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An Examination of the Cs₂NaInCl₆ Luminescence: Interplay of Self-Generated In⁺ and Doped Sb³⁺, Er³⁺/Yb³⁺ Ions

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ABSTRACT

This work introduces a novel explanation of the visible (Vis-) and near-infrared (NIR) Cs₂NaInCl₆ luminescence based on spontaneously formed In³⁺→In⁺ and a doping method by utilizing Er³⁺/Yb³⁺ and Sb³⁺ ions. A combined experimental and theoretical approach has been used to investigate the characteristics of the microcrystals, synthesized through precipitation and hydrothermal techniques. These yielded cubic, Sp.Gr. *Fm* $\bar{3}$ *m*, or tetragonal structure, Sp.Gr. *I4/mmm*, depending on the dopants. In⁺ (5s²) has provoked wide photoluminescence (PL) from ~400–800 nm, and Sb³⁺ (5s²) incorporation has greatly enhanced PL at 450 nm. While Er³⁺ doping has enabled intense NIR emission (~1540 nm), Yb³⁺ sensitization not only improves Er³⁺ PL in the 520–550 nm range (green light) but also adds a band at 980 nm. For Er-doped, RE/Sb-codoped Cs₂NaInCl₆, it is possible to observe not only downconversion but also upconversion (UC) emissions in the 520–550 nm range. DFT calculations have elucidated the dopant and vacancy effects on the band structure and luminescence behavior of the samples. Stable and simple in preparation phosphor-converted LED prototypes have been constructed and characterized in the Vis- to NIR ranges.

1 | Introduction

Recently, lead-free halide double perovskites (DP) have drawn significant research attention as environmentally friendly materials with promising optoelectronic features [1–3]. They are based on the general formula of A^I₂B^{II}B^{III}X₆ (A^I = Rb⁺, Cs⁺; B^I = Na⁺, K⁺, Cu⁺, Ag⁺; B^{III} = In³⁺, Sb³⁺ or Bi³⁺; X = Cl[−], Br[−], or I[−]). Indium-based double perovskites are semiconductors with a direct bandgap structure, high defect tolerance, and environmental stability. Their soft lattice characteristics and significant

electron-phonon coupling generate self-trapped excitons (STE), which contribute to broadband emission with a large Stokes shift.

The Cs₂NaInCl₆ (CNIC) DPs are among the most promising lead-free perovskite candidates due to their 3D structure and direct bandgap of ~5.1 eV. Nevertheless, the optically forbidden transitions associated with dark STEs result in low intrinsic photoluminescence (PL) intensity, limiting their practical use in optoelectronics [4–6]. Recently, in our article, the experimental value of 6.7 eV was established from VUV spectroscopy and is

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assigned to the intrinsic band edge of CNIC. In contrast, the lower-energy optical features reported in the literature could be attributed to defect-induced states within the forbidden gap, associated with vacancies and In^{+} -related centres [7].

Chemical doping is an effective strategy for breaking the parity-forbidden transitions in CNIC. Specifically, doping with ns^2 ions (Sb^{3+} , Bi^{3+}) creates suitable active sites and coordination environments that facilitate $^1\text{P}_1; ^3\text{P}_n$ ($n = 0, 1, 2$) $\rightarrow$ $^1\text{S}_0$ transitions [8, 9].

Another way to modify CNIC excitation and generate more efficient STEs within the near-infrared (NIR) emission range is the use of rare earth (RE) doping. These elements typically exist in trivalent states and prefer octahedral coordination due to their electronic configuration, making them ideal dopants for engineering halide DPs. By tailoring the CNIC composition and structure through codoping of Sb^{3+} , Er^{3+} , and Yb^{3+} , we can realize precise control over emission wavelength, intensity, and lifetime [10–14]. Moreover, it is possible to create high-performance phosphor-converted LEDs (pc-LEDs) through combining these phosphors with commercial blue-chip LEDs (light-emitting diodes) [7, 11, 13].

While most of the researchers mainly focus on the intense downshifting emission [13, 15], we are going to investigate the UC mechanism in the samples when excited near 980 nm NIR light. This process is significantly more efficient than, for example, two-photon absorption due to the presence of an intermediate $4f$ energy level, enabling a sequential excitation mechanism. In contrast, two-photon absorption involves a virtual intermediate state, making it a simultaneous process. As a result, UC requires significantly lower excitation intensity, allowing the use of cost-effective and widely available continuous-wave (CW) laser diodes instead of the expensive femtosecond pulsed lasers typically required for two-photon excitation [16, 17]. Photon UC in RE systems typically involves a sensitizer that transfers energy to an activator ion, such as Er^{3+} . An Yb^{3+} ion could be a proper sensitizer due to its large absorption cross-section at NIR wavelengths, specifically at 980 nm. This way, it is possible to produce green emission through the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (~ 520 nm) and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (~ 550 nm) transitions, and red emission through the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition (~ 660 nm) [18, 19]. These phosphors potentially can be used in diverse types of detectors, complex catalysts, etc. [15, 20]

All in all, the investigation had three objectives: (1) to synthesize the stable PL substances covering the visible-NIR (Vis-NIR) gamut using delicate composition engineering; (2) to prepare pc-LED prototypes and investigate their characteristics; (3) to reveal the distribution of energy levels within Sb^{3+} , $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped CNIC, and the transition pathways between different energy levels to establish the luminescence mechanisms in such materials.

To reach the abovementioned goals, we applied a comprehensive approach combining optical measurements to obtain information about energy level distribution and electron transfer processes. They have provided a practical basis for theoretical calculations and density functional theory (DFT) calculations to simulate the band structure and to understand the luminescence mechanism of the Sb^{3+} , $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped CNIC.

2 | Experimental Section

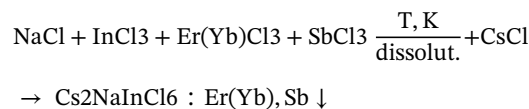
Samples for investigation were synthesized as microcrystalline powders using precipitation and hydrothermal methods. Detailed information on sample synthesis and investigation methods is provided in the [Supporting Information](#). The syntheses were carried out using CsCl , NaCl , InCl_3 , SbCl_3 , ErCl_3 , YbCl_3 , and a 36% HCl solution (Sigma-Aldrich, USA). The starting solutions were prepared by dissolving NaCl or ErCl_3 in 10 mL of 36% HCl at 70°C (Table S1), together with InCl_3 (4.0–4.5 mmol per 10 mL HCl), SbCl_3 (1 mmol per 10 mL HCl), and CsCl (10 mmol per 5 mL HCl).

The obtained powders were characterized by x-ray diffraction (XRD). The crystal structures of the single crystals were determined by single-crystal x-ray diffraction (SCXRD) and refined using the SHELXL package. Morphology, crystal size, and elemental distribution were investigated by scanning electron microscopy (SEM) coupled with energy-dispersive x-ray spectroscopy (EDS). Surface composition and chemical states were analyzed by x-ray photoelectron spectroscopy (XPS). Optical properties were characterized by diffuse reflectance spectroscopy (DRS), photoluminescence (PL), near-infrared (NIR), and up-conversion spectroscopy using UV and laser excitation sources. Electronic structure calculations were performed within density functional theory (DFT) using the VASP code with the PBE exchange-correlation functional and projector augmented wave (PAW) method. The effects of doping and defects were modeled using the virtual crystal approximation (VCA), while spin polarization and spin-orbit coupling (SOC) were included to accurately describe the electronic structure of Sb - and Er -codoped systems (for more details, see the [Supporting Information](#)).

3 | Results and Discussion

3.1 | Sample Preparation and Crystal Structure Characterization

The chloride double perovskites $\text{Cs}_2\text{NaInCl}_6$, $\text{Cs}_2\text{NaIn}_{0.9}\text{Sb}_{0.1}\text{Cl}_6$, $\text{Cs}_2\text{NaIn}_{1-x}\text{Er}_x\text{Cl}_6$ ($x = 0.1, 0.3, 0.5$), $\text{Cs}_2\text{NaIn}_{1-x}\text{Sb}_{0.1}\text{Er}_x\text{Cl}_6$ ($x = 0.1, 0.3, 0.5, 0.7$), $\text{Cs}_2\text{NaIn}_{0.6-x}\text{Sb}_{0.1}\text{Yb}_{0.5}\text{Er}_x\text{Cl}_6$ ($x = 0.1; 0.3$) have been synthesized using precipitation and hydrothermal methods as powders of the microcrystalline range (Figures S1 and S2; Table S1). The following chemical reactions have been employed for the synthesis:



The obtained compositions and crystal structure refinement results for the synthesized powder samples are presented in Table 1.

