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Zhang, M., Khamkaeo, S., Cai, X. et al (2026). Phonon-induced hypersensitive transitions in lanthanide double perovskites. Physical Review B, 114(8). <http://dx.doi.org/10.1103/SS4K-ZYD6>

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Phonon-induced hypersensitive transitions in lanthanide double perovskites

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(Received 5 September 2025; revised 24 March 2026; accepted 4 August 2026; published 28 August 2026)

Lanthanide ions exhibit characteristic emission originating from intra- $4f$ transitions. Among them, hypersensitive transitions (HSTs) are distinguished by their pronounced spectral tunability. Conventional HST emitters typically rely on dilute doping and host-to- $4f$ charge transfer, which are often limited by defect-induced quenching and transfer losses. Here, we observe a highly efficient HST channel independent of a host-to- $4f$ transfer in undoped, intrinsically luminescent europium-based double perovskites, and we identify the mechanisms that govern both the enhancement and loss of HST efficiency. In this system, a thermally activated doubly degenerate phonon mode of the Eu-Cl_6 octahedra relaxes the parity selection rule, thereby strengthening the HST emission. The HST oscillator strength is enhanced by a factor of 2–3 relative to that of the magnetic-dipole transition. Direct excitation into the ^5L_J level bypasses reverse energy transfer and yields a maximum quantum efficiency of nearly 70%. These findings provide insights into the design of efficient and spectrally tunable emission in lanthanide systems.

DOI: [10.1103/ss4k-zyd6](#)

I. INTRODUCTION

The $4f$ - $4f$ electronic transitions of lanthanide ions are characterized by spectrally sharp emission lines, making them attractive for a wide range of light-emitting applications [1–4]. Among these transitions, hypersensitive transitions (HSTs) are especially appealing because their pronounced sensitivity to the local chemical and structural environment enables tunable emission properties [5–8]. Trivalent europium (Eu^{3+}), with strong $4f$ shielding and characteristic red emission, is a well-known example of an HST-active ion [9]. Conventionally, HST activation relies on doping lanthanide ions into host matrices to create dielectric inhomogeneity, which partially relaxes the parity selection rule and facilitates host-to- $4f$ charge transfer [10–13]. However, this strategy has intrinsic limitations, including defect-induced quenching, energy loss during transfer, and challenges in precisely controlling the synthesis. Realizing highly efficient HST emission through intrinsic transition channels, without host-mediated charge transfer, remains an underexplored route for expanding the functional scope of lanthanide emitters.

The emergence of halide perovskites, particularly double perovskites, has provided a promising platform for designing optoelectronic materials with tunable structural and electronic

properties [14]. Their intrinsically soft lattices permit local distortion and symmetry breaking [15–17], which can in principle activate HSTs. Moreover, $A_2^{+}B+B^{3+}X_6^{-}$ -type double perovskites can accommodate trivalent lanthanide ions at high concentrations within a charge-balanced lattice [18,19]. This structure differs from conventional dilute-doping systems and allows strong $4f$ absorption.

In this work, we observe an intrinsic pathway for efficient HST emission in an undoped luminescent Eu^{3+} -based double perovskite system and experimentally identify the physical mechanisms that govern both the enhancement and the loss of HST efficiency. A thermally activated doubly degenerate e_g phonon mode increases the HST oscillator strength by a factor of 2–3 relative to the magnetic-dipole (MD) transition. Conversely, multistep interionic energy migration and $4f$ - $4f$ cross relaxation reduce the HST efficiency. Direct excitation of the $4f$ levels produces a photoluminescence quantum yield (PLQY) of approximately 70%, comparable to that of state-of-the-art Eu^{3+} -doped materials [20,21]. These findings broaden the design space for HST-based emitters and clarify the competing processes that set their efficiency limits.

