

Article

Tunable Luminescence by B-Site Substitution in $\text{Cs}_2\text{NaInCl}_6$

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Abstract

The article presents the synthesis and characterization of double halide perovskites (DHPs) with the nominal composition $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{M}_{0.4}\text{Cl}_6$ ($\text{M} = \text{Si}, \text{Ti}, \text{Zr}$), including photoluminescence (PL), photoluminescence excitation (PLE) spectra measured over a range of temperatures and kinetics of luminescence. The materials were synthesized via a hydrothermal method. The phase purity and elemental composition of the synthesized perovskites were confirmed by X-ray diffraction (XRD), Rietveld refinement, scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) and elemental analysis, which demonstrated that the samples showed a close match to the target stoichiometry. The PL spectra exhibit a systematic shift toward the lower-energy region with substitution from Si to Zr, correlating with the progressive increase in the ionic radii of the substituting cations. All samples display broad, asymmetric emission bands, characteristic of self-trapped excitonic (STE) states. Temperature-dependent PL measurements reveal a gradual decrease in emission intensity with increasing temperature for all samples. The maximum emission intensity is observed in the range of ~160–200 K, corresponding to optimal conditions for radiative recombination, whereas the lowest intensity is recorded at ~80–100 K, where thermal activation of radiative centers is minimal. An increase in temperature is accompanied by a red shift in the PL bands across all compositions. In the Ti-doped DHP, a pronounced blue shift at low temperatures is observed, which can be attributed to the involvement of Ti^{3+} -related electronic states. An analysis of the activation energy of thermal luminescence quenching and the results of time-resolved spectroscopy revealed the activation of thermal processes in the titanium-containing sample and their rapid decay, whereas replacing titanium with silicon leads to more stable luminescence in the crystal under study. Thus, the enhanced luminescence characteristics of double halide perovskites doped with Ti, Si, and Zr highlight their potential for advanced photonic and optoelectronic applications.



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Keywords: double halide perovskites; photoluminescence excitation spectra; photoluminescence spectra; crystalline materials; XRD spectra

1. Introduction

Perovskite materials are a promising class of materials used in many branches of optoelectronics, including solar cells and luminescent materials due to their outstanding optical

and electrical properties. All inorganic halide perovskites are very popular due to their photovoltaic and photoelectric properties, with potential use in solar cells, photodetectors, and light-emitting diodes (LEDs) [1,2].

Double halide perovskites constitute a distinct class of crystalline materials with the general formula $A_2B'B''X_6$ ($A = Cs^+, Rb^+$; $B'(I) = K^+, Na^+, Li^+, Ag^+, Cu^+$; $B''(III) = In^{3+}, Sb^{3+}, Bi^{3+}$; $X = Cl^-, Br^-, I^-$). These compounds are derived from the conventional perovskite structure ABX_3 by replacing the single B-site cation with two different cations (B' and B''), while X represents halide anions (F^-, Cl^-, Br^-, I^-) (Figure 1).

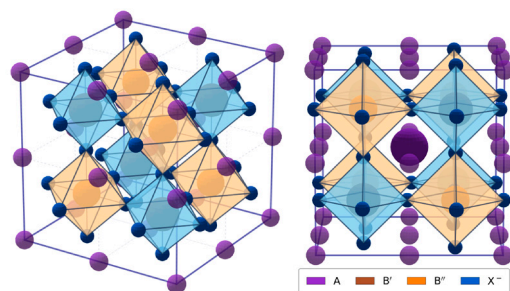


Figure 1. Double perovskite structure [3].

The presence of two chemically distinct cations within the crystal lattice enables fine control over both structural and electronic properties, often resulting in enhanced performance and the emergence of new functionalities. Double halide perovskites are considered an excellent alternative to lead perovskites, which are both toxic and chemically unstable [4].

The broad optical bands of double halide perovskites are associated with the formation of self-trapped excitons (STEs) [5]. Such exciton states can act as effective sensitizers for transition and rare-earth metal ions, transferring absorbed energy to optically active centers and thereby enhancing luminescence [6].

$Cs_2NaInCl_6$ is a lead-free double halide perovskite with a cubic crystal lattice belonging to the $Fm\bar{3}m$ space group and a lattice parameter of a ≈ 10.3 Å. It is a wide-bandgap direct semiconductor (4.8–5.1 eV) and has attracted interest as a potential luminescent material for photoelectronic applications. However, $Cs_2NaInCl_6$ exhibits extremely weak photoluminescence compared with the more extensively studied $Cs_2AgInCl_6$. In $Cs_2AgInCl_6$, Ag^+ ions possess a closed-shell $4d^{10}$ electronic configuration, which leads to a narrower bandgap, stronger orbital hybridization, and consequently more pronounced optical transitions [7–11].

In contrast, Na^+ ions in $Cs_2NaInCl_6$ lack d orbitals, and the valence band is predominantly composed of Cl-3p states. This electronic structure results in a wide bandgap and a very low photoluminescence quantum yield (PLQY). In addition, optical transitions in $Cs_2NaInCl_6$ are parity-forbidden, further suppressing radiative recombination. Consequently, improving the luminescent properties of $Cs_2NaInCl_6$ remains a significant scientific challenge [12,13]. At the same time, these characteristics make $Cs_2NaInCl_6$ an ideal host lattice for dopant-activated luminescence, enabling systematic and wide-range tuning of emission properties while relying on earth-abundant and chemically stable elements.

Moreover, sodium is inexpensive and readily available, and suitable doping or alloying strategies can enhance luminescence efficiency and extend the emission spectral range by several orders of magnitude—effects that cannot be achieved in Ag-based analogs. The incorporation of Na^+ ions disrupts the lattice symmetry, facilitating the formation of self-trapped excitons and leading to a dramatic increase in the STE photoluminescence quantum yield. In alloyed $Cs_2Ag_xNa_{1-x}InCl_6$ systems, the self-trapped exciton is delocalized over

two neighboring octahedra, with the hole localized on the AgCl_6 unit and the electron confined to the InCl_6 octahedron.

