

Article

Electron-Phonon Interaction in Te-Doped $(\text{NH}_4)_2\text{SnCl}_6$: Dual-Parameter Optical Thermometry (100–400 K)

Ting Geng ¹ , Yuhan Qin ¹, Zhuo Chen ², Yuhan Sun ¹, Ao Zhang ¹, Mengyuan Lu ¹, Mengzhen Lu ¹, Siying Zhou ¹, Yongguang Li ^{3,*}  and Guanjun Xiao ^{3,4,*}

¹ College of Basic Education, Beijing Institute of Graphic Communication, Beijing 102600, China; gengting@bigc.edu.cn (T.G.); 16627200577@163.com (Y.Q.); m15901041581@163.com (Y.S.); zhangao@bigc.edu.cn (A.Z.); 19712798920@163.com (M.L.); m19712780632@163.com (M.L.); m19579782042@163.com (S.Z.)

² Optoelectronics Technology Research and Development Center, Institute of Microelectronics of Chinese Academy, Beijing 100029, China; chenzhuo2021@ime.ac.cn

³ College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 311121, China

⁴ State Key Laboratory of High Pressure and Superhard Materials, College of Physics, Jilin University, Changchun 130012, China

* Correspondence: yongguangli@hznu.edu.cn (Y.L.); xguanjun@jlu.edu.cn (G.X.)

Abstract

Lead-free perovskite variants have emerged as promising candidates due to their self-trapped exciton emission. However, in ASnX_3 systems, facile oxidation of Sn(II) to Sn(IV) yields A_2SnCl_6 vacancy-ordered derivatives. Paradoxically, despite possessing a direct bandgap, these variants exhibit diminished photoluminescence (PL). Doping engineering thus becomes essential for precise optical tailoring of A_2SnX_6 materials. Herein, through integrated first-principles calculations and spectroscopic analysis, we elucidate the luminescence mechanism in Te^{4+} -doped $(\text{NH}_4)_2\text{SnCl}_6$ lead-free perovskites. Density functional theory, X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS) confirm Te^{4+} substitution at Sn sites via favorable chemical potentials. Spectral interrogations, including absorption and emission profiles, reveal that the intense emission originates from the triplet STE recombination ($^3\text{P}_1 \rightarrow ^1\text{S}_0$) of Te centers. Temperature-dependent PL spectra further demonstrate strong electron–phonon coupling that induces symmetry-breaking distortions to stabilize STEs. Complementary electronic band structure and molecular orbital calculations unveil the underlying photophysical pathway. Leveraging these distinct thermal responses of PL intensity and peak position, 0.5% $\text{Te}:(\text{NH}_4)_2\text{SnCl}_6$ emerges as a highly promising candidate for non-contact, dual-parameter optical thermometry over an ultra-broad range (100–400 K). This work provides fundamental insights into the exciton dynamics and thermal engineering of optical properties in this material system, establishing its significant potential for advanced temperature-sensing applications.

Keywords: perovskites; electron-phonon coupling; self-trapped excitons; temperature sensors



Academic Editor: Daqin Chen

Received: 30 July 2025

Revised: 4 September 2025

Accepted: 8 September 2025

Published: 16 September 2025

Citation: Geng, T.; Qin, Y.; Chen, Z.; Sun, Y.; Zhang, A.; Lu, M.; Lu, M.; Zhou, S.; Li, Y.; Xiao, G. Electron-Phonon Interaction in Te-Doped $(\text{NH}_4)_2\text{SnCl}_6$: Dual-Parameter Optical Thermometry (100–400 K). *Chemistry* **2025**, *7*, 150. <https://doi.org/10.3390/chemistry7050150>

Copyright: © 2025 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Luminescent all-inorganic metal halides have emerged as versatile optoelectronic platforms due to their tunable electronic structures and crystallographic flexibility [1,2]. Lead halide perovskites represent a prominent subset, achieving near-unity photoluminescence (PL) quantum yields and broad spectral tunability [3]. However, intrinsic lead toxicity and operational instability fundamentally constrain their device implementation. This has

accelerated the development of lead-free alternatives, where ions with analogous electronic structures to Pb^{2+} (e.g., Ge^{2+} , Sn^{2+} , Sb^{3+} and Bi^{3+}) [2,4–8] show promise as B-site substitutes in ABX_3 frameworks.

Tin-based perovskites attract significant interest because of their distinctive self-trapped exciton (STE) emission and environmental benignity [4,9–15]. However, the facile oxidation of Sn(II) to Sn(IV) leads to irreversible phase transformation into vacancy-ordered A_2SnX_6 derivatives. Although thermodynamically stable, these phases typically exhibit severely quenched photoluminescence—a critical limitation attributed to dominant non-radiative recombination pathways.

Doping engineering has proved to be an effective strategy to overcome these limitations. Although $\text{Sb}^{3+}/\text{Bi}^{3+}$ doping has been shown to enable broadband emission [16,17], recent advances demonstrate that tetravalent dopants (e.g., Te^{4+}) are particularly promising for enhancing optoelectronic performance. For instance, Han et al. demonstrated that Te^{4+} -doped Cs_2SnCl_6 serves as an efficient system for CO_2 photoreduction, expanding the materials library for photocatalytic applications [18]. Similarly, Tang et al. achieved intense yellow-green luminescence (580 nm) in $\text{Sn}^{4+}/\text{Te}^{4+}$ ion-exchanged materials via Jahn–Teller distortions, reaching a record PL quantum yield of 95.4% [13]. Despite these advances, Te-doped $(\text{NH}_4)_2\text{SnCl}_6$ remains underexplored, with systematic studies on its optical properties still lacking.

