⁰ This explanation was indirectly supported by the synthesis of non-luminescent Cs₄PbBr₆ NCs that have a strong excitonic absorption in the ultraviolet region.²¹⁻²² However, these CsPbBr₃ NC impurities were undetectable by the powder X-ray diffraction (PXRD) measurements reported in these publications. In independent control experiment, mixing a small amount (0.5 wt %) of CsPbBr₃ NCs in Cs₄PbBr₆ NCs could result in clear CsPbBr₃ features in the XRD pattern.³ This observation is questioning the validity CsPbBr₃ NC impurities scenario. On the other hand, several research groups attributed the green emission to an intrinsic behavior of the 0D perovskite structure. For instance, detailed structural characterizations of emissive and non-emissive Cs₄PbBr₆ NCs demonstrated that these two materials are structurally the same and are free from CsPbBr₃ contaminations.³ Moreover, photoluminescence imaging studies on individual Cs₄PbBr₆

microdisks⁴ and nanocrystals²³ confirmed that photons were not emitted from localized domains containing an emissive impurity, but from the entire 0D film. Therefore, it has been proposed that intrinsic defect states within the band gap may serve as radiative recombination centers for the observed green emission of Cs₄PbBr₆ materials^{3, 24} and blue emission of Cs₄EuBr₆ and Cs₄EuI₆ single crystals.²⁵

Strong evidence for the origin of the emissive defect states of Cs₄PbBr₆ and a detailed theoretical insight on the nature of these defect are thus clearly needed.²⁶ In this Letter, we systematically study the point defects in inorganic Cs-Pb-Br perovskites (CsPbBr₃, CsPb₂Br₅, and Cs₄PbBr₆) based on density functional theory (DFT) calculations. We find that localized-bromide vacancies (V_{Br}) have low formation energy and the proper energy level to act as radiative-charge recombination centers to achieve the green emission in Cs₄PbBr₆. Based on this theoretical finding and guidance, we carefully designed and synthesized green-emissive Cs₄PbBr₆ NCs under different conditions to confirm their pure 0D phase and, perhaps more importantly, to exclude the presence of CsPbBr₃ NCs impurities. We experimentally confirm the existence of V_{Br} -induced defect emissions by demonstrating the increased photoluminescence intensity and lifetime in Br-poor Cs₄PbBr₆ NCs.

Figure 1. (a) Schematic representation of the ternary phase together with paths between precursors (CsBr and PbBr₂) and highlighted compounds (CsPbBr₃, CsPb₂Br₅, and Cs₄PbBr₆). (b) Crystal structures and decomposition energies of orthorhombic- and cubic-phase CsPbBr₃, tetragonal-phase CsPb₂Br₅, and trigonal-phase Cs₄PbBr₆. c Electronic band structures of orthorhombic- and cubic-phase CsPbBr₃, CsPb₂Br₅, and Cs₄PbBr₆ calculated at the HSE+SOC level of theory (Brillouin zone k -path are shown in Figure S1 of the Supporting Information).

The ternary phase diagram of Cs-Pb-Br perovskites (Figure 1a) demonstrates that mixing CsBr and PbBr₂ precursors can produce three different perovskite structures (CsPbBr₃, CsPb₂Br₅, and Cs₄PbBr₆). As shown in Figure 1b, the phase transition of Cs-Pb-Br perovskites occurs by slightly changing the crystal growth conditions, enabling us to achieve low-dimensional phases by carefully controlling the ratios of precursors (CsBr:PbBr₂). PbBr₂-rich conditions lead to the two-dimensional (2D) CsPb₂Br₅ structure where the tetragonal $I4/mcm$ phase has a sandwich structure in which Cs⁺ ions appear between the layers of Pb-Br polyhedra²⁷⁻²⁸. In contrast, in CsBr-rich conditions, 0D Cs₄PbBr₆ with a rhombohedral $R\bar{3}c$ phase forms, in which isolated [PbX₆]⁴⁻

octahedra are separated by Cs^+ ions. In the case of the 3D CsPbBr_3 structure, on the other hand, both cubic ($Pm\bar{3}m$) and symmetry-reduced orthorhombic ($Pnma$) can be obtained and represent room temperature phases for a nanocrystal and powder/thin film, respectively (the experimental and optimized lattice parameters can be found in Table S1 of the Supporting Information).