Pristine $\text{Cs}_2\text{NaInCl}_6$ exhibits very weak photoluminescence, which is mainly associated with the radiative recombination of self-trapped excitons arising from strong electron–phonon coupling and parity-forbidden electronic transitions and therefore rarely discussed in the literature [14,15]. Instead, most studies focus on doped systems, particularly those incorporating Sb^{3+} , Bi^{3+} , or rare-earth ions. For example, $\text{Cs}_2\text{NaInCl}_6$ doped with 1% Sb^{3+} exhibits luminescence with a maximum in the region of 445 nm and a quantum yield of 82% [16]. When the Sb^{3+} concentration is increased to 10%, a slight blue shift to ~442 nm is observed [17]. Doping with erbium and holmium creates narrow-band luminescence in the green (~550 nm) and red (~655 nm) spectral regions, respectively [18,19]. Mn^{2+} ions exhibit green luminescence in a tetrahedral coordination environment and red luminescence in an octahedral coordination environment [20]. One effective way to increase the intensity of the weak luminescence of $\text{Cs}_2\text{NaInCl}_6$ is doping, which allows tuning the optical properties; in particular, the introduction of transition-metal ions significantly enhances the photoluminescence yield of the material. Doping with different ions enables tuning of the band gap as well as the intensity and spectral position of the luminescence bands in the materials under consideration [10].

At high levels of isovalent substitution (up to ~40%), the introduced ions no longer behave as isolated dopants but become integral components of the crystal stoichiometry, effectively altering the chemical formula of the material. Under such conditions, it becomes possible to control the bandgap width, emission peak positions, electron–phonon coupling strength, and absorption spectra—capabilities that are difficult to achieve via conventional low-level doping [21]. Consequently, alloying at both the B' and B'' sites can transform a weakly absorbing and weakly emissive host lattice into a strongly UV-absorbing and highly luminescent material.

When double halide perovskites are alloyed with transition-metal ions, the impurity centers experience an unusually weak crystal field, which favors the emergence of broadband infrared emission—an effect rarely observed in other material systems [22,23].

In the present work, we synthesized a new series of lead-free double perovskites with nominal composition $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{M}_{0.4}\text{Cl}_6$ ($\text{M} = \text{Si}, \text{Ti}, \text{Zr}$), and systematically investigated their optical properties, including photoluminescence and photoluminescence excitation spectra over a wide temperature range, including room temperature. The formation of these compounds proceeds via isovalent substitution, and the choice of substituent elements is motivated by the similarity of their ionic radii to those of indium, enabling partial isomorphic replacement without disrupting the cubic lattice.

These substituents possess distinct electronic configurations (Si : p states; Ti/Zr : d states), allowing modulation of the electronic structure and effective bandgap engineering. A key aspect of this system is charge compensation associated with the substitution $\text{In}^{3+} \rightarrow \text{M}^{4+}$ ($\text{M} = \text{Si}, \text{Ti}, \text{Zr}$). The excess positive charge is compensated by cation vacancies, local lattice distortions, redistribution of electronic density, or coupled substitution involving Ag^+/Na^+ ions. Such charge-compensated defects relax parity-forbidden transitions, introduce localized electronic states, and promote enhanced luminescence through defect-assisted recombination mechanisms [24,25].

Overall, this series enables a comparative investigation of how light (Si), transition (Ti), and heavy (Zr) tetravalent cations influence the optical properties of $\text{Cs}_2\text{NaInCl}_6$ -based double perovskites.

2. Materials and Methods

The double-perovskite samples with nominal composition of $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{M}_{0.4}\text{Cl}_6$, where $\text{M} = \text{Si}, \text{Ti}, \text{Zr}$ were synthesized via a hydrothermal method using Teflon-lined reactors. In this synthesis route the CsCl , AgCl , NaCl , InCl_3 , SiO_2 , TiO_2 , ZrO_2 (Merck, Darmstadt, Germany) were weighed according to the above-mentioned composition, transferred to the reactor and suspended in 10 mL of concentrated HCl solution. After 30 min of stirring, the reactor was placed in a muffle furnace and rapidly heated to 180°C . The temperature of the process was maintained for 12 h and then slowly decreased at a rate of 3.4°C/h until the room temperature was reached. The obtained products in the form of single crystals were collected, washed several times with isopropanol and dried at ambient conditions.

Throughout the manuscript, all chemical formulas for the doped samples are given according to their nominal compositions. Their actual composition was examined by SEM-EDS and ICP-OES and described in Section 3.

The quality and purity of samples were examined using a D2 PHASER (Bruker, Billerica, MA, USA) diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and operating at 30 kV and 10 mA. The XRD patterns were collected using a scanning step of 0.02° and a counting time of 0.4 s per step. The analysis of obtained results was carried out using DIFFRAC.EVA V6.1 software (Bruker, Karlsruhe, Germany) and PDF-5 database, release 2024 (ICDD, Newtown Square, PA, USA). Rietveld refinement was performed using TOPAS Academic software (V.7.0. (2022), Bruker).

The powder samples of double halide perovskites were further investigated by SEM and EDS. Microscopic images of the samples were obtained using a benchtop scanning electron microscope (NANOS, Sempor, Eindhoven, The Netherlands) at the Khoja Ahmed Yasavi International Kazakh-Turkish University (Turkistan, Kazakhstan). The instrument operated in high-vacuum mode at an accelerating voltage of 5–20 kV, depending on the conductivity of the samples. Secondary electron (SE) and backscattered electron (BSE) detectors were used to acquire the images.