In this paper, undoped $(\text{NH}_4)_2\text{SnCl}_6$ and Te-doped $(\text{NH}_4)_2\text{SnCl}_6$ were synthesized and we systematically investigated their structure and photoluminescence properties to reveal the correlated photoluminescence mechanism. The morphology and structure of the samples were characterized using techniques such as TEM, XPS and XRD. UV–Vis absorption spectroscopy and temperature-dependent photoluminescence spectra further confirmed strong electron–phonon coupling, which induces symmetry-breaking distortions that stabilize self-trapped excitons (STEs). DFT calculations revealed linear thermochromic behavior in Te-doped $(\text{NH}_4)_2\text{SnCl}_6$ over a broad temperature range, thereby bridging theoretical and experimental insights into the structure–property relationship. Notably, the pronounced temperature dependence of the emission peak position enables 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$ to achieve highly accurate temperature-sensing across a wide range. Compared with conventional ratiometric thermometry based on emission intensity or intensity ratios, this peak-shift-based approach offers higher measurement accuracy and reduced susceptibility to environmental interference [19,20].

2. Materials and Methods

Chemicals: All reagents and solvents were used without further purification. Ammonium chloride (NH_4Cl ; 99.99%), stannic chloride hydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$; 99.995%) and tellurium tetrachloride (TeCl_4 ; 99.9%) were purchased from Aladdin. Hydrochloric acid (HCl ; 36.0–38.0% in water) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China.

Synthesis of $(\text{NH}_4)_2\text{SnCl}_6$: $(\text{NH}_4)_2\text{SnCl}_6$ polycrystalline powders from small-batch production were prepared by dissolving 1 mmol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in a 3.5 mL HCl solution using constant stirring with a magnetic stir bar under ambient conditions. Then, 2 mmol NH_4Cl in 0.5 mL deionized water was immediately dropped into the above solution. Upon the addition of NH_4Cl , a white polycrystalline precipitate was formed. The product was then extracted from the crude solution via centrifugation (4500 rpm; 3 min, TG16-WS, Beijing North Tech Sichuang Scientific Instrument Co., Ltd., Beijing, China), washed with a HCl solution twice and dried under pressure overnight. The Te-doped $(\text{NH}_4)_2\text{SnCl}_6$ samples were prepared via precipitation reactions following the same procedure with the addition of a nominal amount of TeCl_4 in the HCl solution.

Characterization: The samples were characterized by transmission electron microscopy (TEM). TEM images were obtained using a JEM-2200FS (JEOL, Tokyo, Japan) machine equipped with an emission gun operated at 200 kV.

Optical Measurements: The optical absorption spectra measurements were carried out between 250 and 1000 nm using a deuterium–halogen light source and recorded with an optical fiber spectrometer (QE65000, Ocean Optics, Orlando, FL, USA) and a data collection time of 10 s. The PL experiments were carried out using a 355 nm excitation laser with 10 mW power.

Structural characterization: The structural characterization of the synthesized samples was performed using an X-ray diffractometer (XRD, D8 Advance Bruker, Berlin, Germany) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), scanning over a range of 10–60° (2 θ). The Raman spectra were recorded using a spectrometer equipped with liquid-nitrogen-cooled CCD (iHR 550, Symphony II, Horiba Jobin Yvon, Irvine, CA, USA). A 671 nm single-mode DPSS laser was utilized to excite the sample and the output power was 10 mW. The resolution of the system was 1 cm^{−1}. All the high-pressure experiments were performed at room temperature.

3. Results and Discussion

The (NH₄)₂SnCl₆ and Te:(NH₄)₂SnCl₆ samples were synthesized according to the report in [9]. The details were provided in the experimental section. The transmission electron microscopy (TEM) images reveal that the polycrystalline powders synthesized at room temperature consist of rod-shaped particles with a uniform morphology, having lengths of approximately 15 μm (Figure 1a). Such morphological uniformity plays a critical role in influencing device performance and operational stability. Enhanced structural homogeneity helps to reduce defects, thereby optimizing the functional response of the device (such as response sensitivity and operational stability). As depicted in Figure 1b, lead-free vacancy-ordered (NH₄)₂SnCl₆ perovskite crystallizes in the cubic phase (left panel). Notably, Te is the same periodic element as Sn and they have similar coordination characteristics with halogen, suppressing the doping. This results in a lattice defect and strain as far as possible. After doping the Te⁴⁺ ions, the [SnCl₆]^{2−} octahedron in (NH₄)₂SnCl₆ can be partly substituted by the formed [TeCl₆]^{2−} octahedron (right panel). The [Sn(Te)Cl₆]^{2−} octahedra are isolated from each other, similar to the typical structure of Cs₂SnX₆ (X = Cl, Br and I).

To confirm the successful incorporation of Te without inducing structural phase transitions, the XRD patterns were recorded. The XRD of the as-synthesized undoped (NH₄)₂SnCl₆ sample corresponded well with the standard pattern of (NH₄)₂SnCl₆. No impurity diffraction peaks were observed, indicating that the as-synthesized (NH₄)₂SnCl₆ was pure. No impurity phase was detected in 0.5% Te-doped (NH₄)₂SnCl₆, indicating the high purity of 0.5%Te:(NH₄)₂SnCl₆. The refinement profiles of the (NH₄)₂SnCl₆:xTe (x = 0 and 0.5%) samples showed well-refined simulated patterns (Figure 2a). Furthermore, as is well-established, the ion radius of Te⁴⁺ (VI, 0.97 $\text{\AA}$) is bigger than that of Sn⁴⁺ (VI, 0.69 $\text{\AA}$). With Te doping, the XRD peaks gradually shifted to a smaller diffraction angle, verifying that the partial Sn⁴⁺ was successfully replaced by the bigger Te⁴⁺ in the (NH₄)₂SnCl₆ lattice. Detailed Rietveld refinements are provided in Table S1. Furthermore, the stable oxidation states of Sn⁴⁺ and Te⁴⁺ ensure excellent ambient and thermal stability. As shown in Figure 2b, the absorption spectrum of pure (NH₄)₂SnCl₆ shows a bandgap of 4.26 eV and the strongest band edge absorption, located at 291 nm, is slightly smaller than the reported value of (NH₄)₂SnCl₆ (310 nm). The absorption tail in the long-wavelength region could be attributed to defect or surface states, similar to those observed in Cs₂SnCl₆ NCs. As Te⁴⁺ is incorporated, the absorption spectrum shows two distinct absorption humps at 300–360 nm and 370–500 nm. As shown in Figure S1, the bandgap of 0.5%Te: (NH₄)₂SnCl₆ significantly

reduced to 2.66 eV compared with $(\text{NH}_4)_2\text{SnCl}_6$ (4.26 eV). The newly emerging absorption region between 350 and 500 nm could be assigned to localized $\text{Te } 6s^2 \rightarrow 6s^1p^1$ transitions in $[\text{TeCl}_6]^{2-}$ octahedra. The long-wavelength absorption feature centered at ~ 390 nm can be assigned to the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition of Te^{4+} , which is a doublet caused by the dynamic Jahn–Teller effect. Correspondingly, the peak of the short-wavelength band at ~ 330 nm is assigned to the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ transition.