X-ray powder diffraction (XRD) patterns of the samples doped with a single cation were indexed in cubic symmetry, $\text{Sp.Gr. } Fm\bar{3}m$ (Table 1 and Figures S3; S4a; Tables S2–S4). The incorporation of Sb^{3+} into CNIC does not alter the cubic crystal structure but increases the unit cell size compared to the undoped

TABLE 1 | Compositions of the samples and crystal structure refinement results obtained by powder (Powd.) or single crystal (S.C.) methods.

Compositions	Sp.Gr., lattice parameters (Å)	Calculation method
Cs ₂ NaInCl ₆ (CNIC)	<i>Fm</i> $\bar{3}$ <i>m</i> , <i>a</i> = 10.5359(2)	Powd. ^a
Cs ₂ NaIn _{0.9} Sb _{0.1} Cl ₆	<i>Fm</i> $\bar{3}$ <i>m</i> , <i>a</i> = 10.5398(3)	Powd. ^a
Cs ₂ NaIn _{0.9} Er _{0.1} Cl ₆	<i>Fm</i> $\bar{3}$ <i>m</i> , <i>a</i> = 10.5371(2)	Powd.
	<i>Fm</i> $\bar{3}$ <i>m</i> , <i>a</i> = 10.5196(2)	S.C. ^b
Cs ₂ NaIn _{0.7} Er _{0.3} Cl ₆	<i>Fm</i> $\bar{3}$ <i>m</i> , <i>a</i> = 10.5414(2)	Powd. ^a
Cs ₂ NaIn _{0.5} Er _{0.5} Cl ₆	<i>Fm</i> $\bar{3}$ <i>m</i> , <i>a</i> = 10.5435(2)	Powd.
	<i>Fm</i> $\bar{3}$ <i>m</i> , <i>a</i> = 10.5223(2)	S.C. ^b
Cs ₂ NaIn _{0.8} Er _{0.1} Sb _{0.1} Cl ₆	<i>I4</i> / <i>mmm</i> , <i>a</i> = 7.4647(3), <i>c</i> = 10.5253(6)	Powd. ^a
Cs ₂ NaIn _{0.6} Er _{0.3} Sb _{0.1} Cl ₆	<i>I4</i> / <i>mmm</i> , <i>a</i> = 7.4595(3), <i>c</i> = 10.5321(7)	Powd. ^a
Cs ₂ NaIn _{0.4} Er _{0.5} Sb _{0.1} Cl ₆	<i>I4</i> / <i>mmm</i> , <i>a</i> = 7.4684(3), <i>c</i> = 10.5380(6)	Powd. ^a
Cs ₂ NaIn _{0.2} Er _{0.7} Sb _{0.1} Cl ₆	two-phase	Powd. ^a
Cs ₂ NaIn _{0.3} Er _{0.1} Sb _{0.1} Yb _{0.5} Cl ₆	<i>I4</i> / <i>mmm</i> , <i>a</i> = 7.4653(1), <i>c</i> = 10.5333(2)	Powd. ^a
Cs ₂ NaIn _{0.1} Er _{0.3} Sb _{0.1} Yb _{0.5} Cl ₆	<i>I4</i> / <i>mmm</i> , <i>a</i> = 7.4645(2), <i>c</i> = 10.5411(3)	Powd. ^a

^aThe crystals were too small to examine using the single-crystal method.^bThe crystals were obtained using the hydrothermal method (Figure S1).

CNIC (see Table 1). This is because the ionic radius of Sb³⁺ in six-fold coordination is 0.86 Å compared to 0.80 Å for In³⁺ [21, 22]. Using Er³⁺ as a dopant also preserves the cubic symmetry of the tested crystals, because the Er³⁺ ground state, *a*_{2g} (*f*_{3/2}), is a high-symmetry orbital singlet. Additionally, the HDP crystal field is weaker than the spin-orbit coupling and, therefore, the rearrangement of orbital states does not occur.

Codoped (Sb³⁺ and Er³⁺(Yb³⁺)) samples have been indexed in tetragonal symmetry, Sp.Gr. *I4*/*mmm* (see Table 1; Figures S3 and S4b–d; Tables S5–S7). The parameters of the unit cell correspond with the radii of the cations involved in the substitution (In³⁺ 0.80 Å; Er³⁺ 0.89 Å; Yb³⁺ 0.868 Å; Sb³⁺ 0.86 Å) [21, 22]. Obtained samples belong to the perovskite structure for three reasons: (1) a ratio A:(B^I+B^{III}):X of 1:(0.5+0.5):3 (see Table S8); (2) the B^I, B^{III} cations coordination is octahedral; 3) the [BX₆] octahedra are organized in an all-corner-sharing 3D network [23]. From the previous crystallographic calculation for the derived perovskite structure [24], it is known that the transformation from Sp.Gr. *Fm* $\bar{3}$ *m* to Sp.Gr. *I4*/*mmm* can be realized through Jahn-Teller distortion, as shown in Figure 1a,b. Therefore, we believe that Sb³⁺ and Er³⁺/Yb³⁺ cations incorporate into the crystal structure instead of In³⁺ cations and trigger the formation of Jahn-Teller-distorted halide DPs, decreasing the yield of the reaction product, η (see Table S1).

Meanwhile, in the tetragonal co-doped structures, the In³⁺/RE³⁺-containing octahedral complexes exhibit the Jahn-Teller distortions of the Q₃-type [25]. The displacement of the chlorine ions from their regular positions is 0.31 Å, and a more detailed discussion of this phenomenon is presented in Section 2.5.

The analysis of the XRD patterns for the cubic structure indicates that the shift of the 220 reflections toward the small-angle side is due to the increase in the unit cell following Er³⁺ or Sb³⁺ incorporation (Figure 2a and Table 1). A similar trend is evident in the tetragonal structure, where the lattice parameters also increase

with higher concentrations of Er³⁺/Yb³⁺ and Sb³⁺ (Figure 2b and Table 1). Elemental analysis using energy-dispersive x-ray spectroscopy (EDS) shows that the dopants are homogeneously distributed throughout the powder (Figure S4 and Table S8). Only for the Sb³⁺/Er³⁺/Yb³⁺-codoped samples, traces of unreacted NaCl could be noticed.

Structure determinations using the single crystal x-ray method revealed that Cs₂NaIn_{0.9}Er_{0.1}Cl₆ and Cs₂NaIn_{0.5}Er_{0.5}Cl₆ crystallize in a B-site ordered cubic halide DPs. The complete experimental and refinement details, including the crystallographic data, can be found in the Supporting Information (Tables S9–S12).

The final RE-doped powders and single crystals contain less RE³⁺ than expected (Tables S8 and S13; Figures S4 and S5). This discrepancy could be explained by the difference in the ionic radii of the dopants, as well as the strong anisotropy of the RE³⁺ ions ground state, i.e., [Xe] 4*f*¹¹ for Er³⁺, [Xe] 4*f*¹³ for Yb³⁺, while Sb³⁺ has a highly symmetrical ground state (5*s*²).

For Cs₂NaInCl₆ and Sb³⁺ or/and Er³⁺ doped samples, XPS results show the existence of In⁺ and Cl₂[−] in the crystals (Figure S6). A detailed discussion of the XPS results has been reported in our work [7]. The presence of the In⁺ ions, which have a 5*s*² electron configuration, plays a crucial role in the optical properties of the samples, which are discussed in Section 2.2.