II. RESULTS AND DISCUSSION

The electron configuration of Eu^{3+} is $[\text{Xe}]4f^6$. Owing to electron-electron repulsion and spin-orbit coupling, the $4f$ orbitals split into free-ion energy levels $^{2S+1}L_J$ (Fig. S1; Table S1 in Supplemental Material Ref. [22]). The ground state of Eu^{3+} is $^7F_0$, and the lowest excited state is $^5D_0$. Due to shielding by the outer filled $5s$ and $5p$ orbitals, Eu^{3+} ions behave as chemically isolated species. The $4f$ electrons are highly localized and contribute little to bonding with neighboring ions or the host lattice. This

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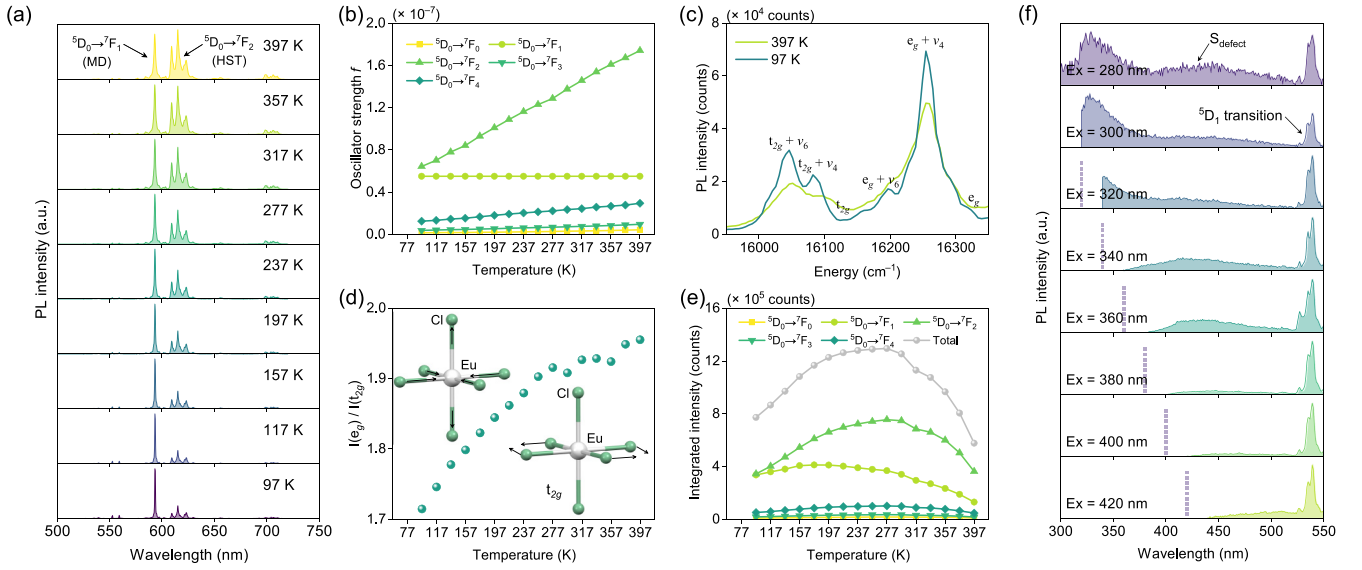


FIG. 1. (a) PL spectra of $\text{Cs}_2\text{NaEuCl}_6$ measured across a temperature range of 97–397 K under 394 nm excitation. (b) Oscillator strengths of the $^5D_0 \rightarrow ^7F_{1-4}$ transitions as a function of temperature. (c) Spectra of the HST zero-phonon region at 97 and 397 K, showing its Stark splitting into the doubly degenerate mode e_g and triply degenerate mode t_{2g} components together with their vibronic sidebands. (d) Intensity ratio $I(e_g)/I(t_{2g})$ as a function of temperature; insets show the degeneracy mode representations of the e_g and t_{2g} states in Eu-Cl_6 octahedron. (e) Integrated PL intensities of the $^5D_0 \rightarrow ^7F_J$ transitions as a function of temperature. (f) Excitation-dependent PL spectra. S_{defect} is the defect state. Vertical dashed lines mark the excitation energies.

localization enables stable incorporation and retention of intrinsic emission properties when size matching is satisfied. $\text{Cs}_2\text{NaEuCl}_6$ was identified as a suitable framework through ionic radius matching and tolerance factor calculations (Tables S2 and S3 [22]). A well-faceted bulk single crystal ($\sim 5 \times 5 \times 3 \text{ mm}^3$) was synthesized via a hydrothermal method with nonlinear cooling optimized for crystallization kinetics. Phase purity was confirmed by energy-dispersive X-ray spectroscopy and X-ray diffraction (Figs. S2–S6 [22]). Due to the thermodynamic stability of double perovskites [23], the sample shows long-term air stability and solution processability (Figs. S7 and S8 [22]). The room-temperature photoluminescence (PL) spectrum shows well-resolved $^5D_0 \rightarrow ^7F_J$ transitions (Fig. S9 [22]), with dominant emission at 610–630 nm [$^5D_0 \rightarrow ^7F_2$, hypersensitive electric-dipole (ED) transition] and 585–600 nm ($^5D_0 \rightarrow ^7F_1$, MD transition); the remaining peaks correspond to nonhypersensitive ED transitions.