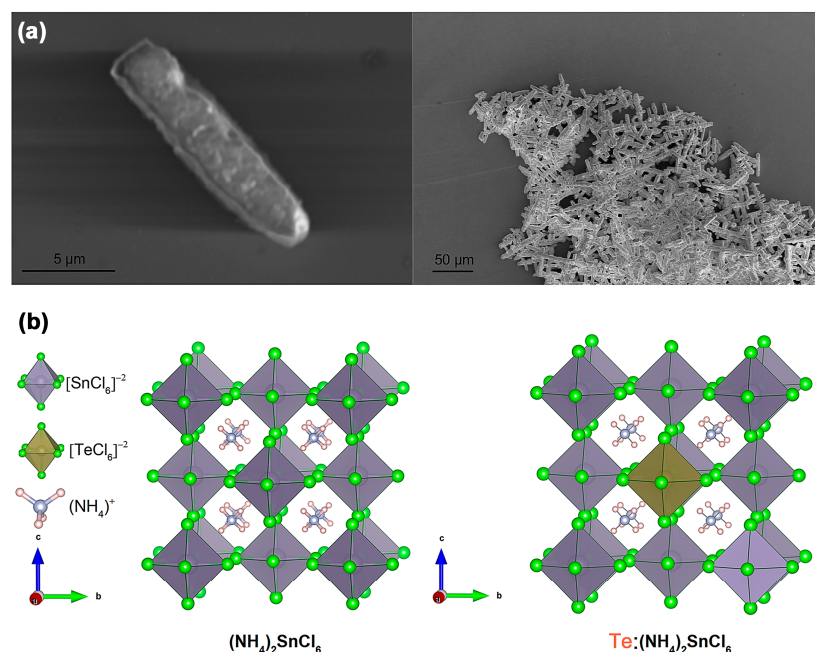


Figure 1. (a) TEM image of 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$. (b) Crystal structure diagram of undoped $(\text{NH}_4)_2\text{SnCl}_6$ and Te-doped $(\text{NH}_4)_2\text{SnCl}_6$ (Te: $(\text{NH}_4)_2\text{SnCl}_6$) vacancy-ordered perovskite. (Purple: Sn atoms; orange: Te atoms; green: Cl atoms; blue: N atoms; pink: H atoms; purple polyhedral: SnCl_6 octahedra; orange polyhedral: TeCl_6 octahedra).

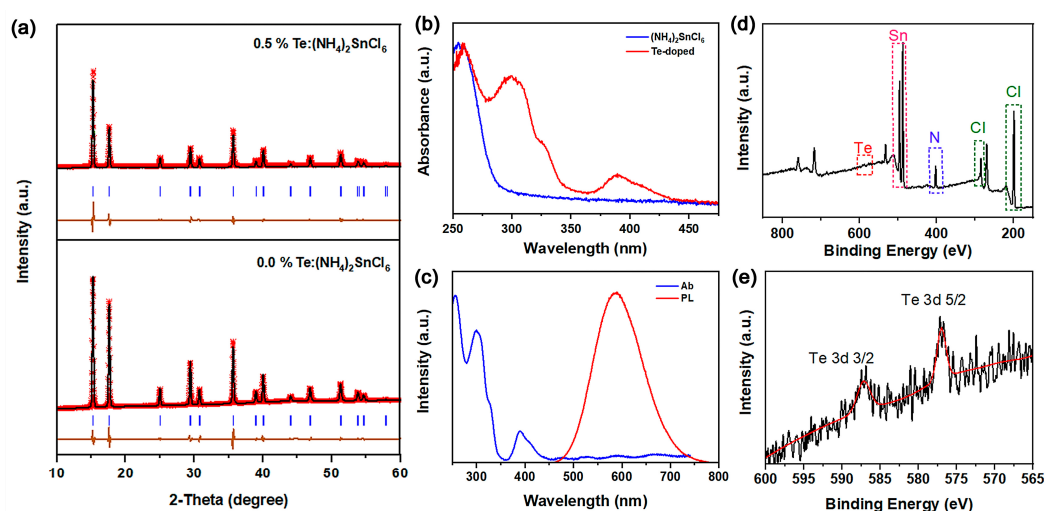


Figure 2. (a) The refinement profiles of undoped $(\text{NH}_4)_2\text{SnCl}_6$ and 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$ (red x: observed data; black solid line: calculated pattern; blue line segment: expected reflection position; brown line: difference curve) and (b) UV–Vis absorption spectra of 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$ and undoped $(\text{NH}_4)_2\text{SnCl}_6$ under ambient conditions, respectively. (c) Absorption spectrum and PL spectrum of 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$ under atmospheric pressure; (d,e) XPS spectra of $x = 0.5\%$ Te: $(\text{NH}_4)_2\text{SnCl}_6$ (red line: fitted; black line: measured).