3.2 | Analysis of UV–Vis Absorption Spectra and PL Properties

To investigate the CNIC absorption mechanism, the absorption spectra were measured (Figure 3a,b). The absorption edge is located at about 240 nm (Figure 3a), corresponding to an optical bandgap of 5.1 eV, which agrees well with Ref. [5]. Additionally, weak absorption peaks were observed, which agreed with data obtained by other authors [14, 26] and explained the induced

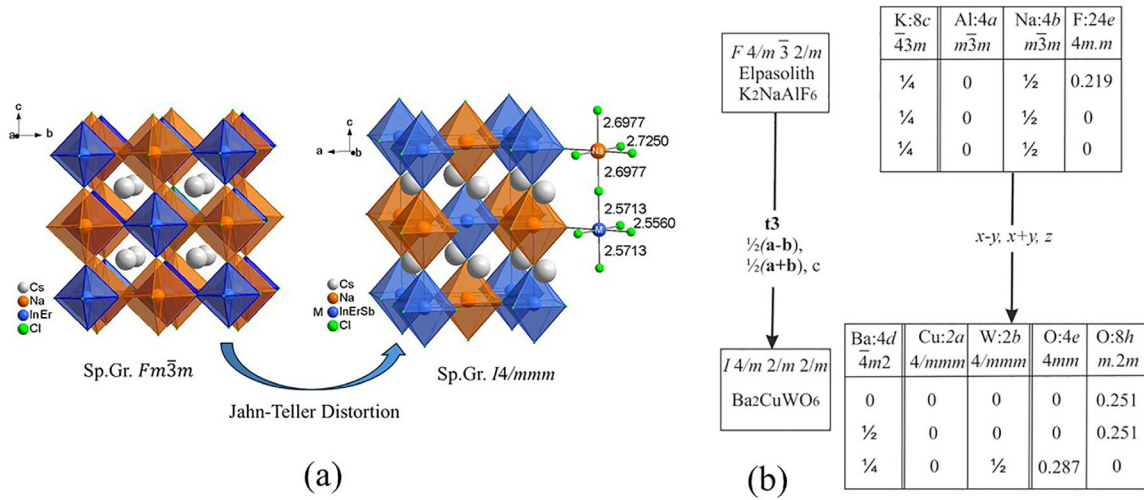


FIGURE 1 | Crystallographic data for the HDPS: (a) schematic diagram of the phase transitions from the cubic structure to the Jahn-Teller-distorted tetragonal double perovskite; (b) group-subgroup relation between Sp.Gr. $Fm\bar{3}m$ and Sp.Gr. $I4/mmm$ [24].

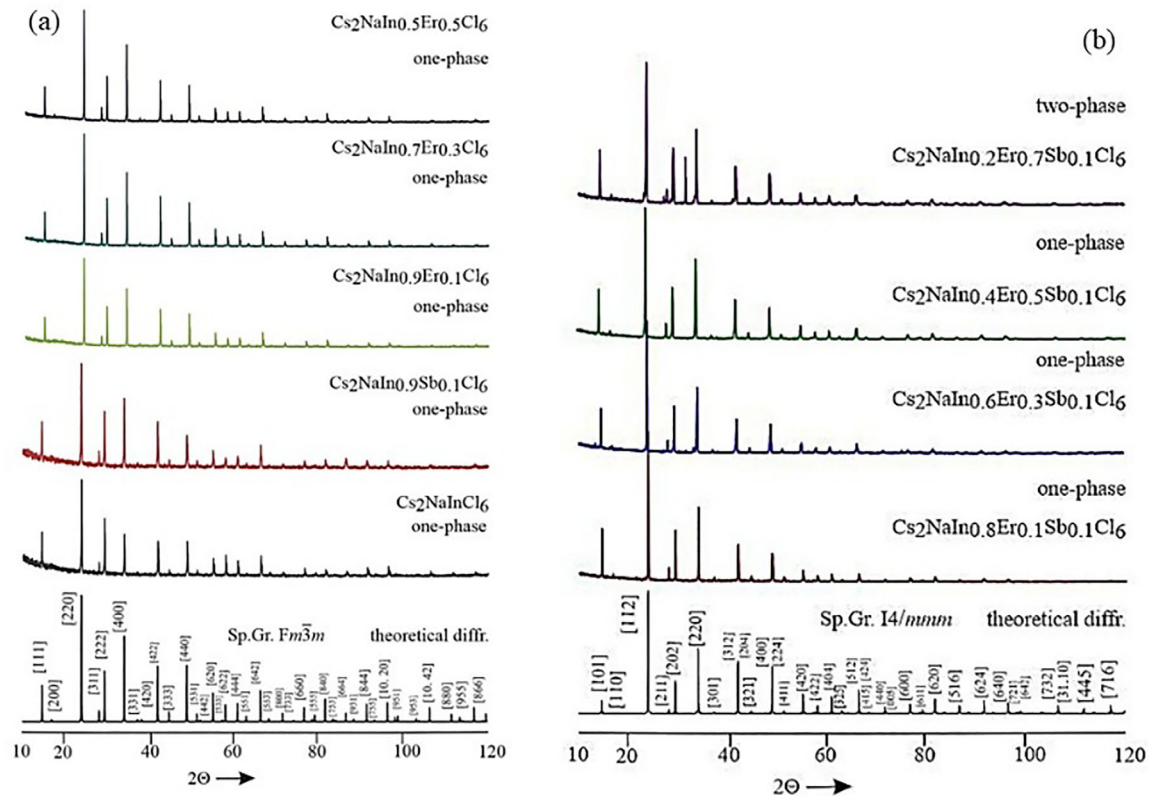


FIGURE 2 | XRD results for (a) Sb^{3+} or Er^{3+} -doped samples and (b) Sb^{3+} and Er^{3+} -codoped samples.

lattice distortion through the subsequent formation of STEs [27]. However, our previous optical measurements of CNIC codoped with Sb^{3+} and Er^{3+} conducted at the Deutsches Elektronen-Synchrotron (DESY) facility between 10 K and 300 K [7] have conclusively shown that the band gap of CNIC is 6.7 eV. Moreover, it was found that the self-generated In^+ ions, as $5s^2$ cations in CNIC, have an unexpected and crucial impact on the formation of the optical spectra observed in CNIC microcrystals. That is why it is important to investigate the roles of these ions, as well

as other mechanisms such as vacancies, to clarify the emission mechanism of CNIC, which is still not fully understood.

In^+ belongs to the large family of ns^2 ions, which exhibit characteristic optical spectra arising from $5s^2 \leftrightarrow 5s^15p^1$ inter-configurational transitions. Unlike transition-metal ions, where crystal-field splitting occurs within the d orbitals, in ns^2 ions the splitting affects the outer p orbitals, while the Jahn-Teller effect and spin-orbit interaction play key roles in determining the

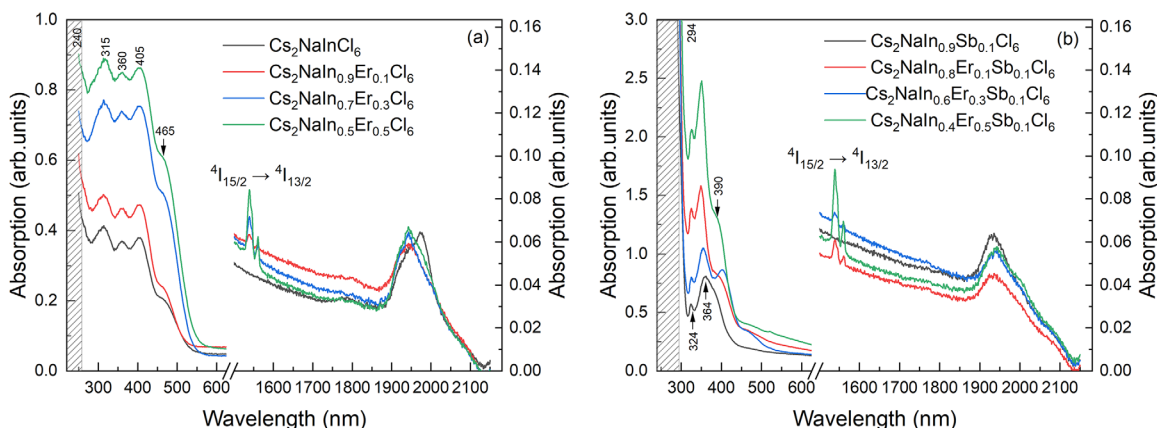


FIGURE 3 | Measured absorption spectra of (a) Er-doped CNIC samples and (b) codoped with Sb and Er CNIC samples.