Microstructure of the synthesized samples was investigated using an Axia ChemiSEM scanning electron microscope (Thermo Fisher Scientific, Eindhoven, The Netherlands). The measurements were performed at an accelerating voltage of 20 kV. To minimize charging effects, the powder samples were deposited onto a conductive carbon tape. The elemental composition and distribution were analyzed using integrated EDS.

Elemental analysis of the samples was performed using a SHIMADZU ICPE-9800 instrument (Shimadzu Corporation, Kyoto, Japan) at the Eco Project Company laboratory in Aktobe, Kazakhstan. Test conditions: temperature $+23.20^\circ\text{C}$, humidity 74%, and pressure 748 mm Hg.

Each sample contains chlorine, but inductively coupled plasma atomic emission spectroscopy (ICP-AES) is not a standard method for determining chlorine in samples. Very high energies are required to excite the emission lines of halogens, since their spectral lines lie in the vacuum ultraviolet (VUV) region, which is absorbed by air. Therefore, chlorine is not detected in most standard ICP-AES systems.

Room temperature (RT) PLE spectra of powder samples were measured with a FluoroMax-4P spectrofluorometer (Horiba Jobin Yvon, Palaiseau, France) equipped with a 150 W xenon lamp as an excitation source and a R928 photomultiplier as a detector, enabling acquisition of PL and PLE spectra in the spectral range of 250–850 nm. During PL measurements, the excitation wavelength was varied from 250 to 300 nm.

For the temperature-dependent PL spectra, the samples were placed in the THMS600 temperature stage (Linkam Scientific, Salfords, UK) equipped with the LNP95 liquid nitrogen cooling pump, allowing measurement in the temperature range of 77–570 K. The

temperature-dependent PL spectra were recorded using a Shamrock SR-750-D1 spectrometer with an iDUS DU420A-OE CCD detector (Andor Technology, Belfast, UK) operating in the 300–1000 nm wavelength range. The excitation source was a 280 nm UV LED combined with a 292 ± 27 nm bandpass optical filter. The PL spectra were corrected for the spectral response of the instrument using an OL 220 calibration lamp.

For kinetics of luminescence measurement, PL spectra were obtained using a Shamrock SR750 D1 grating spectrometer equipped with PIN 420 and an iDus 420 CCD detector (Andor Technology). The spectral range of the spectrometer is 220–1000 nm. The excitation source was a continuous-wave laser IK5352R-D He-Cd (Kimmon Koha, Tokyo, Japan), operating at 442 nm. The excitation part of the equipment for time-resolved spectroscopy consists of a PG 401/SH optical parametric oscillator pumped by a PL2251 YAG:Nd-laser pulse (Ekspla, Vilnius, Lithuania). The optical parametric generator converts the 355 nm pulses produced by the laser into a selected wavelength range from 210 to 2300 nm. The pulse duration is 30 ps. Time-resolved PL spectrum and PL decay profiles were obtained using a 2501S grating spectrometer (Bruker Optics, Ettlingen, Germany) coupled with a C4334-01 streak camera (Hamamatsu Photonics, Hamamatsu, Japan). The luminescent resolution of the sample (spectrally and temporally resolved by the acquisition device) is recorded as image strips of a 640 by 480 pixel CCD array. The time scale available for the measurement range is from 10 ms to 1 ns.

3. Results and Discussion

The XRD of DHP, doped by Zr, Ti, Si are shown in Figure 2.

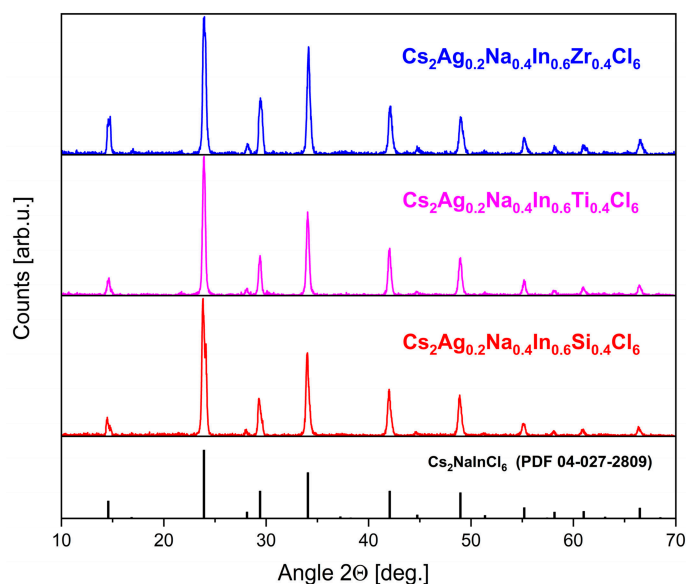
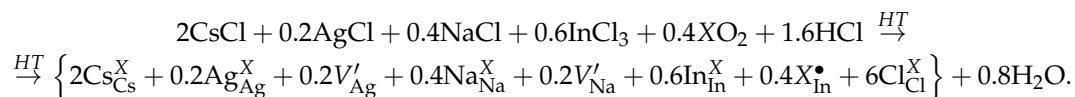


Figure 2. XRD of synthesized samples.

X-ray diffraction patterns of three samples $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{M}_{0.4}\text{Cl}_6$ ($\text{M} = \text{Si}, \text{Ti}, \text{Zr}$), confirms the formation of a single-phase $\text{Cs}_2\text{NaInCl}_6$ (PDF 04-027-2809) and exhibit 100% phase purity. Powder X-ray diffraction (PXRD) analysis confirms that all obtained samples crystallize in the $\text{Cs}_2\text{NaInCl}_6$ structure, in good agreement with the reference pattern.