The hypersensitive character of the $^5D_0 \rightarrow ^7F_2$ transition is revealed by temperature-dependent PL spectroscopy [Fig. 1(a)]. From 97 to 397 K, the intensity of the $^5D_0 \rightarrow ^7F_2$ HST (610–630 nm) increases markedly, while the $^5D_0 \rightarrow ^7F_1$ MD transition (585–600 nm) remains essentially constant and the other ED transitions show only weak growth. This selective enhancement indicates that simple Arrhenius activation of the overall radiative rate is not the main cause of the enhanced HST emission. We quantified transition probabilities using the oscillator strength (f), which in lanthanide systems are described by the Judd-Ofelt theory [5,6,24],

$$f_{J-J'} = \frac{8\pi^2 m_e v}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle J || U^{(\lambda)} || J' \rangle|^2, \quad (1)$$

where m_e is the electron mass, v is the transition wave number, h is Planck's constant, and $2J+1$ is the degeneracy of the

initial state. The Ω_{λ} are phenomenological parameters, and $|\langle J || U^{(\lambda)} || J' \rangle|^2$ is the squared reduced matrix element. These parameters can be obtained from the spontaneous emission rate $A_{J-J'}$ [24,25]:

$$A_{J-J'} = \frac{64\pi^4 e^2}{3h\lambda^3} \chi \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle J || U^{(\lambda)} || J' \rangle|^2. \quad (2)$$

Substituting Eq. (2) into Eq. (1) gives

$$f_{J-J'} = \frac{m_e c \lambda^2}{8\pi^2 e^2} \frac{1}{\chi} A_{J-J'}. \quad (3)$$

Here, χ is the local-field correction factor, $\chi_{\text{ED}} = n(n^2 + 2)^2/9$ for ED transitions and $\chi_{\text{MD}} = n^3$ for MD transitions, where n is the refractive index of the medium. The radiative rate A was extracted from time-resolved PL decay (Fig. S10 [22]), yielding a value of $\sim 223 \text{ s}^{-1}$, corresponding to a lifetime of 4.49 ms. The oscillator strengths (f values) of all seven $^5D_0 \rightarrow ^7F_J$ transitions at different temperatures are shown in Fig. 1(b). At low temperatures, the f values of $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ are comparable. With increasing temperature, the f values of the hypersensitive $^5D_0 \rightarrow ^7F_2$ and sensitive $^5D_0 \rightarrow ^7F_4$ transitions increase approximately linearly, but with distinct slopes. At room temperature (297 K), the f value of $^5D_0 \rightarrow ^7F_2$ becomes 2.4 times that of $^5D_0 \rightarrow ^7F_1$ and increases to ~ 3 times at 397 K. The near-linear trend supports a thermally activated contribution, while the transition-dependent slopes argue against a single Boltzmann-type mechanism. We instead attribute the enhancement to thermally induced vibronic coupling that distorts the local symmetry, relaxes the parity selection rules, and increases the ED transition probabilities.

Soft lattice characteristics are well established in double perovskites, arising from large A -site free volumes, weak

halide bonding, and abundant low-frequency phonon modes [15–17,26]. Thermal perturbation can induce lattice fluctuations in $\text{Cs}_2\text{NaEuCl}_6$. The fluctuation of Cs^+ ions originates from large voids beyond the octahedral framework, while the fluctuation amplitudes of Na^+ , Eu^{3+} , and Cl^- ions are influenced by vibronic frequencies and atomic mass. Given that m_{Na} (22.99 u) and m_{Cl} (35.45 u) are much smaller than m_{Eu} (151.96 u), the resulting time-dependent local fields

$$\mathbf{E}_{\text{loc}}(t) = \mathbf{E}_{\text{Cs-Eu}}(t) + \mathbf{E}_{\text{Na-Eu}}(t) + \mathbf{E}_{\text{Cl-Eu}}(t) \quad (4)$$