spectral structure. The ground state of In^{3+} is the 1S_0 state. Due to the strong spin-orbit interaction, the 3P and 1P terms of the $5s^15p^1$ excited electron configuration split into four multiplets: 3P_0 , 3P_1 , 3P_2 , and 1P_1 . In the cubic crystal field, the fifth-fold degenerated 3P_2 term splits into a triplet T_{2u} and a doublet E_u . The other two terms remain unsplit: $^3P_1(T_{1u})$ and $^1P_1(T_{1u})$. The $^1S_0 \rightarrow ^1P_1(T_{1u})$, $^3P_1(T_{1u})$, $^3P_2(T_{2u})$ transitions correspond to the C, B, and A absorption bands (Figure S7) [28]. The C band is spin-allowed, whereas the B and A bands are spin-forbidden. However, in crystals the selection rules are partially relaxed due to spin-orbit coupling, particularly through the mixing of the 3P_1 and 1P_1 states. Thus, only three intense bands can be partially observed in the measured spectra: the $^1S_0 \rightarrow ^3T_{1u}$ transition (~ 315 nm), the $^1S_0 \rightarrow ^3T_{2u}$ transition (~ 290 nm), and the $^1S_0 \rightarrow ^1T_{1u}$ transition (~ 260 nm) (Figure 3a). The absorption band at 360 nm (3.44 eV) can be attributed to defects in the anion sublattice, which is consistent with our theoretical calculations (see Section 2.5). However, the absorption spectrum of CNIC is more complex, suggesting that the In-containing octahedral complexes undergo low-symmetry distortions associated with a Jahn-Teller effect in the excited state [7]. According to the Jahn-Teller theorem, the orbitally degenerate electronic state $^3T_{1u}$ is unstable due to the low-symmetry lattice vibrations, which result in E_g - or/and T_{2g} -distortions of an ideal cubic crystal. A more detailed analysis of the CNIC absorption spectrum is presented in Ref. [7].

The ion vacancies can form two of the most important point defects responsible for optical absorption, known as V_k and F centres, which absorb visible light and give the crystal a color [29]. The obtained EDS results (see Table S8) demonstrate a lack of chlorine anions, and this fact supports the idea of the probability of defect centres formation (trapped electron). Absorption bands at 405 nm (3.03 eV) and 465 nm (2.68 eV) correspond to blue and violet color absorption of the CNIC crystals and probably lead to their yellowish color (Figure S8).

In the literature, there is also information about the vacancy-type hole state formation (V_k) in HDPs [30] and CsPbI_3 [31]. It could be a self-trapped hole in the halide sublattice site, which strongly distorts the lattice, pulling two neighboring anions closer together, forming a diatomic anion: X_2^- . In Ref. [30], theoretical modelling for HDPs has confirmed the formation of the stable Cl_2^- defect. It introduces a hole-trapping state within the bandgap

and band structure calculations, at different Cl–Cl distances (from ~ 2.8 Å to ~ 2.01 Å), and gives the corresponding acceptor level from 0.21 to 1.8 eV. In the measured absorption spectra (Figure 3a,b), we noticed the intense bands at ~ 1980 nm (0.63 eV), which could support the idea of the acceptor level formation in the investigated samples. Our assumption aligns with Ref. [27], where broadband emission was observed for CNIC and its low efficiency was explained by the recombination of photoexcited electrons with holes through phonon emission.

We can conclude that deficiency of Cl^- anions in the crystal structure of the synthesized CNIC leads to the formation of F centers (trapped electrons), V_k centers (trapped holes), and influences the valence state of In^{3+} ($\text{In}^{3+} + 2e^- \rightarrow \text{In}^+$ formation) and Cl_2^- dimers appearance ($2\text{Cl}^- + h^+ \rightarrow \text{Cl}_2^-$). These valence states were confirmed by our XPS results (see Figure S6), agrees with Refs. [30, 31] and were discussed in detail in Ref. [7].

After doping with Er^{3+} , the absorption is enhanced compared to the undoped sample, which can be attributed to a higher density of defects. These results are consistent with the findings in Ref. [11], where the authors, through theoretical simulations, have established that Er^{3+} doping introduces a new localized valence band maximum, forms nanoelectronic domains, and breaks the symmetry of the In^{3+} site.

Figure 3b shows that Sb^{3+} doping rearranges the absorption spectrum within the 250–460 nm wavelength range, red-shifting the absorption edge to 294 nm, which corresponds to a narrower band gap of 4.2 eV (see Section 2.5). From the literature review, it is known that $5s^2$ electrons of a Sb^{3+} cation transit into the excited $5s^1p^1$ state in the octahedral coordination of six Cl^- ligands, thus forming $[^1P_1 \text{ singlet state}] > [^3P_2 > ^3P_1 > ^3P_0 \text{ triplet state}] > [^1S_0 \text{ ground state}]$ energy levels. In the crystal field of CNIC, the doublet with peaks at 325 and ~ 350 nm corresponds to the $^1A_{1g} \rightarrow ^3T_{1u}$ transition (A band, Figure S7) and agrees with data from Refs. [5, 32, 4]. The absorption band observed in the NIR range at 1540 nm corresponds to the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition in Er^{3+} ions of the Er-doped samples (Figure 3a,b) and agrees with the data of [33].

In Ref. [27], the broadband emission with a PL maximum at 550 nm under 265 nm light excitation was observed for CNIC,

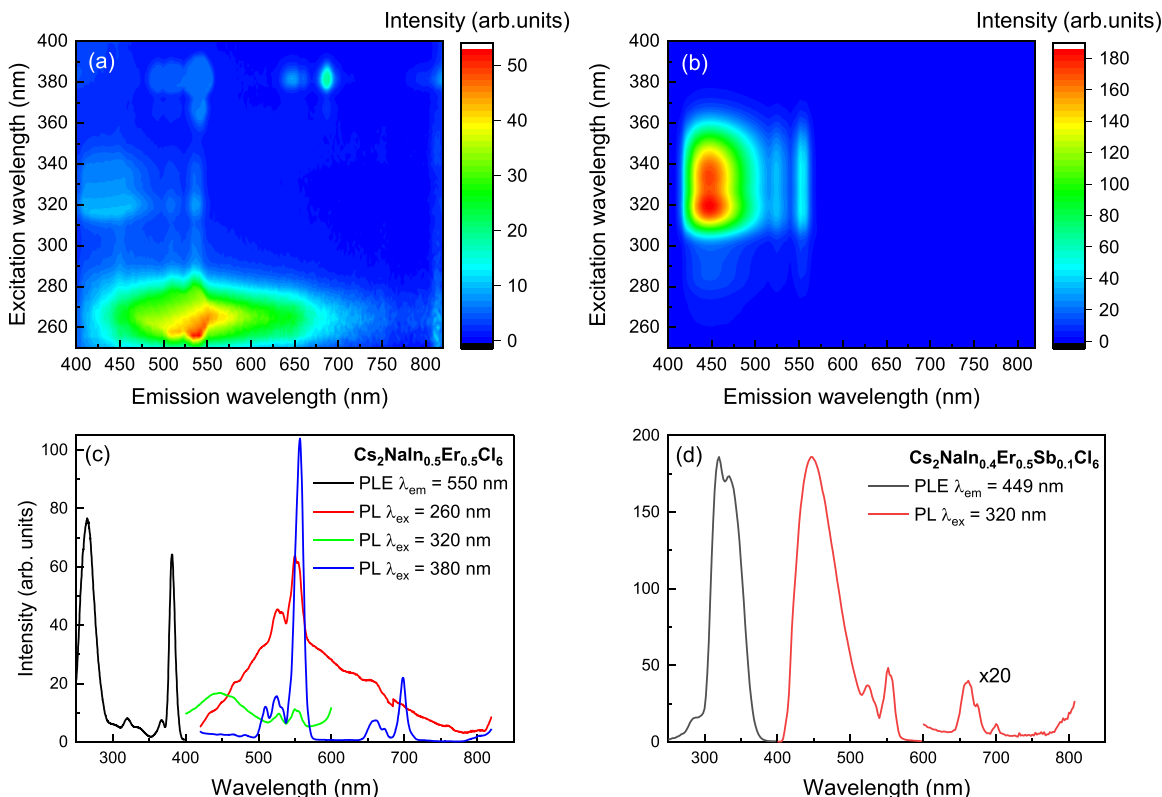


FIGURE 4 | Measured spectra for Er-doped and Er/Sb-codoped CNIC samples: (a) 2D PLE map of the 0.5 Er-doped CNIC; (b) 2D PLE map of the $\text{CNi}_{0.4}\text{C}_{0.5}\text{Er}/0.1\text{Sb}$; (c) excitation and emission spectra of 0.5 Er-doped CNIC; (d) excitation and emission spectra of $\text{CNi}_{0.4}\text{C}_{0.5}\text{Er}/0.1\text{Sb}$.

which agrees with our data (Figure S9a–c), while in Ref. [26] the undoped CNIC displays no visible PL at room temperature. In article [11], blue STE emission at 450 nm was reported under 335 nm light excitation, which is also observed in the 2D spectra of CNIC obtained by us, albeit with very weak intensity, together with broadband white emission of CNIC, which can be decomposed into ~ 450 nm, 568 nm, and 652 nm (Figure S9b). This could be explained by the influence of optically active In^+ ions as $5s^2$ centers, the existence of which was established based on XPS results (Figure S6). Additionally, we cannot rule out the influence of self-trapped excitons, which are formed due to structural defects and contribute to the formation of the optical spectrum. XPS results as well as In^+ influence on the optical properties of CNIC have been discussed in detail in our article [7].