At room temperature, Sn(IV)-based compounds are more stable in air than tin(II)-based counterparts. However, the absence of ns^2 active lone pairs cannot effectively promote the formation of Jahn–Teller-like STEs; thus, the pure Sn(IV)-based halides of the $(\text{NH}_4)_2\text{SnCl}_6$ white powder showed no emission under a 355 nm UV lamp. Upon the exchange of Sn/Te ions, the introduction of Te^{4+} ions with active $5s^2$ lone pairs effectively promotes the formation of Jahn–Teller distortions in the lattice structure [13]. The Jahn–Teller distortions formed during the expansion process are conducive to the improvement in light emission performance. Hence, after doping the Te^{4+} ions, the formed 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$ perovskite emits a strong yellow light under a 355 nm UV lamp. As shown in Figure 2c, the photoluminescence (PL) spectra show a bright broadband orange emission peak at 585 nm with a full width at half maximum (FWHM) at about 116 nm and a large Stokes shift. The broadband PL spectrum profile and large Stokes shift are due to the intense lattice distortion and robust Jahn–Teller effect. Hence, a significant improvement in photoluminescence was observed from the Te^{4+} substitution. Moreover, the exact element content was determined by XPS. In Figure 2d,e, the peaks located at 597.78 and 587.48 eV belong to Te^{4+} $3d_{3/2}$ and $3d_{5/2}$, respectively. These XPS profiles indicate that Te prefers to replace the Sn site, forming the TeCl_6 octahedron in 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$ perovskite variants.

To further clarify the emission mechanism, the PL emission spectra at different temperatures were measured from 80 K to 420 K (Figure 3a,b). A 2D projection of the emission spectra with contour lines demonstrated the evolution of luminescence with temperature (Figure 3c). The emission intensity first increased as the temperature increased from 80 K to 280 K, but then decreased with temperatures from 280 K to 420 K (Figure 3d). Such behavior suggests that PL could originate from thermally activated delayed fluorescence, which involves reverse intersystem crossing (RISC) from long-lived triplet-excited states back to short-lived singlet-excited states [21] via the thermally activated non-radiative recombination. A comparison with the previous commonly observed PL shifts with temperature in ABX_3 and $\text{A}_2\text{BB}'\text{X}_6$ perovskites ($\text{X} = \text{Cl}, \text{Br}$ and I) [22–24] revealed that this abnormal PL blue shift monotonically corresponds with increasing temperatures and is ascribed to important thermal lattice expansion [22]. As shown in Figure 3e, the variation in PL intensity with temperature can be expressed as follows:

$$I = I_0 / (1 + A \exp^{-E_a/k_B T})$$

where I_0 and I are the emission intensities at 0 K and measurement temperature, respectively. E_a is the thermal activation energy, which is considered to evaluate the exciton binding energy [25]. k_B is the Boltzmann constant. The E_a of 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$ was calculated to be 553 meV, which is much higher than Te: Cs_2SnCl_6 (270 meV) and Rb_2TeCl_6 (117 meV) [10,11]. The E_a of 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$ is much higher than the thermal energy at room temperature and indicates the formation of stable STEs with highly localized behavior. The electron–phonon coupling degree can be effectively reflected by the variation in FWHM with temperature (Figure 3f). The temperature-dependent FWHM can be fitted as follows:

$$\text{FWHM}(T) = 2.36 \sqrt{S \hbar \omega_{\text{phonon}}} \sqrt{\coth \frac{\hbar \omega_{\text{phonon}}}{2k_B T}}$$

where S is the electron–phonon coupling parameter, $\hbar \omega$ is the phonon frequency and k_B is the Boltzmann constant. The S of 7.5 and $\hbar \omega$ of 46.2 meV were obtained by fitting. The $\hbar \omega$ value is consistent with the Raman spectra (Figure S2). Such a value of S indicates robust electron–phonon coupling, implying prominent lattice distortion and the resulting Jahn–Teller effect in 0.5%Te: $(\text{NH}_4)_2\text{SnCl}_6$.

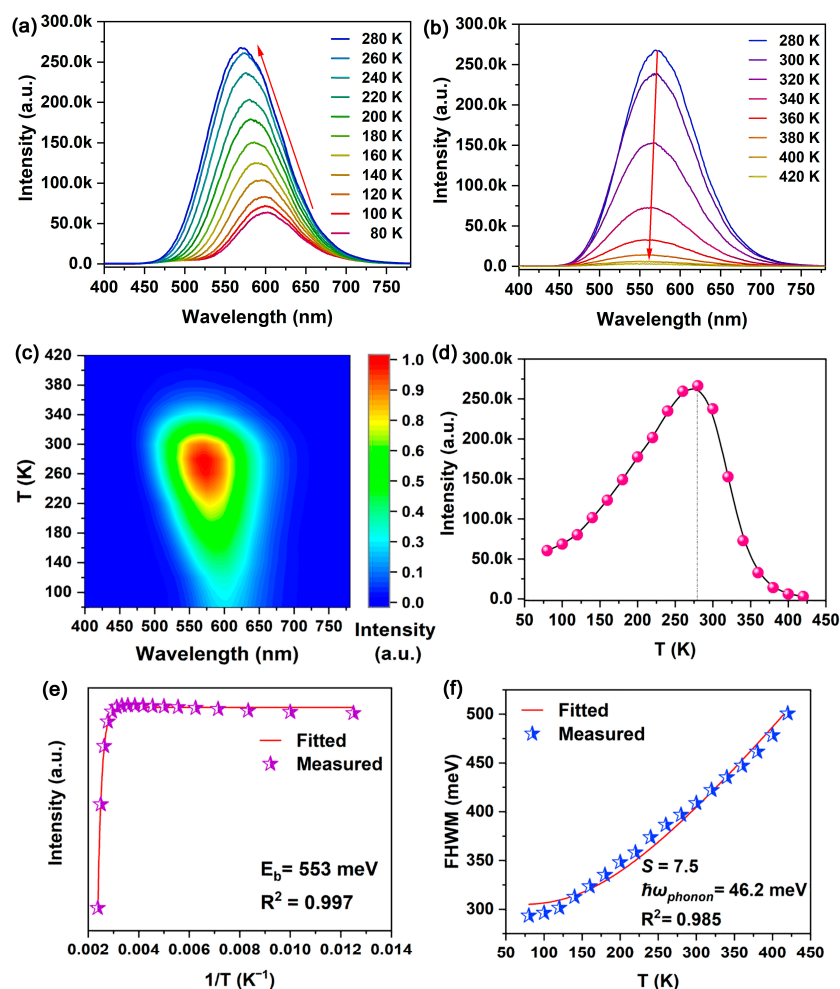


Figure 3. (a,b) Temperature-dependent emission spectra of 0.5%Te:(NH₄)₂SnCl₆. (c) Pseudocolor mapping of temperature-dependent wavelength and emission intensity. (d) Temperature-dependent intensity of emission spectra. (e) PL intensity vs. 1/T and the linear fitting result. (f) Fitting results of the FWHM as a function of temperature.