It is worth noting here that the incorporation of tetravalent dopants X^{4+} ($\text{X} = \text{Si}, \text{Ti}$ and Zr) into the In^{3+} sites leads to the formation of excessive positive charge in the crystal lattice due to creation of $\text{X}_{\text{In}}^\bullet$ species. According to the principle of electroneutrality, this excessive charge has to be compensated by the creation of negatively charged defects. Thus, the chemical composition of the matrix was intentionally modified by reducing the total occupancy of the B' sublattice (incorporation of 0.2 mole Ag and 0.4 mole Na instead of

0.4 and 0.6, respectively, in relation to the nominal composition of the parent material $\text{Cs}_2\text{Ag}_{0.4}\text{Na}_{0.6}\text{InCl}_6$). This change in the concentration of the aforementioned cations in the B' sublattice results in the formation of 0.4 mol of the negatively charged cation vacancies (V'_{Na} and V'_{Ag}), which compensate the excess positive charge associated with the formation of 0.4 mol of substitutional defects ($X_{\text{In}}^\bullet$). Considering the defect chemistry, the nominal stoichiometry of the reacted ions and the synthesis of doped materials under hydrothermal treatment (HT) can be expressed using the following equation (the nominal composition of the desired product is presented in the curly brackets):



To quantitatively characterize the crystal structure we performed a quantitative analysis and performed a Rietveld refinement (Figures 3–5). The quantitative results of the analysis are summarized in Table 1.

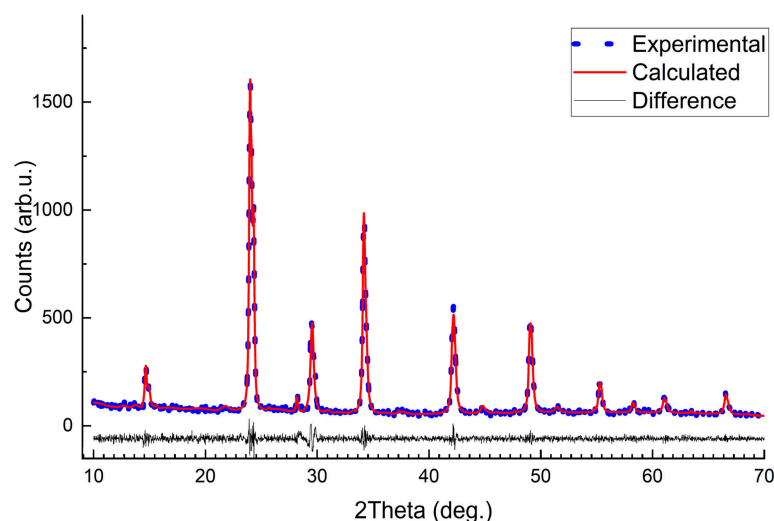


Figure 3. Rietveld refinement of samples with nominal composition $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Si}_{0.4}\text{Cl}_6$.

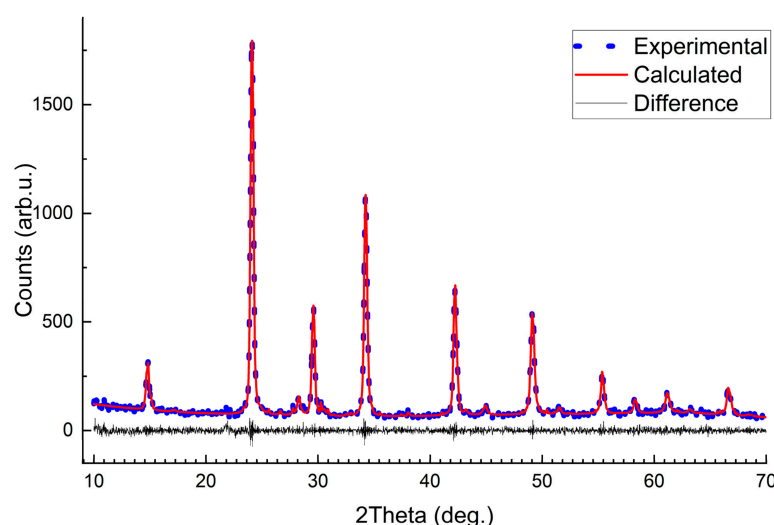


Figure 4. Rietveld refinement of samples with nominal composition $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Ti}_{0.4}\text{Cl}_6$.

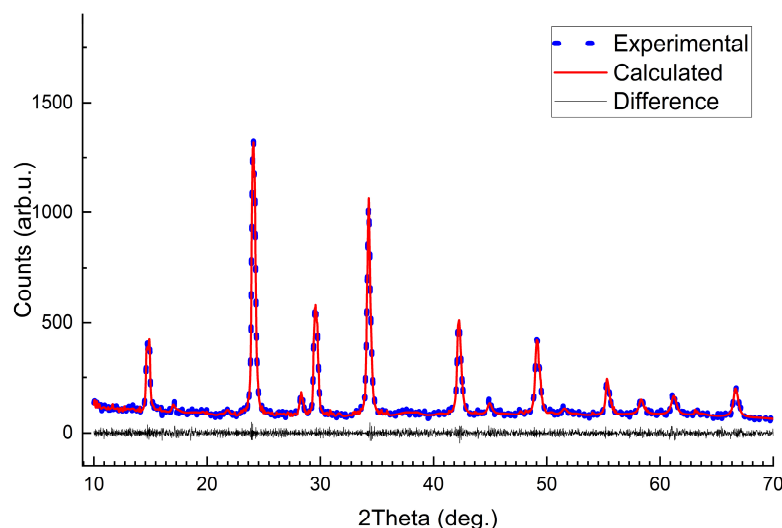


Figure 5. Rietveld refinement of samples with nominal composition $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Zr}_{0.4}\text{Cl}_6$.

Table 1. Quantitative parameters of Rietveld refinement of samples with nominal composition $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{M}_{0.4}\text{Cl}_6$.