For Er-doped samples, the PL spectra at 265 nm excitation (Figure 4a,c) were less intense, and this agrees well with the assumption [11] that Er^{3+} incorporation generates more defects, STEs, increases the radiative recombination rate, phonon activity, and exciton-phonon coupling. In the Er-doped samples, the 450 nm weak PL was obtained under 320 nm excitation (similar to results for CNIC in work [11]), and the reason for this peculiarity relates to the complicated nature of halide DPs and the interaction between In^+ , defects, STE, and dopants [14, 15, 18, 32]. Under 380 nm excitation (to excite electrons to $^4\text{I}_{15/2} \rightarrow ^2\text{G}_{7/2}$ – a higher-lying energy levels of Er^{3+}), the Er^{3+} bands at 520 ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$), 550 ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$), 660 nm ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) were registered, while the registered band at 690 nm correspond to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{13/2}$ transition. The same bands are additionally present on the

emission spectra of the 0.5Er-doped CNIC (0.5Er means 5 at.% Er) at 265 nm excitation (Figure 4a,c).

Analyzing the photoluminescent excitation spectra of the Sb-doped CNIC (Figure S9d) we can conclude that the two maxima at 320 nm and ~ 336 nm correspond to $5s^2 \rightarrow 5s^1p^1$ transitions of the $[\text{SbCl}_6]^{3-}$ octahedra because of the Jahn-Teller distortion, and the measured bands correlate well with literature data [5, 8, 32, 4] and absorption spectra (Figure 3a,b). For example, the weak band at 280 nm (Figure S9d) corresponds to the $^1\text{A}_{1g} \rightarrow ^3\text{T}_{2g}$ transition (B band, Figure S7), and the bands at 320 and 336 nm are associated with the $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1u}$ transition (A band, Figure S7).

Under 320 nm excitation, the Sb-doped CNIC sample reveals a broad blue PL (Figure S9e,f) with very high intensity. Additionally, the Sb/Er-codoped CNIC samples show the narrowband emission of Er^{3+} ions at ~ 520 , 550, and 660 nm, which corresponds to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ f - f transitions, respectively, and agrees with [11, 14, 33] (Figure 4b,d).

The NIR PL bands from Er^{3+} -doped CNIC and $\text{Sb}^{3+}/\text{Er}^{3+}$ -codoped CNIC were measured from 370 nm laser excitation (Figure 5a). All the PL emissions exhibit distinct peaks at 1510–1520, 1530, 1547, and 1562 nm, corresponding to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ f - f transition of Er^{3+} . Such multiple features have been observed in Er^{3+} emissions in previous studies and attributed to an equivalent four-level model with Stark splitting [34].

To avoid the competition between two PL excitation channels, like the CNIC crystals and the Er^{3+} ions, the samples were

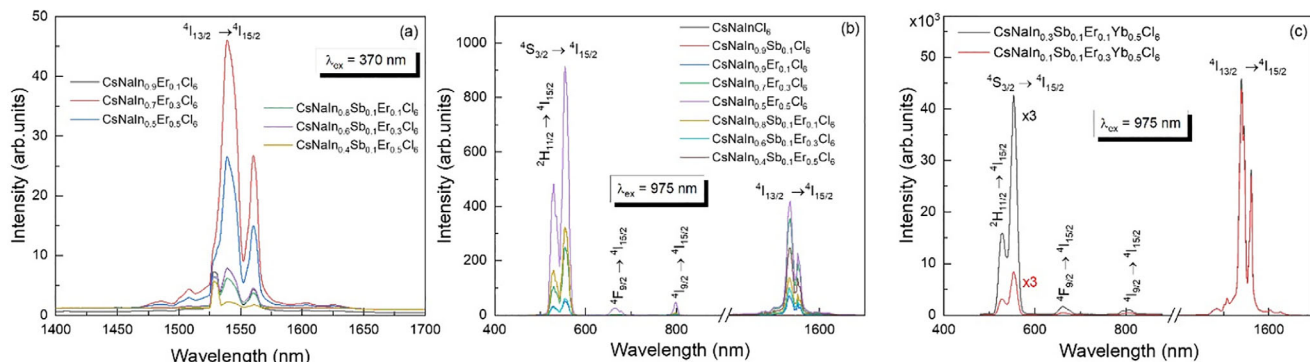


FIGURE 5 | Measured spectra in NIR region: (a) PL spectra under 370 nm excitation; (b) Stokes and anti-Stokes luminescence under 975 nm excitation in Er/Sb/Er-doped CNIC samples; (c) Stokes and anti-Stokes luminescence under 975 nm excitation in Sb/Er/Yb-codoped CNIC samples.

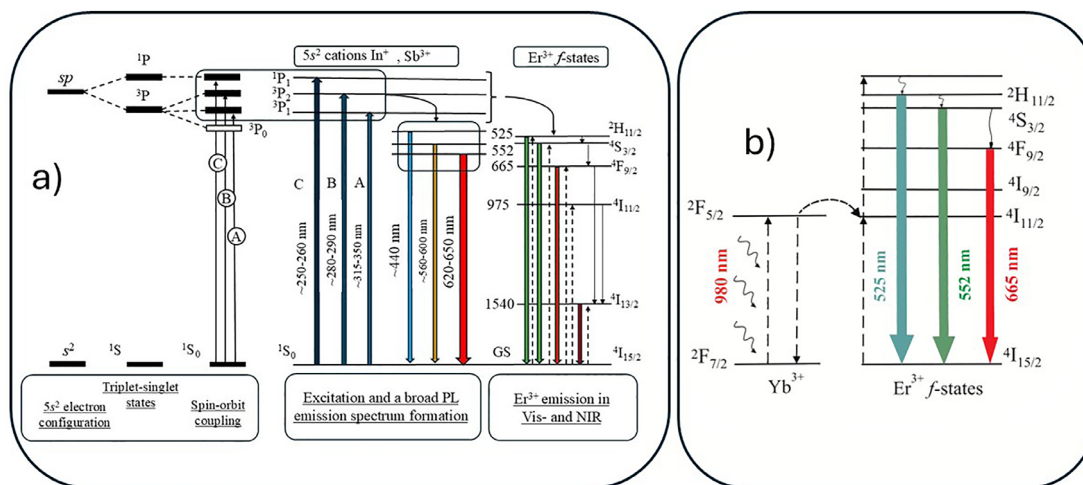


FIGURE 6 | Schematic energy transfer between CNIC and Er^{3+} ion because of In^{3+} or/and Sb^{3+} as $5s^2$ cations excitation (a), and between Yb^{3+} and Er^{3+} in the Er/Sb/Yb codoped samples with laser excitation at 975 nm (b).

also irradiated at the 975 nm excitation wavelength, which corresponds to the transitions from the $^4\text{I}_{15/2}$ level to the $^4\text{I}_{11/2}$ level within Er^{3+} . In this case, the two types of luminescence were measured: Stokes luminescence, with a peak at 1540 nm (Figure 5b), exhibiting multiple features, and anti-Stokes luminescence (upconversion, UC), with peaks at 525 and 550 nm (Figure 5b and Figure S10). The same was measured for the Sb/Er/Yb-codoped samples at the 975 nm excitation wavelength (Figure 5c). Additionally, the 2D spectra were measured for them (Figure S11) and show intense green PL (Figure S2g) for the CNIC sample doped with 0.1Sb/0.3Er/0.5Yb, which was used for pc-LED prototype construction (see Section 2.4).