Generally, the DFT calculations provide an insight into the optical properties and energy band structure of undoped (NH₄)₂SnCl₆ and Te-doped (NH₄)₂SnCl₆ (Figure 4a,b). In the undoped compound, the VBM mainly consists of Cl-*p* orbitals, while the conduction band minimum (CBM) is dominated by Cl-*p* and Sn-*s* orbitals. The NH₄⁺ ions do not contribute near the band edges. Upon Te doping, the electronic density of states reveals a new VBM above the original valence band. The bandgap is abruptly reduced to 1.78 eV, which is mainly attributed to the newly formed VBM, consisting of states of the Cl 3*p* and filled pseudo-closed Te 5*s* orbitals. It is well-established that the STE emission of Te-doped perovskites is likely a result of the interplay between the 5*s*² lone pair of Te⁴⁺ [11]. As an ion whose outer electron configuration is *s*², the energy bands of Te⁴⁺ are generally composed of ground state ¹S₀, singlet-excited state ¹P₁ and triplet-excited state ³P_{*n*} (*n* = 0, 1 and 2) [26]. In combination with the above results, the luminescence mechanism diagram of 0.5%Te:(NH₄)₂SnCl₆ is illustrated in Figure 4d,e. Due to the soft lattice structure of 0.5%Te:(NH₄)₂SnCl₆, the excited carriers are readily localized to form bound excitons, which then relax to the trap state. Electrons are emitted through energy transfer to the Te⁴⁺ triplet STEs, followed by non-radiation relaxation, resulting in STE emission. For the Te⁴⁺ of *s*² electron configuration, ¹S₀ → ³P₁ and ¹S₀ → ¹P₁ are parity-allowed due to spin-orbit coupling. The electrons are transferred to the singlet state with high energy, then undergo the intersystem crossing (ISC) process from singlet STEs to triplet STEs. Finally,

the compound from triplet STEs to the ground state results in a wide emission band with a large Stokes shift [24]. At low temperatures (80–280 K), the 3P_1 state is partially frozen because the thermal energy is insufficient to overcome its energy barrier. As the temperature rises from 80 K to 280 K, this state becomes thermally activated, enhancing the reverse intersystem crossing (RISC) and leading to an increase in the photoluminescence (PL) intensity. However, a further increase in temperature beyond 280 K enhances non-radiative recombination pathways, which subsequently quenches the PL emission. Therefore, the emission intensity of 0.5%Te:(NH₄)₂SnCl₆ reaches a maximum at 280 K. The emission blue shift monotonically corresponding with increasing temperature is ascribed to important thermal lattice expansion and enhanced electron–phonon coupling. The electron–phonon coupling coefficient is basically scaled to the temperature because of atom motion in the lattice. There is also a positive correlation between the electron–phonon coupling coefficient and temperature in perovskites. Previous studies prove that higher temperatures lead to a larger electron–phonon coupling constant [27], resulting in a blue shift of the emission. However, the influence of the electron–phonon coupling constant on emission intensity is non-linear: a strong coupling constant contributes to enhanced emission intensity, whereas an excessively large coupling constant promotes non-radiative recombination, leading to diminished emission intensity. With an increase in temperature from 280 K to 420 K, the excessively large electron–phonon coupling accounts for the crossover between the GS and the STEs, promoting phonon-assisted non-radiative recombination and thereby reducing the emission intensity of 0.5%T Te:(NH₄)₂SnCl₆.

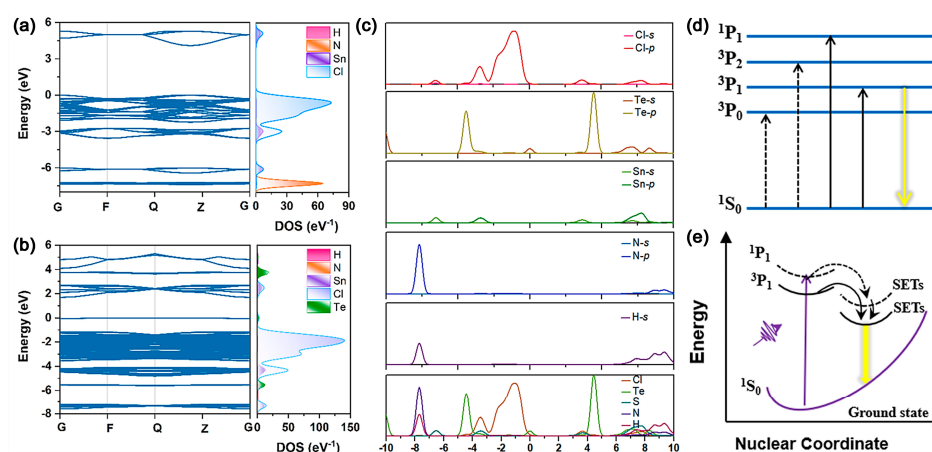


Figure 4. (a) Electronic band structure and PDOS of (NH₄)₂SnCl₆. (b) Electronic band structure and PDOS of Te:(NH₄)₂SnCl₆. (c) Calculated band structure and projected density of states (DOS) of Te:(NH₄)₂SnCl₆. (d) Schematic diagram of the potential energy curves as well as the transition and luminescence processes in a configuration space. The arrow indicates the energy level transition. (e) Schematic diagram of proposed energy-transfer model.