Based on the electronic band structure calculations of these Cs-Pb-Br perovskites using the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional and accounting for spin-orbit coupling (*i.e.*, the HSE + SOC level), we find that the bandgaps of these Cs-Pb-Br perovskites increase as the dimensionality decreases (Figure 1c); both CsPbBr_3 and Cs_4PbBr_6 exhibit a direct bandgap (*calc*: 2.35 and 3.90 eV; *expl*: 2.35 and 3.95 eV), while CsPb_2Br_5 shows an indirect bandgap (*calc*: 3.13 eV; *expl*: 3.10 eV). Based on these results, the observed green emission in the CsPbBr_3 nanomaterials could be attributed to direct electron-hole radiative recombination, while Cs_4PbBr_6 has an intrinsic large band gap due to the negligible electronic couplings between $[\text{PbBr}_6]^{4-}$ octahedra, indicating that the green emission band (centered at ~ 2.4 eV) in Cs_4PbBr_6 originates from a mid-gap state instead of a direct band-to-band transition. Therefore, the different crystal and electronic structures of these Cs-Pb-Br perovskites allow us to distinguish the origin of green emission in Cs_4PbBr_6 from that in CsPbBr_3 . Moreover, the cubic-phase CsPbBr_3 has a slightly lower dissociation energy (0.21 eV) than does its orthorhombic-phase, and Cs_4PbBr_6 is the most stable structure among these perovskites with a dissociation energy up to 0.69 eV, which agrees well with recent work on Cs_4PbBr_6 single crystals²⁹.

Figure 2. (a) Illustrations of Br, Pb, and Cs vacancies (V_{Br} , V_{Pb} and V_{Cs}). (b) Calculated defect formation energies for orthorhombic- CsPbBr_3 , CsPb_2Br_5 , and Cs_4PbBr_6 at Br-rich/Pb-poor, moderate, and Pb-rich/Br-poor conditions. (c) Defect charge-transition levels of CsPbBr_3 , CsPb_2Br_5 and Cs_4PbBr_6 . (d) charge density distributions of V_{Br} defect states for CsPbBr_3 , CsPb_2Br_5 and Cs_4PbBr_6 calculated at the GGA/PBE level of theory. The bandgaps were corrected using the HSE+SOC method.

To explore and decipher the origin of defect-induced green luminescent centers and its nature in Cs_4PbBr_6 and higher dimensional structures, we calculated the point defect formation energy and corresponding charge-transition levels for all structures using well-established methods³⁰, which have been applied to guide the experimental design of high luminescent inorganic perovskites by controlling the defect concentration (*e.g.*, CsSnI_3 ³¹ and CsPbCl_3 ³²). As illustrated in Figure 2a and Figure S3a, we focus on three vacancies (V_{Cs} , V_{Pb} , and V_{Br}) and three antisites (Pb_{Cs} , Pb_{Br} , and Cs_{Br}) since they are potentially dominant defects formed in inorganic perovskite materials³³⁻³⁴. The details of the calculations on the defect formation energies and charge-transition levels can be

found in the Supporting Information; and the calculated chemical potential regions (points A, B, and C correspond to Br-rich/Br-poor, moderate, and Br-rich/Pb-poor conditions) are also shown in Figure S2 of the Supporting Information. As illustrated in Figure 2b, under Br-rich/Pb-poor conditions, V_{Cs} has the lowest defect formation energy in all Cs-Pb-Br perovskites and is the dominant defect. V_{Br} has a much larger formation energy than V_{Pb} , especially in orthorhombic-phase CsPbBr_3 . In moderate conditions, the dominant defect is still V_{Cs} in both CsPbBr_3 and Cs_4PbBr_6 , but with an increased formation energy (up to 1.5 eV), while both the in-plane and out-of-plane Br vacancies (*i.e.*, V_{Br1} and V_{Br2} as illustrated in Figure 2a) are the dominant defects in CsPb_2Br_5 . The overall defect concentration in moderate conditions would be much smaller than that in Br-rich conditions. As the chemical potential point shifts from the Br-rich/Pb-poor to Pb-rich/Br-poor side, the defect formation energies of V_{Pb} and V_{Cs} increase, while that of the donor vacancy V_{Br} largely decreases. Thus, under the Pb-rich/Br-poor conditions, V_{Br} becomes the dominant defect in all cases, with formation energies of less than 1.5 eV. For antisite defects (Figure S3), only Pb_{Cs} is expected to form in Cs_4PbBr_6 given its much lower formation energy compared to other antisites in the Cs-Pb-Br perovskites; this supports our conclusion that in Cs_4PbBr_6 antisite Pb_{Cs} defect are mainly responsible for the intrinsic Pb^{2+} ion emission in the UV spectral range when they occupy Cs^+ sites¹⁷. The overall formation energies of antisite defects remain much larger than the vacancy defects, indicating that the ions are energetically difficult to misplace in the Cs-Pb-Br perovskites, regardless of lattice dimensionality.