3.3 | Emission Mechanisms for Different Compositions

Based on the obtained results, the following energy transfer mechanisms could be proposed (Figure 6a,b): (1) interaction of the CNIC host structure with Er^{3+} doped ions; (2) interaction of the CNIC host structure with Sb^{3+} and Er^{3+} dopants; (3) interaction with CNIC structure and three dopants, like Sb^{3+} , Er^{3+} and Yb^{3+} .

In the first type of mechanism, the $^1\text{S}_0 \rightarrow ^1\text{P}_1$, $^3\text{P}_{1,2}$ transitions (C, B, A bands of $5s^2$ In^{3+} ions) become partially permitted and can be observed in optical spectra (Figure 6a). This energy partially emits in broad wavelength region (400 – 800 nm) and transfers to Er^{3+} ions to emit characteristic bands in Vis- and NIR regions: $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (~520 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (~550 nm), $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (~660 nm), and $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ (~1540 nm) transitions in the f -shell of Er^{3+} ions, which agrees with [17, 35]. Decomposed into sub-bands at 450, 568, and 652 (Figure S9b), the luminescence spectrum of CNIC indicates the possibility of emitting light with wavelengths close to those of Er^{3+} f - f transitions. Due to the weaker emission of CNIC, there is sufficient energy to significantly excite transitions at 1540 nm, whilst the emissions at 520 and 550 nm are very low (Figures 4c and 5a).

In the second type, under 320 nm radiation, electrons in the Sb^{3+} -doped CNIC are excited from the ground state to the excited state, producing intense PL at 450 nm (emission of Sb^{3+}) (Figure S9e,f). Also, there is energy transfer from Sb^{3+} doped CNIC matrix to the Er^{3+} ions, which also emit radiation in Vis- and NIR regions, $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$ (490 nm), $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (520 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (550 nm), $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (660 nm), and $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ (1540 nm) because of energy transitions in the f -shells of Er^{3+} ions

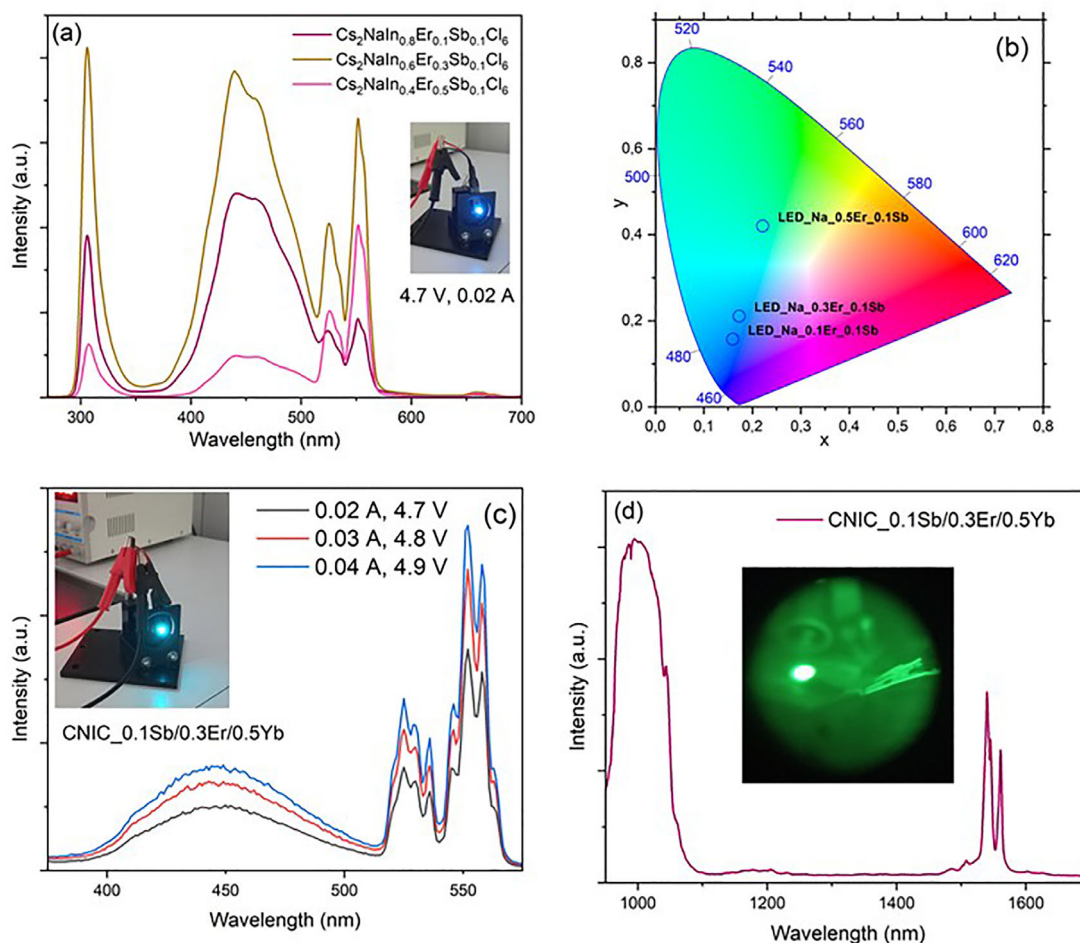


FIGURE 7 | Measured spectra of the pc-LED based on the synthesized samples as the luminophore material: (a) the spectrum of the pc-LED and a photo under bias (4.7 V, 0.02 A); (b) CIE chromaticity diagram of the Er/Sb-codoped samples; (c) measured spectrum of the pc-LED based on the CNIC doped with Er/Sb/Yb in the Vis-region under bias (4.7–4.9 V, 0.02–0.04 A) and the pc-LED photo under measurement; (d) measured spectrum of the pc-LED based on CNIC doped with Er/Sb/Yb in the NIR region and a dark photo from the NIR camera under bias (4.9 V, 0.04 A).

(Figures 4b,d, 5b and 6a). This mechanism aligns with our earlier investigation of halide DPs doped with Er^{3+} [35] and other research data [14, 19]. The emissions $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (525 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (550 nm) of Er^{3+} in this case are more intense than in the first type of the transition energy mechanism.

In the third type of transition mechanism, in addition to the energy transfer channels of the matrix to Yb^{3+} and Er^{3+} , there is an energy transfer between Yb^{3+} and Er^{3+} . Although power-dependent UC measurements were not performed in the present work, the observed green UC emission under 975 nm excitation is consistent with the established $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ energy-transfer UC mechanism reported for RE-doped chloride perovskites. According to [18, 36], Yb^{3+} ions efficiently sensitize Er^{3+} through sequential energy-transfer processes, leading to UC Er^{3+} emission. After excitation of Yb^{3+} ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$), the first transfer populates the $\text{Er}^{3+} ^4\text{I}_{11/2}$ level, and a second transfer excites Er^{3+} to higher states ($^4\text{F}_{7/2}$), followed by relaxation to the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ emitting levels, responsible for the green and red emission, correspondingly (Figure 6b and Figure S12).

The photoluminescence quantum yield (PLQY) measurements reveal a strong influence of Sb^{3+} , Er^{3+} , and Yb^{3+} doping on the

luminescence efficiency of the CNIC host (Table S14). The significant decrease in the visible-range PLQY upon Yb^{3+} co-doping suggests efficient excitation-energy transfer to the $\text{Er}^{3+}/\text{Yb}^{3+}$ subsystem, likely accompanied by population of the NIR emitting states, outside the detection range of the PLQY measurements (Figure S12b). Therefore, it provides indirect evidence for energy-transfer processes involving Sb^{3+} , Er^{3+} , and Yb^{3+} ions in the co-doped samples. Moreover, comparison of the UC spectra shows that the Yb-containing sample exhibits the highest UC intensity among the investigated compositions, significantly exceeding those of the Er-doped and Er/Sb-codoped samples (Figure S12a). This observation further supports the role of Yb^{3+} as an efficient sensitizer that enhances excitation-energy transfer and promotes the population of Er^{3+} excited states responsible for UC emission.