Additionally, temperature-dependent luminescence data were processed to generate plots depicting the evolution of the peak position and full width at half maximum (FWHM) as functions of temperature (Figure 5a,b). The emission peak exhibits a linear blue shift with increasing temperature according to $\lambda = -0.14 T + 615.6 \text{ nm}$ ($R^2 = 0.99$), where T denotes temperature in Kelvin. This temperature sensitivity corresponds with an absolute temperature sensitivity. Therefore, to quantify observed changes, the absolute temperature sensitivity can be determined as $S_A = \frac{\Delta\lambda}{\Delta T}$, with $\Delta\lambda$ representing the spectral shift per temperature increment of ΔT . The absolute sensitivity (S_A) is 0.14 nm/K and relative sensitivity (S_r) is 0.23% K⁻¹ at 100 K. Concurrently, the FWHM of the Te-doped emission broadens linearly as $\text{FWHM} = 0.11T + 73.5 \text{ meV}$ ($R^2 = 0.99$). Based on the research findings, 0.5%Te:(NH₄)₂SnCl₆ demonstrates significant potential as a promising candidate for

non-contact dual-parameter thermometry across a wide temperature range of 100–400 K. The chromaticity coordinates of 0.5%Te:(NH₄)₂SnCl₆ can effectively be controlled by temperature, ranging from orange-yellow to light yellow, which can be observed from the emission color changes throughout the temperature-increase process (Figure 5c). Moreover, the CIE coordinates are (0.5439, 0.4303) at 80 K and (0.3943, 0.5195) at 420 K. The CIE(x,y), CCT(K) and CRI of 0.5%Te:(NH₄)₂SnCl₆ at different temperature are presented in Table S2. In addition, the typical thermochromism behavior, linear variation in the emission wavelength and FWHM of the emission band with temperature make it a promising candidate for temperature sensors (Figure 5d). The linear thermochromic behavior of the material originates from temperature-dependent changes in the crystal structure. DFT calculations were performed to simulate the crystal structures at various temperatures and the lattice parameters were plotted as a function of temperature (Figure S4). The results indicate a nearly linear expansion of the lattice parameters with an increasing temperature. This structural expansion is identified as the primary mechanism responsible for the observed linear thermochromism. Temperature variations can alter the crystallinity and interfacial stress of a material, thereby affecting its performance. Given that perovskite materials possess a soft lattice structure, reversible structural and optical changes are achievable within a certain temperature range. The XRD patterns of (NH₄)₂SnCl₆ and 0.5%Te:(NH₄)₂SnCl₆ were observed before and after storing them under ambient conditions for 20 months. All patterns show a pure-phase crystal structure, indicating no structural evolution and, therefore, good stability of the materials under ambient conditions (Figure S3). Furthermore, the sample can withstand the extreme condition of immersion in water without any pretreatment and maintain a bright luminescence. This stability significantly broadens its application in the field of temperature-sensing. These results suggest that the luminescence behavior of 0.5%Te:(NH₄)₂SnCl₆ can be promoted by modulating the temperature, which makes it a potential candidate for modern highly efficient and visual (colorimetric) optical temperature sensors.

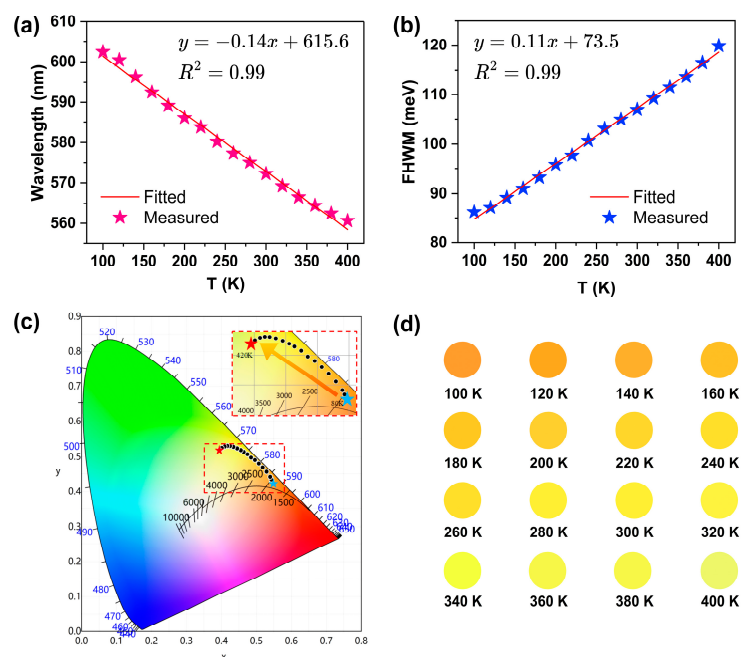


Figure 5. (a) The peak and (b) FWHM of the emission band of 0.5%Te:(NH₄)₂SnCl₆ as a function of temperature. (c) CIE coordinate diagram of emission of 0.5%Te:(NH₄)₂SnCl₆ at different temperatures. The chromaticity coordinates of the material shift along the path of the arrow with increasing temperature from 100 K to 400 K, with the black dots denoting their locations at specific corresponding temperatures. (d) Photos of 0.5%Te:(NH₄)₂SnCl₆ at different temperatures.

4. Conclusions

In summary, we investigated the structural evolution and optical properties of 0.5%Te:(NH₄)₂SnCl₆ as a function of temperature from 80 K to 400 K. At low temperatures (80–280 K), the ³P₁ state is partially frozen because the thermal energy is insufficient to overcome its energy barrier. As the temperature rises from 80 K to 280 K, this state becomes thermally activated, leading to an increase in the photoluminescence (PL) intensity. However, a further increase in temperature beyond 280 K enhances non-radiative recombination pathways, which subsequently quenches the PL emission. Therefore, the emission intensity of 0.5%Te:(NH₄)₂SnCl₆ reaches a maximum at 280 K. The emission blue shift monotonically corresponding with increasing temperature is ascribed to important thermal lattice expansion and enhanced electron–phonon coupling. When increasing the temperature from 280 to 420 K, the excessively large electron–phonon coupling accounts for the crossover between the GS and the STEs, promoting phonon-assisted non-radiative recombination and thereby reducing the emission intensity of 0.5%Te:(NH₄)₂SnCl₆. Based on the research findings, 0.5%Te:(NH₄)₂SnCl₆ demonstrates significant potential as a promising candidate for non-contact dual-parameter thermometry across a wide temperature range of 100–400 K. Our study delivers fundamental insights into the optical properties and band structure of 0.5%Te:(NH₄)₂SnCl₆ while establishing this material as a promising platform for non-contact thermometry across an ultra-broad temperature range (100–400 K).