Comparing the defect formation energies between cubic- and orthorhombic-phase CsPbBr_3 (see Table S2 of the Supporting Information), cubic- CsPbBr_3 has much lower V_{Br} and V_{Cs} formation energies than the orthorhombic phase, but a much higher formation energy of V_{Pb} . The different vacancy formation energies in CsPbBr_3 are likely due to the larger octahedral tilting in the

orthorhombic phase compared with the cubic one. Although it has been suggested that CsPbBr₃ is highly defect tolerant due to the shallow character of the vacancy-related states,³³ the dominant vacancy defects can reduce the photoluminescence quantum yield through nonradiative recombination of photoexcited excitons in the nanocrystals synthesized from solution processes, especially V_{Pb} defects in CsPbBr₃ nanocrystals with the cubic phase. This is supported by recent work on CsSnI₃ nanocrystals, in which the photoluminescence lifetime increased by decreasing the concentration of V_{Sn} defects³¹.

We further studied the charge-transition levels of these vacancy and antisite defects. As shown in Figure 2c, for both cubic- and orthorhombic-CsPbBr₃, only antisite Pb_{Br} corresponds to a deep transition level, while the other studied defects (V_{Br}, V_{Cs}, V_{Pb}, and Pb_{Cs}) show shallow transition levels. The formation of deep transition levels in CsPbBr₃ is difficult due to the large formation energies, but shallow defects are dominant, in agreement with previous predictions on orthorhombic-phase CsPbBr₃.³³ After reducing the dimensionality into 2D CsPb₂Br₅, Pb_{Br} retains its shallow features, but some shallow defects (V_{Cs} and V_{Pb}) become deep ones. For Cs₄PbBr₆, only deep defects are observed; V_{Br} and Cs_{Br} have a transition level energy of ~2.3 eV above the VBM; both V_{Pb} and V_{Cs} exhibit a deep transition level at -0.5 eV below the VBM; the other antisites all have deep transition levels within the bandgap. Since the formation energy of Cs_{Br} is much larger in all growth conditions, the V_{Br} defect becomes the only reasonable origin for the green emission observed in Cs₄PbBr₆ materials. In addition, the electronic characteristics of the V_{Br} defect in Cs₄PbBr₆ is different from those of the other two Cs-Pb-Br perovskites (Figure 2d). In CsPbBr₃, the V_{Br}-introduced charge density is delocalized over several lattice units surrounding the Br vacancy, and a similar delocalized feature is observed within one layer in CsPb₂Br₅. In contrast, for the Cs₄PbBr₆ structure, the presence of V_{Br} leads to a small structural change of [PbBr₅]³⁻ unit

and the surrounding $[\text{PbBr}_6]^{4-}$ retain in octahedral form, and the charge density is highly localized within the octahedron carrying a defect.

Figure 3. (a) Experimental X-ray diffraction (XRD) pattern, (b) normalized photoluminescence spectra according to the absorbance in the excitation wavelength of 375 nm, and (c) time-resolved photoluminescence (excitation wavelength = 400 nm) of Cs₄PbBr₆ NCs under different growth conditions, including Br-poor, Br-slightly poor, moderate, Br-slightly rich, and Br-rich conditions. (d) Temperature-dependent integrated PL intensity of green emission for CsPbBr₃ and Br-poor Cs₄PbBr₆ NCs using 470-nm excitation.

Therefore, based on these theoretical results, the V_{Br} defects in Cs_4PbBr_6 can be considered to act as recombination centers and achieve green emission due to the following reasons: *i*) V_{Br} has a much smaller formation energy under Br-poor conditions, *ii*) the V_{Br} transition level matches well with the green emission energy, and *iii*) the V_{Br} electronic charge density is highly localized. These results on the energetics of intrinsic point defects in Cs_4PbBr_6 supercells highlight the importance of minimizing V_{Br} defect formation energy during the synthesis of large Cs_4PbBr_6 NCs with increased volume-to-surface ratio. To support this conclusion, we decided to experimentally induce more defects under extremely Br-poor conditions in order to increase the V_{Br} concentration and consequently improve the photoluminescence quantum efficiency of Cs_4PbBr_6 NCs.