can acquire an appreciable odd-parity component. These perturbed local fields affect the local symmetry, which we quantify by analyzing multiplet degeneracy. In an octahedral crystal field (O_h), the $4f$ Hamiltonian contains only

$$\hat{H}_{\text{CF}}^{(O_h)} = B_4^0 C_0^{(4)} + B_6^0 C_0^{(6)}. \quad (5)$$

Under such symmetry, the ${}^7F_2$ level ($2J + 1 = 5$) splits as follows [Fig. 1(c)] [27,28],

$$\Gamma({}^7F_2) = e_g \oplus t_{2g}. \quad (6)$$

The doubly degenerate e_g phonon mode corresponds to axial distortions of the octahedral framework (elongation or compression) [Fig. 1(d) inset], while the triply t_{2g} mode is primarily associated with octahedral tilting or rotation [29,30]. Given that Eu^{3+} occupies the center of the Eu-Cl_6 octahedron, an e_g -type distortion directly lowers the Eu-site symmetry, whereas a rigid t_{2g} -type tilt largely preserves the internal octahedral geometry and therefore produces a weaker perturbation of the local crystal field. For an ideal cubic lattice with an Eu site of O_h symmetry, the intensity ratio between the e_g and t_{2g} components of the ${}^5D_0 \rightarrow {}^7F_2$ transition is expected to remain constant. However, we observe a steady increase in the $I(e_g)/I(t_{2g})$ ratio with rising temperature [Fig. 1(d)]. These experimental results indicate increasingly strong thermally activated local e_g -type axial distortions, which contribute to relaxing the parity selection rule.

A nonmonotonic temperature dependence of PL intensity is observed, featuring activation followed by quenching. The integrated emission intensity increases with temperature and peaks at ~ 177 K for the ${}^5D_0 \rightarrow {}^7F_1$ MD transition, while all ED transitions peak at ~ 277 K [Fig. 1(e)]. The earlier quenching onset of the ${}^5D_0 \rightarrow {}^7F_1$ line is consistent with its MD character: as a parity-allowed transition, it does not require local symmetry breaking and therefore reaches its maximum at a lower temperature. By contrast, ED transitions, enabled by vibronically induced local symmetry breaking, reach their maxima at higher temperatures. These trends are not readily explained by a simple excitonic or free-carrier recombination channel. Both the increasing and decreasing regions are well described by an Arrhenius relation,

$$I(T) = I_0 \exp\left(-\frac{E_a}{k_B T}\right), \quad (7)$$

where $I(T)$ is the PL intensity at temperature T , I_0 is the reference intensity, E_a is the activation energy, and k_B is Boltzmann's constant. Fitted activation energies (Fig. S12 [22]) are ~ 2.5 meV for ${}^5D_0 \rightarrow {}^7F_1$ (MD) and ~ 10 meV for the ED transitions. In contrast, thermal quenching above 277 K yields comparable activation energies (~ 100 meV) for all

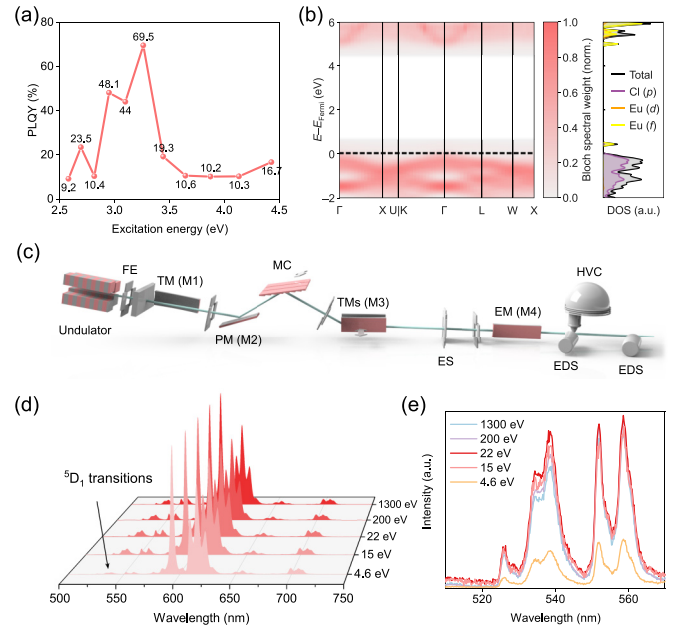


FIG. 2. (a) Excitation-dependent PLQY of $\text{Cs}_2\text{NaEuCl}_6$. (b) Effective band structure and density of states (DOS) in the paramagnetic phase. (c) Synchrotron-based monoenergetic photon excitation system at the FinEstBeAMS beamline. FE: front end; TM: toroidal mirror; PM: plane mirror; MC: plane grating; ES: exit slit; EM: ellipsoidal mirror; HVC: high vacuum chamber; EDS: end station. (d) Emission spectra collected under high-energy-photon excitation. (e) Detail of the ${}^5D_1 \rightarrow {}^7F_{0-2}$ transitions.