	M = Si	M = Ti	M = Zr
a (Å)	10.23	10.33	10.41
V (Å ³)	1073	1105	1128
R _{wp}	9.07	8.83	8.53
R _p	6.48	6.41	6.33
R _{exp}	8.49	7.93	7.73
Goff (χ ²)	1.07	1.11	1.1

As shown by the fit profiles (Figures 3–5), the calculated diffractograms demonstrate satisfactory agreement with the experimental data. The obtained R-factor values fall within acceptable limits. The relatively flat nature of the difference curves indicates that the constructed structural models are sufficiently reliable. The observed local disturbances and fluctuations in the difference profile are associated, in particular, with the presence of individual single reflections for which a complete mathematical match could not be achieved within the framework of the ideal cubic model, confirming the presence of a single phase. Furthermore, when comparing the profiles, slight systematic shifts in the positions of some peaks are observed, which confirms the successful incorporation of dopants. This effect may be attributed to local microstresses and slight lattice distortions caused by the mismatch in the ionic radii of the matrix cations and dopants. As can be seen from the table, the observed changes in the lattice constants are in good agreement with the ionic radii and the Vegard's law and confirm that the dopants have successfully incorporated into the lattice. Accordingly, based on the $\text{Cs}_2\text{NaInCl}_6$ reference pattern, the lattice constant is $a \simeq 10.533$ Å. Nevertheless, these features are local in nature and do not disrupt the overall macroscopic cubic symmetry of the framework (space group Fm-3m).

Figure 6 presents SEM images and EDS elemental analysis results.

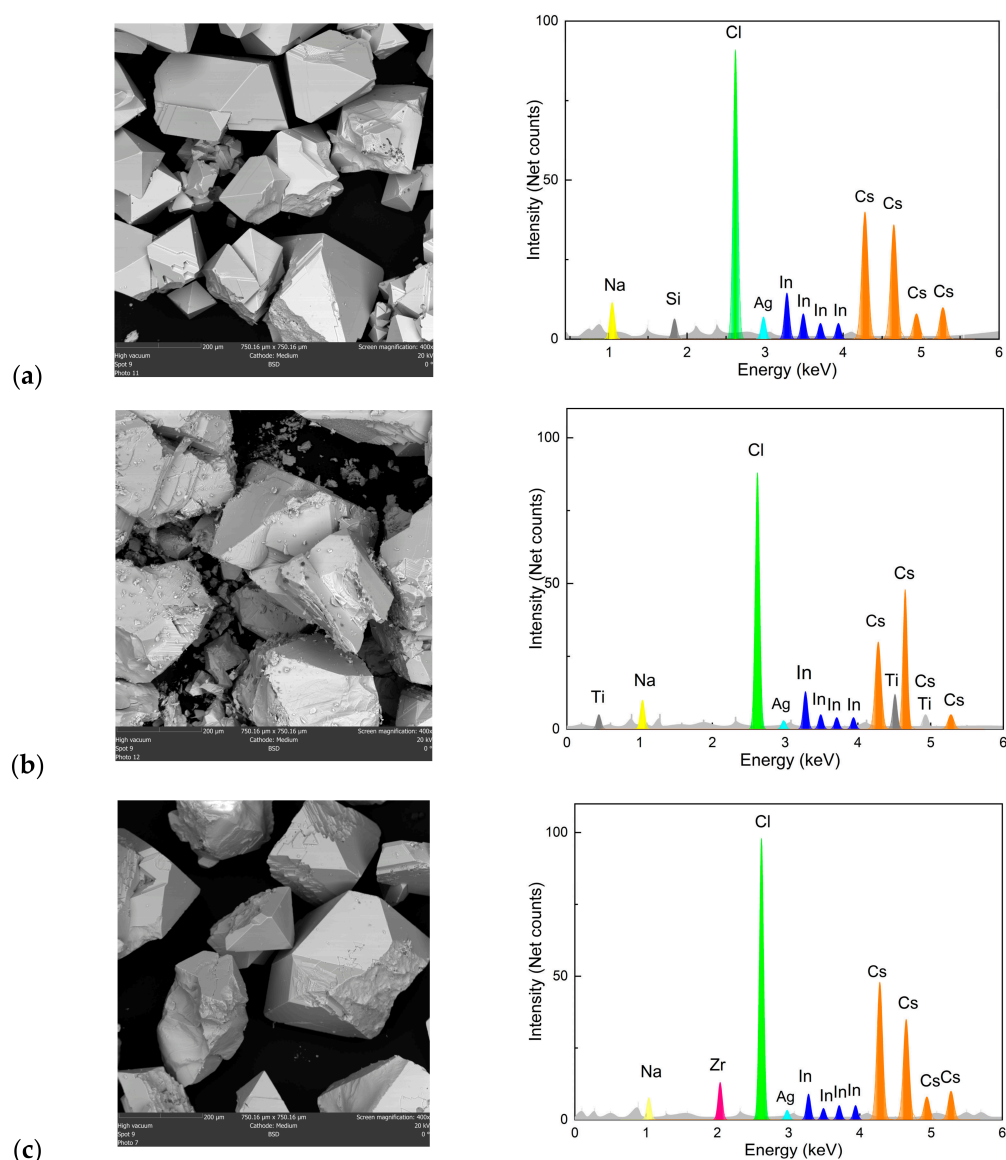


Figure 6. SEM images and results of EDS of samples with nominal composition $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{M}_{0.4}\text{Cl}_6$. (a) $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Si}_{0.4}\text{Cl}_6$. (b) $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Ti}_{0.4}\text{Cl}_6$. (c) $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Zr}_{0.4}\text{Cl}_6$.

As can be seen from the micrographs, the hydrothermal synthesis conditions facilitated the formation of a well-defined, highly crystalline morphology. For samples doped with Si and Zr (Figure 6a,c), the crystals exhibit a pronounced cubic and octahedral habit with exceptionally smooth faces and sharp, well-defined edges. The characteristic size of these isolated single-crystal blocks ranges from approximately 150 to 300 μm . The titanium-doped sample (Figure 6b) exhibits a more aggregated microstructure consisting of larger, interconnected crystalline blocks of similar sizes (150–300 μm). In the interstitial space, a small fraction of ultradisperse light-colored material (“dust-like” fractions and nanoscale crystallites) is observed. Such microstructural features are characteristic of titanium-containing double halide systems obtained by the hydrothermal method and may be associated with secondary nucleation effects or trace amounts of nanoscale unreacted precursors [26]. Nevertheless, these small surface formations do not affect the bulk crystal structure of the matrix.