3.4 | Investigation of the pc-LEDs

To produce the pc-LED prototype, the $\text{CNIC}_{0.9-x}\text{C} \cdot 0.1\text{Sb}^{3+}/x\text{Er}^{3+}$, $x = 0.1, 0.3, 0.5$ phosphor was combined with silicon resin and placed on a 320 nm LED driven by a 0.02 A current. The luminescence spectrum and performance characteristics of the pc-LED prototypes were measured (Figure 7a). The CIE

TABLE 2 | Lattice parameters and the total energy of the atom systems based on the CNIC crystal structure.

Sample	a, Å	Total energy, eV	Total energy/atom, eV
CNIC	10.3744	5787	144.68
CNIC + Er ³⁺	10.7100	4608	115.20
CNIC + Sb ³⁺	10.7560	4615	115.38
CNIC + V _{Cl} ⁻	10.7340	5796	148.62
CNIC + V _{Na} ⁺	10.6375	5490	140.77
CNIC + V _{In} ³⁺	10.6392	4634	118.82

chromaticity diagram (Figure 7b) of CNIC_{0.9-x}C·0.1Sb³⁺/xEr³⁺, x = 0.1, 0.3, 0.5 Er shows different colors, ranging from blue to more greenish, corresponding to an increasing amount of Er³⁺.

For the Sb/Er/Yb codoped samples, the dependence of the intensity on voltage was measured (Figure 7c), where the green color appeared to become more dominant. Finally, the spectra in the NIR region were investigated for CNIC·0.1Sb/0.5Yb/0.3Er, and bands at 980 nm from Yb³⁺ and 1540 nm from Er³⁺ were noted (Figure 7d). These results make the pc-LED a promising prototype for a Vis-NIR light source, featuring a simple preparation method and the capability to produce broadband and effective NIR emissions.

3.5 | Computational Details

Quantum-chemical calculations were conducted on the doped and defective materials based on the CNIC DPs featuring Er³⁺ and Sb³⁺ dopants. The necessity to perform the spin-dependent calculations is explained in the SI (see Section 1). Firstly, geometry optimization was performed to determine the lowest total energy. The resulting lattice parameters and total energy per atom are presented in Table 2. The initial geometry of the CNIC was a cubic structure with $a = 10.5359$ Å, and after its optimization, it remained cubic with $a = 10.3744$ Å. The change in the unit cell parameters is 1.34%, indicating that the chosen computer modelling method enables us to reproduce the geometric parameters of the CNIC crystal structure. It was confirmed that Er³⁺ and Sb³⁺ dopants increase the unit cell volume, stabilizing the CNIC structure at nearly the same level (Table 2).

Additionally, the defective structure of the CNIC was examined by modelling the chloride (V_{Cl}⁻), sodium (V_{Na}⁺), and indium (V_{In}³⁺) vacancies, which enhance the lattice parameters (Table 2). The V_{Na}⁺ and V_{In}³⁺ defects stabilize the CNIC crystal structure, while the V_{Cl}⁻ defects raise the total energy of the crystal, destabilizing the structure. This contrasting effect of Er, Sb dopants and vacancies on structural stability might explain why the precipitated crystals contain less chlorine (Table S8) and why the yield of the reaction product varies (Table S1). After doping with Sb and Er, the yield of the reaction product increases from 66% for CNIC to 84% and 76%, respectively. However, increasing the amount of Er from 1 at.% to 5 at.% decreases the quantity of precipitates. This fact could be related to the larger radius of the

TABLE 3 | The E_g values and nature of the energy band structure of the calculated atomic systems. The $\uparrow\downarrow$ arrows define the spin-up and spin-down configuration.

Material	E_g , eV		Nature of the energy band gap	
CNIC	5.61 $\uparrow\downarrow$		$\Gamma \rightarrow \Gamma \uparrow\downarrow$	
CNIC + Er ³⁺	5.32 $\uparrow$	5.36 $\downarrow$	$\Gamma \rightarrow L \uparrow\downarrow$	
CNIC + Sb ³⁺	3.60 $\uparrow$	3.34 $\downarrow$	$\Gamma \rightarrow \Gamma \uparrow$	$L \rightarrow L \downarrow$
CNIC + V _{Cl} ⁻	3.54 $\uparrow$	3.30 $\downarrow$	$\Gamma \rightarrow \Gamma \uparrow$	$\Gamma \rightarrow L \downarrow$
CNIC + V _{In} ³⁺	5.45 $\uparrow\downarrow$		$\Gamma \rightarrow \Gamma \uparrow\downarrow$	
CNIC + V _{Na} ⁺	4.01 $\uparrow\downarrow$		$\Gamma \rightarrow L \uparrow\downarrow$	

Er ion ($r_{In3+} = 0.80$ Å; $r_{Er3+} = 0.89$ Å) [21, 22], which appears to have a more significant effect in this case.

The optimized structures of the investigated samples were used as the atomic geometries for calculations of their electronic properties. The energy band structure calculated for CNIC is presented in our recently published article [7] and in Figure S13a (Table 3). Based on the calculation, the CNIC cubic crystal is a direct semiconductor with a calculated band gap (E_g) of 5.61 eV. According to the computational methodology, the GGA/PBE functional underestimates the energy gap. It agrees well with the experimental E_g of 6.7 eV estimated from VUV spectroscopy, which was assigned to the intrinsic band edge of CNIC [7]. The lower-energy optical features (5.1 eV) reported in the literature [4, 5] were derived from the optical absorption edge of real samples containing intrinsic defects, which are not taken into consideration in the calculated band structure presented in Figure S13a. The DFT calculations for the ideal crystal do not include these defect states and therefore describe the fundamental electronic structure of stoichiometric CNIC.

Electron properties, particularly the energy band distribution, depend on spin polarization. Pristine CNIC is a non-magnetic material, and the spin-polarized calculations converge to identical spin-up and spin-down electronic structures. The energy band structures calculated for Er³⁺ or Sb³⁺-doped CNIC crystals are presented in a spin-restricted regime (Figure 8). For both dopants, the VB is formed by Cl 3p electrons in the spin-up configuration. In the spin-down configuration, the Na 2p electrons contribute to the top of the VB. The electrons from the Er³⁺ ions create the bottom of the CB, without significantly altering the E_g of the CNIC crystal, which agrees with the absorption spectra (Figure 3a). The Sb³⁺ ion hybridizes with the Cl⁻ ion to form the top of the VB. Additionally, the Sb³⁺ 5p electrons, together with the Cl⁻ 3s electrons, form a donor trapping level, significantly reducing the E_g of the crystal, which agrees with the absorption spectra (Figure 3b). The bottom of the CB is established by the In 5s electrons supported by the Cl⁻ 3s ions. Er³⁺ introduces localized 4f and 5d states near the host band gap, which weakly hybridize with the host CB, creating the indirect band gap (Figure 8a,b). Intense spin-orbit coupling (SOC), because of heavy Er³⁺, keeps the energy gap indirect, introducing the expected splitting of the Er-derived electronic states (Figure 8e). Consequently, the calculated band gap of the Er-doped CNIC decreases slightly