transitions, suggesting a common nonradiative loss pathway, which we assign to reverse energy transfer. Evidence for the reverse-transfer state is obtained from excitation-dependent PL spectra [Fig. 1(f)]. A weak PL peak near 325 nm is observed under 280 nm excitation, corresponding to band-to-band radiative recombination. Most of the excitation energy is funneled to excite the strong ${}^5D_{0,1} \rightarrow {}^7F_J$ emissions. A defect-related PL peak near 420 nm is observable at room temperature only under excitation wavelengths shorter than 380 nm (energy > 3.26 eV), but it vanishes at low temperatures (< 250 K). This behavior is consistent with the ~ 100 meV reverse-activation energy, attributed to overcoming the barrier gap, extracted under 394 nm (3.15 eV) excitation.

The PLQY of $\text{Cs}_2\text{NaEuCl}_6$ was measured at room temperature over excitation energies from 2.5 to 4.5 eV, with a maximum of 70% at ~ 3.25 eV within a narrow 3.1–3.3 eV window [Fig. 2(a); Fig. S13 [22]], notably below the band-gap energy of $\text{Cs}_2\text{NaEuCl}_6$ ($E_g \sim 3.5$ eV; Fig. S14 [22]). This trend indicates efficient direct excitation of $4f$ states, which reduces energy losses associated with host-to- $4f$ energy transfer. Density function theory (DFT) calculations augmented with Hubbard U (DFT + U) reveal a dense manifold of Eu $4f$ states in the effective band structure [Fig. 2(b)]. The calculated Bloch spectral weight is significantly higher than that observed in conventional Eu^{3+} -doped materials [31], consistent with prior calculations on lanthanide double perovskites [32], supporting enhanced $4f$ -state optical accessibility. To further probe excitation-pathway dependence in the high-energy regime, we performed

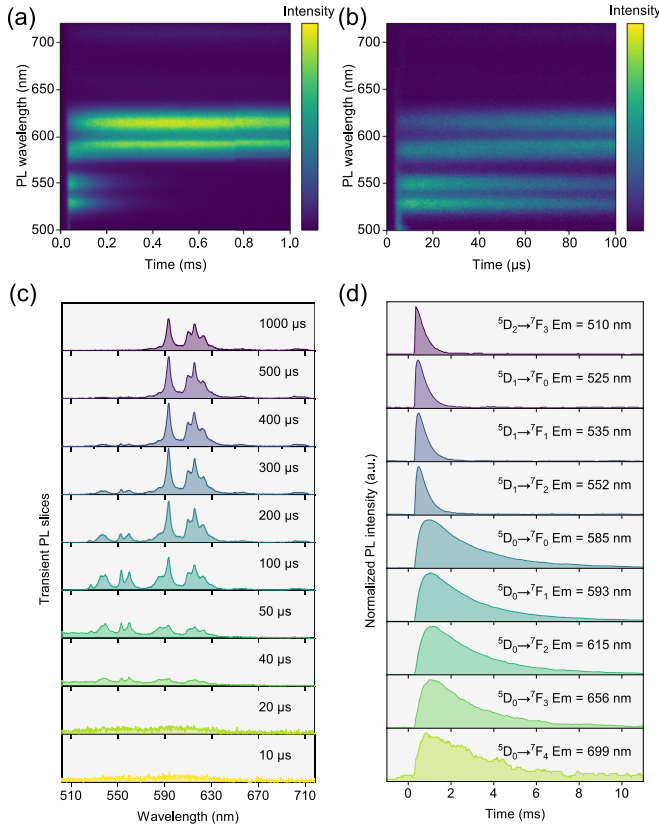


FIG. 3. Time-resolved PL mappings of $\text{Cs}_2\text{NaEuCl}_6$ under 340 nm excitation, covering the emission range of 500–720 nm over two distinct timescales: (a) 0–1 ms; (b) 0–100 μs . (c) Spectral slices extracted within the 0–1 ms window. (d) Decay profiles of emissions from the $^5D_2$, $^5D_1$, and $^5D_0$ levels within 0–10 ms.