The results of the quantitative elemental analysis obtained using the EDS method are presented in Table 2.

Table 2. The elemental percentage of samples with nominal composition $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{M}_{0.4}\text{Cl}_6$ (EDS).

Element	Line	M = Si	M = Ti	M = Zr
		Nominal/Measured/Deviation (at.%)	Nominal/Measured/Deviation (at.%)	Nominal/Measured/Deviation (at.%)
Cs	L	20.83/17.7 ± 4.1/−3.13	20.83/23.4 ± 6.9/+2.57	20.83/21.7 ± 1.4/+0.87
Ag	L	2.08/3.9 ± 3/+1.82	2.08/1.6 ± 0.4/−0.48	2.08/1.8 ± 0.4/−0.28
Na	K	4.17/5.7 ± 4.5/+1.53	4.17/5.4 ± 2.3/+1.23	4.17/3.8 ± 0.8/−0.37
In	L	6.25/6.8 ± 2.8/+0.55	6.25/6.3 ± 4.5/+0.05	6.25/5.2 ± 0.4/−1.05
M (Si, Ti, Zr)	L	4.17/3.2 ± 1.7/−0.97	4.17/5.7 ± 1.8/+1.53	4.17/6.6 ± 0.4/+2.43
Cl	K	62.5/62.7 ± 8.7/+0.5	62.5/57.6 ± 9/−4.9	62.5/60.9 ± 1.4/−1.6

A comparative analysis of the theoretical and experimental stoichiometry (Table 2) showed that the obtained compositions are close to the calculated values. In general, for the vast majority of the analyzed elements, the calculated deviations fall well within the acceptable limits of experimental error. The chlorine content in all samples is ~60 at.%, which corresponds to the stable phase of the double perovskite. The observed deviations in the Zr concentration (2.43 at.%) and In concentration (1.05 at.%) exceed the equipment error, and the corresponding deviations may be due to the specific distribution of element on the surface of the agglomerates, as determined by the EDS method. The relatively high standard deviations for light elements (Na) and low-concentration dopants (Si, Ag) are due to instrumental limitations of the energy-dispersive spectroscopy (EDS) method and the low intensity of their characteristic X-ray radiation against the background of the complex double perovskite matrix.

To overcome the instrumental limitations of EDS and accurately determine the bulk stoichiometry, quantitative elemental analysis by ICP-OES was performed (Table 3).

Table 3. The elemental analysis of samples with nominal composition $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{M}_{0.4}\text{Cl}_6$ (ICP-OES).

Element	Nominal Stoichiometry	Measured Composition (mg/kg)			Experimental Stoichiometry/Deviation		
		Ti	Si	Zr	Ti	Si	Zr
Cs	2	308,643	274,611.07	296,418	2.23/+0.23	2.13/+0.13	2.27/+0.27
Ag	0.2	15,850.3	16,198.55	18,344.1	0.14/−0.06	0.15/−0.05	0.17/−0.03
Na	0.4	8928.9	8365.46	8535.5	0.37/−0.03	0.37/−0.03	0.38/−0.02
In	0.6	61,234.7	64,994.64	59,910.9	0.51/−0.09	0.58/−0.02	0.53/−0.07
M (Si, Ti, Zr)	0.4	16,890.4	9850.343	22,529.6	0.34/−0.06	0.36/−0.04	0.25/−0.15

Elemental analysis confirmed that the actual dopant incorporation correlates well with the nominal compositions and is consistent with the structural parameters determined by Rietveld refinement.

Overall, XRD and Rietveld refinement confirmed the formation of the target double halide perovskite phase and phase purity, while EDS and ICP-OES demonstrated that the experimental elemental composition is in good agreement with the nominal stoichiometry. Minor local deviations in the concentrations of light components, attributed to the surface sensitivity of SEM-EDS and instrumental background effects of ICP-OES, remain within acceptable experimental errors. The overall crystal framework remains intact, with no secondary phases detected.

The room-temperature photoluminescence (PL) spectra of the crystals $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{M}_{0.4}\text{Cl}_6$ (M = Si, Ti, Zr) were recorded at excitation wavelengths of 250 and 300 nm. The results are shown in Figure 7.

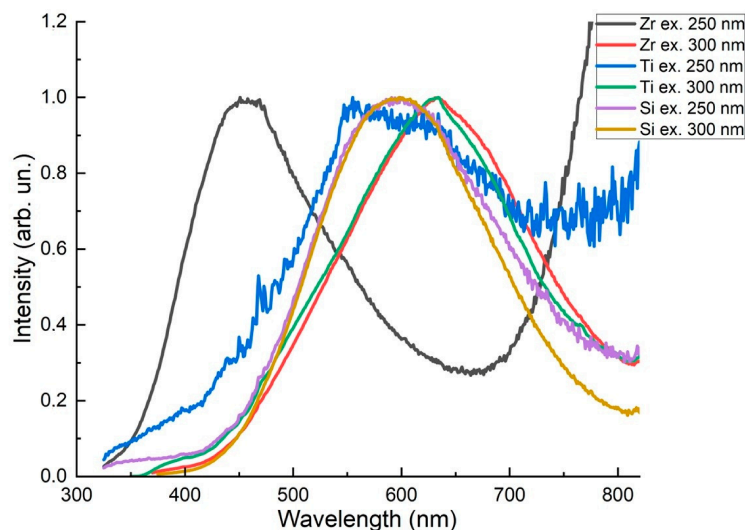


Figure 7. PL spectra of DHPs doped with different ions at different excitation wavelengths.