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemistry7050150/s1>, Figure S1: Tauc plot of undoped (NH₄)₂SnCl₆ and Te-doped (NH₄)₂SnCl₆, respectively; Figure S2: Raman spectra of undoped (NH₄)₂SnCl₆ and the Te-doped (NH₄)₂SnCl₆. Figure S3: The XRD patterns of (NH₄)₂SnCl₆ and (NH₄)₂SnCl₆:0.5%Te before and after storing them in ambient conditions for 20 months, the ambient temperature ranged between 20–32 °C and the relative humidity varied from 45% to 85%. Figure S4: Temperature-dependent Cell parameters. Table S1: The detailed Rietveld refinement of (NH₄)₂SnCl₆ and Te-doped (NH₄)₂SnCl₆; Table S2: The CIE(x,y), CCT(K) and CRI Te-doped (NH₄)₂SnCl₆ at different temperature [28].

Author Contributions: Conceptualization, T.G. and Z.C.; methodology, T.G., G.X. and Y.L.; software, Y.S., A.Z. and Y.S.; validation, Z.C., A.Z., Y.L. and G.X.; formal analysis, Y.Q.; investigation, T.G.; data curation, Z.C., A.Z., Y.L. and G.X.; writing-original draft preparation, T.G., Y.S., M.L. (Mengyuan Lu), M.L. (Mengzhen Lu) and S.Z.; writing-review and editing, T.G., Y.S., M.L. (Mengyuan Lu), M.L. (Mengzhen Lu) and S.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Science Foundation of China (12174144 and 12474009), the Zhejiang Provincial Natural Science Foundation of China (LR22B010001), the BIGC Project (NO: Ea202412 and 27170124039), the Open Project of State Key Laboratory of High Pressure and Superhard Materials, Jilin University (No.202505) and the Innovation and Entrepreneurship Training Program (202510015027 and S202510015044).

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare that they have no conflicts of interest.

References

1. Wang, C.; Xiao, J.; Yan, Z.; Niu, X.; Lin, T.; Zhou, Y.; Han, X. Colloidal synthesis and phase transformation of all-inorganic bismuth halide perovskite nanoplates. *Nano Res.* **2023**, *16*, 1703–1711. [CrossRef]
2. Acharyya, P.; Ghosh, T.; Pal, K.; Rana, K.S.; Dutta, M.; Swain, D.; Etter, M.; Soni, A.; Waghmare, U.V.; Biswas, K. Glassy thermal conductivity in Cs₃Bi₂I₆Cl₃ single crystal. *Nat. Commun.* **2022**, *13*, 5053. [CrossRef]