To experimentally confirm the V_{Br} point defect emission, we synthesized green-emissive Cs_4PbBr_6 NCs under different conditions (Br-poor, Br-slightly poor, moderate, Br-slightly rich, and Br-rich) through controlling the HBr amount using our modified micro-emulsion method^{2, 35} (see Methods in the Supporting Information). The HRTEM images show that the as-grown Cs_4PbBr_6 NCs show a quasi-hexagon shape with dimensions of 40-60 nm (Figure S4 of the Supporting Information). X-ray diffraction (XRD) patterns with peaks at 12.5°, 20.0°, 25.3°, 28.5°, and 30.2° (Figure 3a) confirm the pure 0D rhombohedral phase of Cs_4PbBr_6 (JPCDS No.73-2478), without any featured peaks (15.5°, 21.8° and 31.0°) from cubic-phase CsPbBr_3 (Figure S7a). The energy-dispersive X-ray (EDX) spectroscopy analysis (Figure S5) demonstrates that the elemental ratio of Br:Pb was found to be 5.6:1 for Br-poor Cs_4PbBr_6 NCs, smaller than that in the moderate sample (Br:Pb = 6.4:1), demonstrating the high Br deficiencies in the Br-poor sample. The Cs_4PbBr_6 samples all show a long Urbach tail in the absorption and photoluminescence excitation (PLE) spectra (Figure S6), arising from the localized sub-band-gap state-mediated absorption of photons³⁶. Based on the different absorption and PLE features between Cs_4PbBr_6 and CsPbBr_3

NCs (Figure S6 and Figure S7b), we can further exclude the possibility of CsPbBr₃ impurities emerged in Cs₄PbBr₆ NCs. As shown in Figure 3b, Cs₄PbBr₆ NCs obtained under different conditions show narrow photoluminescence bands located in the green region (509-514 nm) with full width at half-maximum values of 19-20 nm, regardless of their slightly different shapes. The PL intensity increased when increasing the concentration of Br defects (from Br-rich to moderate to Br-poor conditions), and the highest photoluminescence quantum yield (PLQY, ~46%) was achieved in Br-poor Cs₄PbBr₆, and a slightly red-shift of PL peak might be due to the strong interactions between charged [PbBr₅]³⁻ units in the 0D lattice once the population of V_{Br} increases.

Time-resolved photoluminescence (TRPL) measurements were conducted to better understand the role of defects in the charge carrier dynamics in Cs₄PbBr₆ NCs. The TRPL intensity of Cs₄PbBr₆ NCs are fitted to a biexponential with different lifetimes. Similar to Cs₄PbBr₆ nanoplates⁴, Cs₄PbBr₆ NCs show a fast PL lifetime component of ~3.7 ns, which may be originated from a charged exciton due to spin-orbit coupling; while the long component of PL lifetimes is determined by the V_{Br} concentration. The Br-poor Cs₄PbBr₆ NCs exhibit a significantly longer PL lifetime than do the Br-rich ones: $\tau_1 = 3.68 \pm 0.01$ and $\tau_2 = 15.4 \pm 0.06$ ns for Br-rich Cs₄PbBr₆ NCs (blue curve), and $\tau_1 = 3.85 \pm 0.02$ and $\tau_2 = 36.4 \pm 0.19$ ns for Br-poor Cs₄PbBr₆ (red curve). Note that the lifetimes of Cs₄PbBr₆ NCs are different than those of the CsPbBr₃ NCs, with PLQY of ~70% and PL lifetimes of $\tau_1 = 1.92 \pm 0.01$ and $\tau_2 = 9.08 \pm 0.07$ ns (Figure S7c). As given in Figure 3d, the exciton binding energy (137 ± 15 meV) of Cs₄PbBr₆ NCs, derived from temperature-dependent integrated PL intensity (Figure S8 of the Supporting Information), is much larger than that of the CsPbBr₃ NCs (51 ± 10 meV), which agrees well with previous reports (100-350 meV^{2, 29, 35}). Moreover, our previous study¹⁷ showed that Cs₄PbBr₆ has strong exciton-phonon couplings due to extra Pb-Br rocking modes in the [PbBr₆]⁴⁻ octahedron compared to rigid CsPbBr₃ with

horizontal and vertical Pb-Br stretching modes. Since the trapping of electrons occurs at Br vacancies followed by the recombination with holes, the V_{Br} defect can act as a trap state making the exciton recombination centers more efficient for green emission in Cs_4PbBr_6 NCs. Thus, the enhancement in the steady-state PL measurements are accompanied by lifetime increment in Br-poor Cs_4PbBr_6 NCs with a high concentration of V_{Br} defects. Moreover, V_{Br} -induced excitons in the Cs_4PbBr_6 lattice host could predominantly couple to these Pb-Br rocking and stretching modes, promoting resonant energy transfer from the $[PbBr_6]^{4-}$ octahedra to the V_{Br} luminescent centers using high-energy excitation.