As shown in Figure 7, the photoluminescence of the samples typically consists of a broad band, centered close to 600 nm, with a remarkably high full width at half maximum (FWHM) of ~ 200 nm. The PL band is attributed to self-trapped excitons, similar to the prototypical $\text{Cs}_2\text{AgInCl}_6$ [5]. The precise location of the maximum varies somewhat with the chemical composition and excitation wavelength, the latter suggesting some inhomogeneous broadening effects in the samples. In the case of $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Si}_{0.4}\text{Cl}_6$ the emission varies little while switching the excitation from 250 to 300 nm; however this is not the case for $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Zr}_{0.4}\text{Cl}_6$ and $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Ti}_{0.4}\text{Cl}_6$ samples.

In the case of $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Ti}_{0.4}\text{Cl}_6$ the emission cannot efficiently be excited by 250 nm wavelength, resulting in weak and distorted shape of the PL band. The 300 nm excitation, however, still results in efficient emission centered in the red region (635 nm). The most atypical behavior was, however, observed for the $\text{Cs}_2\text{Ag}_{0.2}\text{Na}_{0.4}\text{In}_{0.6}\text{Zr}_{0.4}\text{Cl}_6$ sample. Upon excitation at 300 nm the sample exhibits STE emission with a maximum at ~ 635 nm, whereas under excitation at 250 nm, the photoluminescence band of the Zr-doped sample is heavily blueshifted, resulting in an emission band at ~ 450 nm. Such behavior indicates the possibility of two distinct self-trapped excitonic states with different trapping depths, which are selectively excited depending on the excitation energy [27]. Under 250 nm excitation, additional transitions or high-energy states are promoted, whereas at 300 nm excitation, the low-energy STEs are more pronounced [28].

The low symmetry of the emission band, characterized by a long-wavelength tail, indicates energy transfer occurring from shallower to deeper STE state. This phenomenon can be exploited for spectral tuning depending on the excitation wavelength.

As shown in Table 4, the FWHM of the photoluminescence band increases in the sequence Si–Ti–Zr under 300 nm excitation. This trend is attributed to the progressive enhancement of exciton–phonon coupling [29]. For Si^{4+} substitution, exciton localization is relatively weak due to the predominance of p states, resulting in smaller local lattice distortions. This effect becomes more pronounced for Ti and Zr substitutions owing to the presence of d states, which promote exciton self-trapping and lead to broader photoluminescence bands. Therefore, an increase in the atomic mass and d-character of the substituting cation enhances the localization of the excited state.

Table 4. Comparative PL data of DHPs.

Sample Composition	FWHM (nm)	Peak Position (nm)	Relative Intensity (arb.un)
Cs ₂ Ag _{0.2} Na _{0.4} In _{0.6} Si _{0.4} Cl ₆ (250 nm)	220	599	10.35
Cs ₂ Ag _{0.2} Na _{0.4} In _{0.6} Si _{0.4} Cl ₆ (300 nm)	197	598	3.47
Cs ₂ Ag _{0.2} Na _{0.4} In _{0.6} Ti _{0.4} Cl ₆ (250 nm)	267	555	1.5
Cs ₂ Ag _{0.2} Na _{0.4} In _{0.6} Ti _{0.4} Cl ₆ (300 nm)	210	634	1.35
Cs ₂ Ag _{0.2} Na _{0.4} In _{0.6} Zr _{0.4} Cl ₆ (250 nm)	170	451	10.6
Cs ₂ Ag _{0.2} Na _{0.4} In _{0.6} Zr _{0.4} Cl ₆ (300 nm)	218	635	1.3

From Table 4, it is evident that the photoluminescence intensities under 250 nm excitation are higher than those under 300 nm excitation. This effect is most pronounced for the Si- and Zr-containing samples. Taking into account the bandgap of the material in the range of ~5 eV, one can assume that excitation at 250 nm involves transitions closer to the band-edge states, whereas excitation at 300 nm predominantly involves transitions within the tail states of the density of states, where part of the excitation energy is presumably lost through trapping processes. Notably, the relative photoluminescence intensity reaches its maximum for the Si-containing sample under 300 nm excitation, where d states are absent. In this case, reduced lattice distortions provide more efficient charge compensation, thereby increasing the probability of radiative recombination.

For the interpretation and understanding of relaxation processes in DHPs, we recorded PLE spectra at selected emission wavelengths (Figure 8).

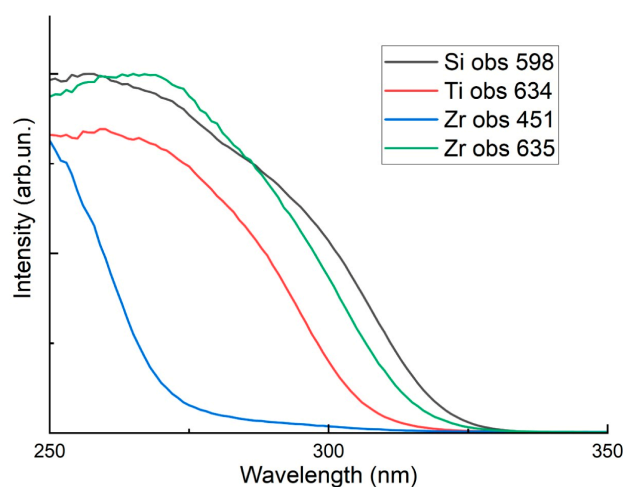
**Figure 8.** PLE spectra of DHPs recorded at selected emission wavelengths.