3. Wang, F.; Yang, J.; Geng, T.; Lv, P.; Zhao, D.; Li, Y.; Dong, Q.; Xiao, G.; Zou, B. Pressure-induced emission and remarkable piezochromism of two-dimensional cesium antimony bromide perovskites. *Mater. Res. Lett.* **2024**, *12*, 500–506. [\[CrossRef\]](#)
4. Das Adhikari, S.; Echeverria-Arrondo, C.; Sanchez, R.S.; Chirvony, V.S.; Martínez-Pastor, J.P.; Agouram, S.; Mora-Seró, I. White light emission from lead-free mixed-cation doped Cs₂SnCl₆ nanocrystals. *Nanoscale* **2022**, *14*, 1468–1479. [\[CrossRef\]](#)
5. Zhou, L.; Liao, J.F.; Qin, Y.; Wang, X.D.; Wei, J.H.; Li, M.; He, R. Activation of self-trapped emission in stable bismuth-halide perovskite by suppressing strong exciton–phonon coupling. *Adv. Funct. Mater.* **2021**, *31*, 2102654. [\[CrossRef\]](#)
6. Zhou, B.; Liu, Z.; Fang, S.; Zhong, H.; Tian, B.; Wang, Y.; Shi, Y. Efficient white photoluminescence from self-trapped excitons in Sb³⁺/Bi³⁺-codoped Cs₂NaInCl₆ double perovskites with tunable dual-emission. *ACS Energy Lett.* **2021**, *6*, 3343–3351. [\[CrossRef\]](#)
7. Liu, Q.; Yin, J.; Zhang, B.B.; Chen, J.-K.; Zhou, Y.; Zhang, L.-M.; Wang, L.-M.; Zhao, Q.; Hou, J.; Shu, J.; et al. Theory-guided synthesis of highly luminescent colloidal cesium tin halide perovskite nanocrystals. *J. Am. Chem. Soc.* **2021**, *143*, 5470–5480. [\[CrossRef\]](#)
8. Jing, Y.; Liu, Y.; Li, M.; Xia, Z. Photoluminescence of singlet/triplet self-trapped excitons in Sb³⁺-based metal halides. *Adv. Opt. Mater.* **2021**, *9*, 2002213. [\[CrossRef\]](#)
9. Li, Z.; Zhang, C.; Li, B.; Lin, C.; Li, Y.; Wang, L.; Xie, R.-J. Large-scale room-temperature synthesis of high-efficiency lead-free perovskite derivative (NH₄)₂SnCl₆:Te phosphor for warm wLEDs. *Chem. Eng. J.* **2021**, *420*, 129740. [\[CrossRef\]](#)
10. Zeng, R.; Bai, K.; Wei, Q.; Chang, T.; Yan, J.; Ke, B.; Huang, J.; Wang, L.; Zhou, W.; Cao, S.; et al. Boosting triplet self-trapped exciton emission in Te (IV)-doped Cs₂SnCl₆ perovskite variants. *Nano Res.* **2021**, *14*, 1551–1558. [\[CrossRef\]](#)
11. Zhao, W.; Ma, Z.; Shi, Y.; Fu, R.; Wang, K.; Sui, Y.; Xiao, G.; Zou, B. Pressure tailoring electron-phonon coupling toward enhanced yellow photoluminescence quantum yield and piezochromism. *Cell Rep. Phys. Sci.* **2023**, *4*, 101663. [\[CrossRef\]](#)
12. Wang, J.; Wang, L.; Wang, F.; Jiang, S.; Guo, H. Pressure-induced bandgap engineering of lead-free halide double perovskite (NH₄)₂SnBr₆. *Phys. Chem. Chem. Phys.* **2021**, *23*, 19308–19312. [\[CrossRef\]](#)
13. Tan, Z.; Chu, Y.; Chen, J.; Li, J.; Ji, G.; Niu, G.; Tang, J. Lead-free perovskite variant solid solutions Cs₂Sn_{1–x}Te_xCl₆: Bright luminescence and high anti-water stability. *Adv. Mater.* **2020**, *32*, 2002443. [\[CrossRef\]](#)
14. Jing, Y.; Liu, Y.; Zhao, J.; Xia, Z. Sb³⁺ doping-induced triplet self-trapped excitons emission in lead-free Cs₂SnCl₆ nanocrystals. *J. Phys. Chem. Lett.* **2019**, *10*, 7439–7444. [\[CrossRef\]](#)
15. Geng, M.; Pan, X.; Zhao, J.; Wang, X.; Liu, R.; Xu, Z.; Ma, N.; Gao, M.; Shao, M.; Li, J. Regulating crystal growth of Cs₂SnCl₆ perovskite for rapid response and durable humidity-triggered non-contact sensor. *Chem. Eng. J.* **2024**, *486*, 150222. [\[CrossRef\]](#)
16. Chang, J.; Xu, S.; Liu, A.; Li, Y.; Liu, B.; Chen, B. White light emission in Bi³⁺/Te⁴⁺ co-doped Cs₂SnCl₆ for adjustable daily lighting and visible light communication. *J. Am. Ceram. Soc.* **2025**, *108*, 20159. [\[CrossRef\]](#)
17. Jin, M.; Zheng, W.; Gong, Z.; Huang, P.; Li, R.; Xu, J.; Cheng, X.; Zhang, W.; Chen, X. Unraveling the triplet excited-state dynamics of Bi³⁺ in vacancy-ordered double perovskite Cs₂SnCl₆ nanocrystals. *Nano Res.* **2022**, *15*, 6422–6429. [\[CrossRef\]](#)
18. Wei, H.; Sun, J.; Mao, X.; Wang, H.; Chen, Z.; Bai, T.; Han, K. Cs₂SnCl₆: To emit or to catalyze? Te⁴⁺ ion calls the shots. *Adv. Sci.* **2023**, *10*, 2302706. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Xu, Q.; Qian, W.; Muhammad, R.; Chen, X.; Yu, X.; Song, K. Photoluminescence and temperature sensing properties of Bi³⁺/Sm³⁺ co-doped La₂MgSnO₆ phosphor for optical thermometer. *Crystals* **2023**, *13*, 991. [\[CrossRef\]](#)
20. Guan, M.; Hao, J.; Qiu, L.; Molokeev, M.S.; Ning, L.; Dai, Z.; Li, G. Two-dimensional hybrid perovskite with high-sensitivity optical thermometry sensors. *Inorg. Chem.* **2024**, *63*, 3835–3842. [\[CrossRef\]](#)
21. Liu, S.; Yang, B.; Chen, J.; Wei, D.; Zheng, D.; Kong, Q.; Deng, W.; Han, K. Efficient thermally activated delayed fluorescence from all-inorganic cesium zirconium halide perovskite nanocrystals. *Angew. Chem.* **2020**, *132*, 22109–22113. [\[CrossRef\]](#)
22. Ke, B.; Zeng, R.; Zhao, Z.; Wei, Q.; Xue, X.; Bai, K.; Zou, B. Homo- and heterovalent doping-mediated self-trapped exciton emission and energy transfer in Mn-doped Cs₂Na_{1–x}Ag_xBiCl₆ double perovskites. *J. Phys. Chem. Lett.* **2019**, *11*, 340–348. [\[CrossRef\]](#)
23. Zeng, R.; Zhang, L.; Xue, Y.; Ke, B.; Zhao, Z.; Huang, D.; Zou, B. Highly efficient blue emission from self-trapped excitons in stable Sb³⁺-doped Cs₂NaInCl₆ double perovskites. *J. Phys. Chem. Lett.* **2020**, *11*, 2053–2061. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Zhao, Z.; Zhong, M.; Zhou, W.; Peng, Y.; Yin, Y.; Tang, D.; Zou, B. Simultaneous triplet exciton–phonon and exciton–photon photoluminescence in the individual weak confinement CsPbBr₃ micro/nanowires. *J. Phys. Chem. C* **2019**, *123*, 25349–25358. [\[CrossRef\]](#)
25. Wei, J.-H.; Liao, J.-F.; Wang, X.-D.; Zhou, L.; Jiang, Y.; Kuang, D.-B. All-inorganic lead-free heterometallic Cs₄MnBi₂Cl₁₂ perovskite single crystal with highly efficient orange emission. *Matter* **2020**, *3*, 892–903. [\[CrossRef\]](#)
26. Chang, T.; Wei, Q.; Zeng, R.; Cao, S.; Zhao, J.; Zou, B. Efficient energy transfer in Te⁴⁺-Doped Cs₂ZrCl₆ vacancy-ordered perovskites and ultrahigh moisture stability via a-site Rb-alloying strategy. *J. Phys. Chem. Lett.* **2021**, *12*, 1829–1837. [\[CrossRef\]](#) [\[PubMed\]](#)

27. Peng, H.; Zou, B. Effects of electron-phonon coupling and spin-spin coupling on the photoluminescence of low-dimensional metal halides. *J. Phys. Chem. Lett.* **2022**, *13*, 1752–1764. [[CrossRef](#)]
28. Jansen, E.; Schäfer, W.; Will, G. *R* values in analysis of powder diffraction data using Rietveld refinement. *J. Appl. Cryst.* **1994**, *27*, 492–496. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.