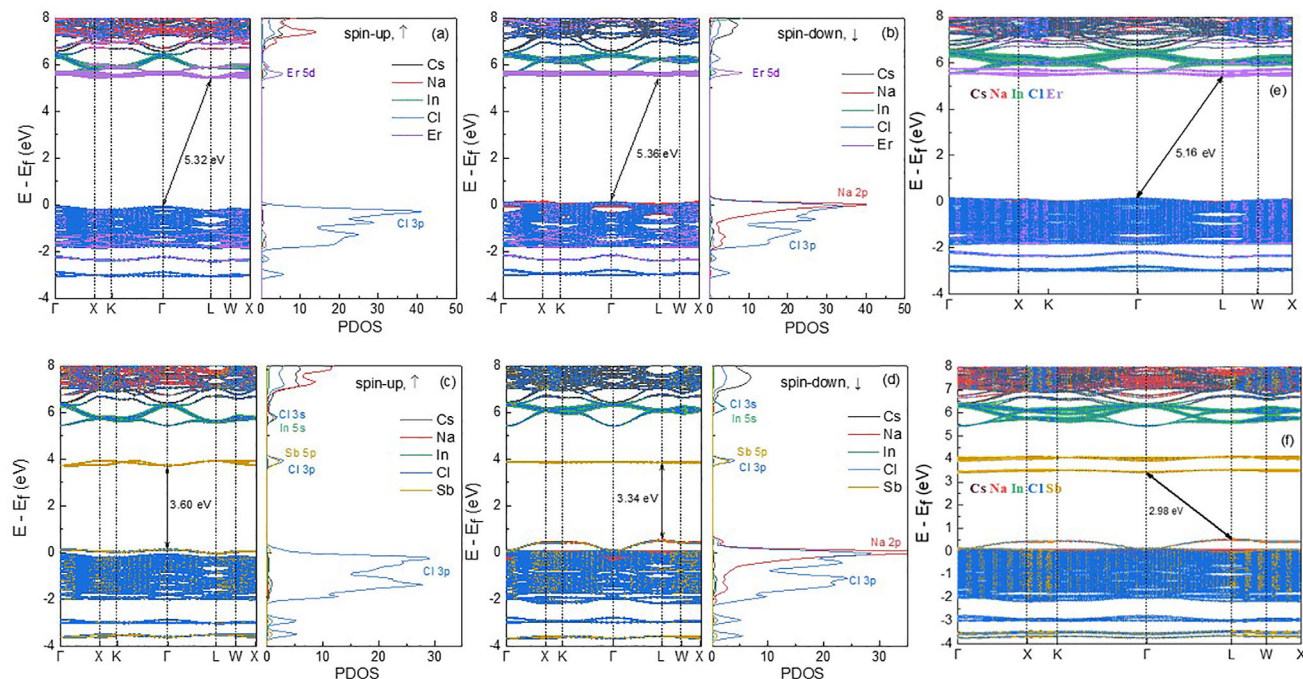


FIGURE 8 | The energy band structure calculated by the GGA/PBE method for the CNIC crystal doped by Er^{3+} with spin up (a) and spin down (b), for the CNIC crystal doped by Sb^{3+} with spin up (c) and spin down (d), and the energy band structure calculated by the GGA/PBE+SOC method for the CNIC crystal doped by Er^{3+} (e) and Sb^{3+} (f).

from 5.32 eV (spin-up) and 5.36 eV (spin-down) to 5.16 eV when SOC is explicitly included. Moreover, Er^{3+} ions serve as luminescence centers: electrons excited into the host CB transfer energy nonradiatively to the Er^{3+} 4f shells, resulting in emission from intra-4f transitions. Since the host gap has become indirect, host band-edge PL weakens, but sharp Er^{3+} f-f emission prevails.

Analyzing results of the spin-polarized calculations, the Sb dopant does not significantly perturb the CBM position across the Brillouin zone (Figure 8c,d). The band gap remains direct but effectively narrows due to the Sb-induced intermediate band; considering SOC, the energy gap becomes indirect. Here, the energy gap is equal to 2.98 eV compared to the 3.60 eV (spin-up) and 3.34 eV (spin-down) values calculated by the spin-polarized GGA/PBE method. SOC acts mainly on Sb 5p electrons and causes splitting of these states, and strong new absorption appears in the visible region because electrons can be excited from Cl 3p $\rightarrow$ Sb 5p states (instead of only Cl 3p $\rightarrow$ In 5s) (Figure 8f). Photoluminescence intensifies and broadens in the visible spectrum, consistent with direct transitions into and from Sb-related states, which agrees with PL spectra of Sb-doped samples (Figure S9).

The electron properties of the defective CNIC crystal were also investigated, considering the V_{Cl}^- , V_{Na}^+ , and V_{In}^{3+} vacancies (Figure S13 and Table 3). In the case of V_{Cl}^- (Figure S13b,c), the created donor trapping levels decrease the E_g . Spin-up and spin-down configurations reach E_g values of 3.54 eV and 3.30 eV, respectively. The V_{Cl}^- structures possess a donor level composed mainly of the In 5s electrons. The localization of the donor electrons on In 5s orbitals surrounding the chloride vacancy is consistent with the formation of reduced indium (In^+) centers inferred from the optical spectroscopy and XPS measurements (see Section 2.2). Therefore, within the adopted VCA methodol-

ogy (see SI, Section 1), the V_{Cl}^- model provides indirect theoretical support for the experimentally proposed self-generated In^+ luminescence centers. The spin-polarized calculations do not give any difference in the case of V_{In}^{3+} and V_{Na}^+ vacancies, so only spin-up configuration results are presented for the V_{In}^{3+} and V_{Na}^+ possessing structures (Figure S13d,e and Table 3).

Removing In^{3+} from the crystal lattice results in one center being locally missing, but the CBM still originates from the s-orbital of the remaining In^{3+} atoms; the symmetry and character of the conduction band in k -space do not change significantly (there are simply fewer states, but with the same shape) (Figure S13d). Therefore, the gap value may vary, but its character remains unchanged because the band topology stays the same (Table 3). In the case of the V_{Na}^+ vacancies, a donor trapping level is created by the Na 2p electrons (Figure S13e). The V_{Na}^+ changes the nature of the energy gap in $\text{Cs}_2\text{NaInCl}_6$ because it modifies the global electrostatic potential and the relative energies of states at different points of the Brillouin zone, shifting the global minimum of the CBM.

4 | Conclusions

Using precipitation or hydrothermal techniques, it is possible to obtain one-phase Er-doped CNIC powder samples that crystallize in the ordered cubic symmetry, Sp. Gr. $Fm\bar{3}m$. In the case of Sb, Er/Yb codoping, a tetragonal structure could be obtained, Sp.Gr. $I4/mmm$ due to Jahn-Teller distortion. It affects the powder yields, which become lower in the case of Sb/ RE^{3+} codoping.

The method of synthesis (precipitation or hydrothermal method) and its duration (20 min or 2 h) determine the surface quality of

microcrystals, phase compositions of the samples, and defects of cations and anions. Lack of Cl^- stimulates the F centers (trapped electrons), V_k centers (trapped holes), and Cl_2^- dimers formation ($2\text{Cl}^- + \text{h}^+ \rightarrow \text{Cl}_2^-$), which could be the color centres. In^{3+} ions could act as electron-trapping centers, and form In^+ ions ($\text{In}^{3+} + 2\text{e}^- \rightarrow \text{In}^+$). These conclusions are supported by the XPS results, the measured absorption spectra, and the DFT calculations. The possible existence of STEs, vacancies, and the formation of the relevant subbands can explain the complex character of the absorption spectra of the CNIC or doped-CNIC samples.

The self-generated In^+ and doped Sb^{3+} both have a $5s^2$ configuration, and in the excited states, they can undergo the $^1\text{S}_0 \leftrightarrow ^1\text{P}_1$, $^3\text{P}_{1,2}$ transitions (C, B, A bands), which form a broad PL spectrum in the visible region. Sb^{3+} doping significantly enhances the band at 450 nm, while In^+ increases the band at 568 nm. This explanation accounts for why the Sb-doped CNIC exhibits PL at lower wavelengths (450 nm) compared with CNIC (568 nm), even though the Sb-doped CNIC has a narrower band gap (3.6 eV) compared to undoped CNIC (6.7 eV).

Er doping decreases the PL intensity of the CNIC, because the band gap changes from direct to indirect, but practically does not change the band gap value (5.32 eV–5.36 eV). Also, Er-doped CNIC gives a weak Er emission in the visible ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (520 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (550 nm), $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (660 nm)) but intense luminescence in the NIR range, because of $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ f - f transition (~ 1540 nm). For Er-doped, RE^{3+}/Sb -codoped CNIC, it is possible to observe not only downconversion, but also UC emissions. Yb-doping enhances Er PL in the visible region (520, 550, and 665 nm) and NIR region, as Yb acts as a sensitizer.

All in all, halide DP powder samples can be used as luminescence materials in the Vis- and NIR regions and are suitable for doping with ns^2 ions (e.g., Sb^{3+}) and RE^{3+} ions (Er^{3+} and Yb^{3+}). Unfortunately, defects decrease the PL intensity; however, a doping strategy improves their PL properties, covering the entire Vis-NIR spectrum with high efficiency. Based on them, pc-LED prototypes as proof-of-concept demonstration devices have been obtained. The DFT calculation results enhance our understanding of the crystal field influence of ns^2 ion dopants, such as Sb^{3+} , and the band gap structures of complex phases, like halide double perovskites. These findings contribute to a fundamental understanding of the luminescence behavior and support the development of advanced optoelectronic materials.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: adom71826-sup-0001-SuppMat.docx.