synchrotron-based monoenergetic photon-excitation experiments [Fig. 2(c)]. High-energy photons generated by a permanent magnet undulator were monochromatized with a plane-grating monochromator and focused onto the crystal surface [33]. The excitation energy was stepped from 4.6 eV (band-to-band regime) to 15, 22, 200, and 1300 eV, where progressively deeper inner-shell ionization becomes available. Under 4.6 eV excitation, the emission profile is essentially identical to that observed above. In contrast, under 15–1300 eV excitation, the 525–565 nm emission, corresponding to $^5D_1 \rightarrow ^7F_{0,1,2}$ transitions, increases markedly, whereas the $^5D_0 \rightarrow ^7F_J$ transitions remain nearly unchanged [Figs. 2(d) and 2(e)]. This selective response indicates that high-energy excitation affects feeding into upper 4*f* excited states, while the terminal $^5D_0$ emissive channel remains comparatively stable.

To understand the origin of the observed asynchronous response between upper 4*f* levels and terminal $^5D_0$ level, we performed transient PL measurements and tracked emission from 500 to 720 nm over two time windows, 0–1 ms and 0–100 μs [Figs. 3(a) and 3(b)]. As shown by the time-resolved spectral slices [Fig. 3(c)], emission in the higher-energy region dominates at early times, with distinct peaks at 525, 535, 552, and 560 nm. These features are typically weak in steady-state spectra because they are rapidly overwhelmed by the longer-lived peaks at 593, 610, 615, 624, 703, and 710 nm, corresponding to $^5D_0 \rightarrow ^7F_{1-4}$ transitions. Based on

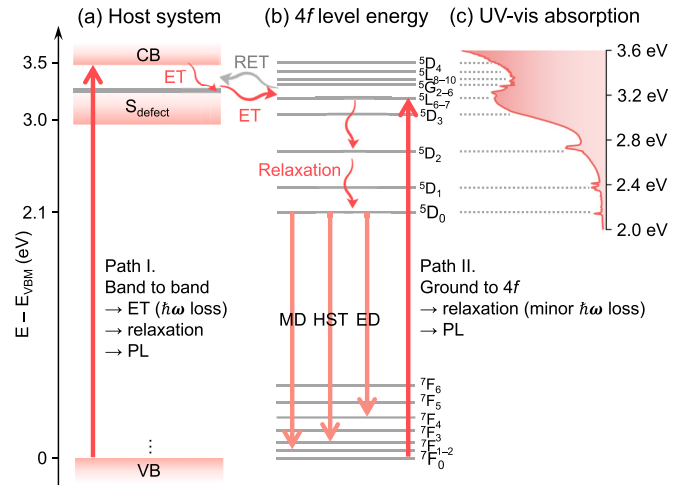


FIG. 4. Energy-level diagram and photophysical pathways. CB: conduction band; S_{defect} : defect state; VB: valence band; ET: energy transfer; RET: reverse energy transfer. $\hbar\omega$: thermalization.

established Eu^{3+} 4*f* level assignments, the short-lived peaks are attributed to $^5D_1 \rightarrow ^7F_0$ transitions (~ 527 nm), $^5D_1 \rightarrow ^7F_1$ (~ 539 nm), and $^5D_1 \rightarrow ^7F_2$ (~ 553 and ~ 560 nm). Their emergence and decay sequence provides direct evidence for stepwise relaxation from $^5D_1$ to $^5D_0$. Additional evidence is provided by time-resolved decay profiles of emissions from $^5D_2$, $^5D_1$, and $^5D_0$ [Fig. 3(d)]. The rise of $^5D_1$ emission coincides with the decay of $^5D_2$, followed by the rise of $^5D_0$ as $^5D_1$ decays, consistent with a cascade transfer pathway, $^5D_2 \rightarrow ^5D_1 \rightarrow ^5D_0$. Lifetime fitting yields a ~ 1 μs timescale for $^5D_2 \rightarrow ^5D_1$ and ~ 100 μs for $^5D_1 \rightarrow ^5D_0$ (Fig. S15 [22]). These steps are much faster than the final $^5D_0$ radiative decay on the millisecond timescale, indicating efficient intra-4*f* relaxation within upper 4*f* levels before terminal emission. Overall, these results support sequential 4*f* level relaxation rather than direct host-to-terminal population and explain why excitation into higher Eu 4*f* states does not introduce substantial additional loss before $^5D_0$ emission.