Figure 4. Drift-corrected HRTEM image of (a) non-emissive and (b) green-emissive Cs_4PbBr_6 NC. The fast Fourier transform (FFT) patterns are shown as insets; (c) high angle annular dark field (HAADF)-STEM image of green-emissive Cs_4PbBr_6 NC; and (d) HAADF-STEM images and fast Fourier transform patterns of selected areas 1 and 2 in (c).

To further substantiate the conclusion, we have used the recently developed low-dose HRTEM and data processing methods³⁷ to acquire images of both non-emissive and green-emissive Cs_4PbBr_6 samples with extremely low beam doses ($\sim 30\text{--}40\text{ e}/\text{\AA}^2$). The drift-corrected HRTEM images were obtained by removing the drift between successive frames (Figures 4a, 4b). The lattice periodicity of non-emissive Cs_4PbBr_6 NC can be clearly resolved; by taking a fast Fourier transform (FFT) pattern, two diffraction spots are confirmed as the (110) and (002) planes of Cs_4PbBr_6 . Notably, two selected regions of green-emissive Cs_4PbBr_6 NCs show the same FFT patterns as the non-emissive case. In fact, similar FFT pattern can be obtained from different regions over different nanocrystals (see more images of different NCs from the same Cs_4PbBr_6 sample batch in Figure S9 of the Supporting Information), indicating the pure Cs_4PbBr_6 crystallographic phase; the presence of small dark points/domains is due to the unavoidable beam damage on the nanocrystal surface during HRTEM measurements. To further confirm this, HAADF-STEM imaging was performed at 300 kV on a probe-corrected Titan 60-300 kV microscope (the probe convergence angle was 17 mrad and the collection angle was 50~250 mrad). As shown in Figures 4c and 4d, the FFT patterns from both bright and dark contrast regions in HAADF-STEM image exhibit the same pattern along $\langle 110 \rangle$ zone axis of Cs_4PbBr_6 0D phase. Although the point defects (*e.g.*, V_{Br}) cannot be resolved at the atomic level in the HRTEM images, we can confirm the pure 0D phase of green-emissive Cs_4PbBr_6 NCs and completely exclude the appearance of the CsPbBr_3 phase in both non-emissive and green-emissive Cs_4PbBr_6 samples.

In most inorganic semiconductors, including CsPbBr_3 , point defects with deep transition levels work as carrier traps, resulting in non-radiative recombination channels and, usually, broadband emissions. It should be noted that the shallow levels largely preserve the bulk electronic structure and do not degrade the optoelectronic properties. However, for Cs_4PbBr_6 , although the V_{Br} defect has a deep energy level of ~ 2.3 eV within the band gap, the V_{Br} -induced narrow band emission retains a high PL quantum yield. Interestingly, this emission feature (narrow bandwidth and few ns lifetime) is similar to small organic molecules, confirming the molecular behavior of Cs_4PbBr_6 where the excitons are directly generated in the isolated $[\text{PbBr}_5]^{3-}$ under sub-band gap energy excitation. We should emphasize that these V_{Br} defects in Cs_4PbBr_6 will not lead to large lattice distortions since the formed trap-state $[\text{PbBr}_5]^{3-}$ is well separated from other complete octahedra. The photogenerated excitons are trapped and strongly localized in those isolated traps for radiative recombination, preventing exciton-exciton annihilation in Br-deficient Cs_4PbBr_6 NCs.

In summary, we have identified the nature of the dominant defect in Cs-Pb-Br perovskites by DFT calculations on the defect formation energies and transition levels. We have identified the origin of green luminescence in Cs_4PbBr_6 by proving that the V_{Br} defect-induced states act as radiative recombination centers to capture excitons in Br-deficient Cs_4PbBr_6 NCs. From atomic-resolution TEM measurements using low-beam doses, we confirm the 0D-phase Cs_4PbBr_6 and exclude the presence of CsPbBr_3 NCs impurities. We suggest that the precise control of defect concentration under halogen-poor conditions leading to stable 0D perovskites allows the achievement of high photoluminescence quantum yields. Our findings can extend the scope of use of point defect emission in these bulk quantum 0D perovskite materials.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Experimental and computational methods; crystal lattice parameters and Brillouin zone paths of Cs-Pb-Br compounds; stability regions and represent active points; antisite defect formation energy; TEM images, EDX and steady-state absorption spectra of Cs₄PbBr₆ NCs; optical characterizations of CsPbBr₃ NCs; temperature-dependent PL spectra; low-doss HRTEM images of Cs₄PbBr₆ NCs.

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Notes

The authors declare no competing financial interests.

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