Combining these results, we propose an energy-level diagram to interpret the photophysical pathways (Fig. 4). In $\text{Cs}_2\text{NaEuCl}_6$, the Eu^{3+} 4*f* levels, especially the $^5L_{6-7}$ levels at ~ 3.2 eV, serve as efficient excitation centers. For excitation above or near the band gap (Path I), charge carriers are initially generated in the host and subsequently transfer their energy to Eu^{3+} ions during carrier recombination via the charge transfer state located below the band gap. However, this pathway is subject to energy back transfer because of the relatively small energy barrier (~ 100 meV). Alternatively, the Eu^{3+} ions can be directly excited to the $^5L_{6-7}$ levels through absorption of incident photons or energy deposition by energetic particles, such as through hot-electron impact (Path II). Rapid intra-4*f* relaxation then populates the lowest stable emissive $^5D_0$ state, bypassing reverse energy transfer and resulting in a markedly enhanced PLQY.

III. CONCLUSIONS

In summary, we identify a mechanism for efficient hypersensitive emission in an undoped Eu^{3+} -based double

perovskite. The experimentally observed doubly degenerate phonon mode relaxes the parity selection rule, thereby strengthening HST emission. Furthermore, the excitation experiments confirm that the $\text{Eu}^{3+} \ ^5L_6 - ^5G_3$ levels at 3.1–3.3 eV can be efficiently populated by direct energy absorption. Direct excitation within this energy window populates these $4f$ absorption states, followed by rapid intra- $4f$ relaxation to the $^5D_0$ state. This process avoids reverse energy transfer and thereby enhances the PLQY. Unlike the random dopant distribution in typical doped semiconductors, Eu^{3+} ions in $\text{Cs}_2\text{NaEuCl}_6$ occupy well-defined lattice sites. Thermally activated vibronic distortions enable HSTs, while the ordered lattice favors direct $4f$ excitation and mitigates Auger-type losses. Furthermore, $\text{Cs}_2\text{NaEuCl}_6$ is a promising candidate for electrically pumped perovskite laser diodes: its band gap can supply carrier-recombination energy to raise Eu^{3+} from $^7F_0$ to $^5L_6$, enabling optical gain in an efficient three-level scheme. Although wide-band-gap hosts such as SiC and GaN have comparable gaps, their limited Eu solubility and the crystal damage associated with high-dose implantation constrain practical implementation. Overall, our results establish a viable strategy to expand the functional scope of lanthanide-based emitters by coupling lattice dynamics to symmetry-controlled $4f$ transitions.

ACKNOWLEDGMENTS

This work was financially supported by the Knut and Alice Wallenberg Foundation (Grant No. KAW 2019.0082),

the ERC Consolidator Grant (LEAP, Grant No. 101045098), the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (faculty Grant SFO-Mat-LiU No. 2009–00971), and the Centre in Nanoscience and technology at LiTH, CeNano. We acknowledge the MAX IV Laboratory for beamtime on the FinEstBeAMS beamline under Proposal No. 20220670. Research conducted at MAX IV, a Swedish national user facility, is supported by Vetenskapsrådet (Swedish Research Council, VR) under Contract No. 2018–07152, Vinnova (Swedish Governmental Agency for Innovation Systems) under Contract No. 2018–04969 and Formas under Contract No. 2019–02496. S.I.S. acknowledges support from VR (Grant No. 2023-05247). U.S. acknowledges funding support from the Swedish e-Science Research Centre (SeRC). The theoretical computations were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS), partially funded by VR (Grant No. 2022-06725). M.K. and P.P. acknowledge support from VR (Grant No. 2021-04808) and Wallenberg Initiative Materials Science for Sustainability, as funded by the KAW Foundation. F.G. and I.A.A. acknowledge support as Wallenberg Scholars.

DATA AVAILABILITY

The raw data that support the findings of this article are openly available [34]. Further details are provided in the Supplemental Material [22], which includes Refs. [35–49].

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