Figure 8 presents the PLE spectra of the Zr, Ti, and Si samples, measured at the central wavelength of PL. In case of Ti- and Si-modified samples, the observation wavelength was the peak of the orange emission (598–634 nm). In case of Zr sample, the PLE spectra of blue and orange emission (shallow and deep exciton) were measured separately. The PLE spectra corresponding to the deep exciton emission for all samples (Zr, Ti, Si) are qualitatively similar, with the PLE maximum around 260 nm. The presence of shoulders and fine structure features in the PLE band indicate some splitting of the excitation bands; however, the structure is not well resolved. In the case of the shallow exciton emission of the Zr-modified sample, the excitation band is shifted towards higher energies, in accordance with the blueshift of the emission. The excitation band maximum for the shallow exciton emission is shifted beyond the accessible spectral range of the Xe-lamp-based measurement system.

In general, all three samples are effectively excited in the ultraviolet region (250–270 nm). In this spectral range, absorption and subsequent luminescence generation are attributed to high-energy electronic transitions, such as edge interband transitions or excitonic absorption, corresponding to photon energies of approximately 4.4–5.0 eV.

The sequence of substitutions $\text{Si} \rightarrow \text{Ti} \rightarrow \text{Zr}$ leads to a gradual decrease in luminescence intensity under identical excitation conditions. This trend correlates with systematic changes in the local structural environment caused by cation substitution. Partial substitution of In^{3+} ions with Si^{4+} , Ti^{4+} , or Zr^{4+} ions leads to a red shift in both the excitation and emission spectra; the emission is observed in the range of 589–640 nm, while the bulk crystal structure is preserved.

The introduction of Si^{4+} , Ti^{4+} , and Zr^{4+} ions causes increasingly pronounced distortions of the crystal lattice, which significantly affects the photoluminescence characteristics. As the ionic radius increases in the series Si^{4+} (0.40 Å) $\rightarrow$ Ti^{4+} (0.605 Å) $\rightarrow$ Zr^{4+} (0.72 Å), enhanced local structural distortion is expected, promoting deeper exciton localization as suggested by the broadening of the PL bands. This effect is consistent with the observed reduction in emission energy and the corresponding red shift in the luminescence spectra.

The excitation (PLE) spectra of DHP doped with Si, Ti, and Zr ions display well-defined excitation bands in the ultraviolet region (256–266 nm). These bands can be attributed to ligand-to-metal charge-transfer transitions involving Cl^- (3p) states and the empty p orbitals of Si^{4+} , as well as the empty d orbitals of Ti^{4+} and Zr^{4+} [30,31]. The photoluminescence of the doped samples is broadband across the visible region and is consistent with emission originating from self-trapped excitons.

The red shift observed in both the excitation and emission spectra follows the substitution sequence $\text{Si} \rightarrow \text{Ti} \rightarrow \text{Zr}$ and correlates with the increasing involvement of d orbitals, which are absent for Si^{4+} and progressively more extended for Ti^{4+} (3d) and Zr^{4+} (4d).

X-ray diffraction analysis does not reveal significant structural differences among DHP samples doped with different ions, indicating that the observed variations in the luminescence bands are not associated with changes in the long-range crystal structure. Instead, these variations are attributed to local octahedral distortions and corresponding modifications of the ligand field, as reported previously [32].

To evaluate the thermal stability and performance of the phosphors, temperature-dependent photoluminescence spectra of DHP doped with Si, Ti, and Zr were recorded over the range from 80 to 480 K (Figures 9–11). To ensure reproducible excitation conditions throughout the experiment, the temperature-dependent PL spectra were acquired under UV-LED excitation of 280 nm.

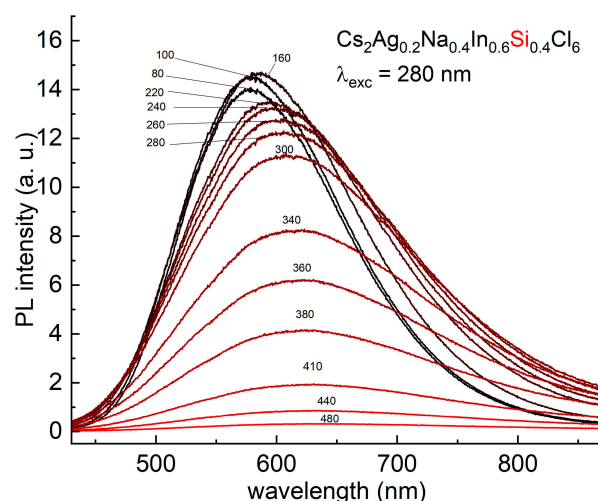


Figure 9. The PL of DHP doped with Si.

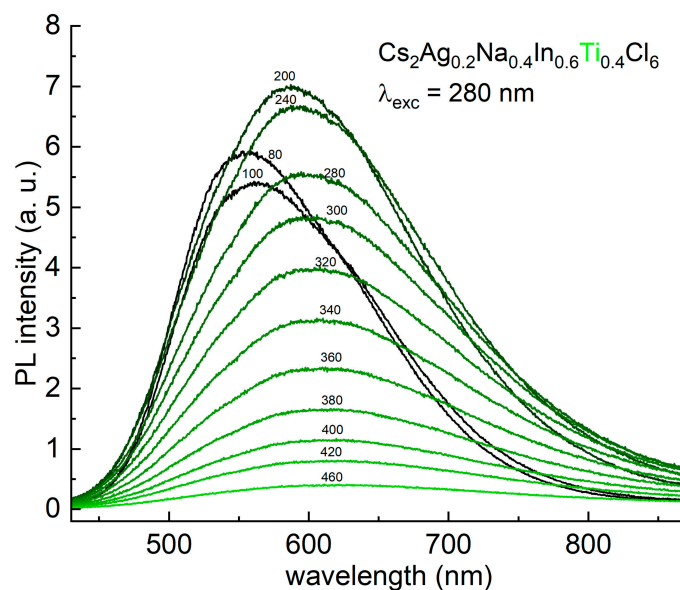


Figure 10. The PL of DHP doped with Ti.

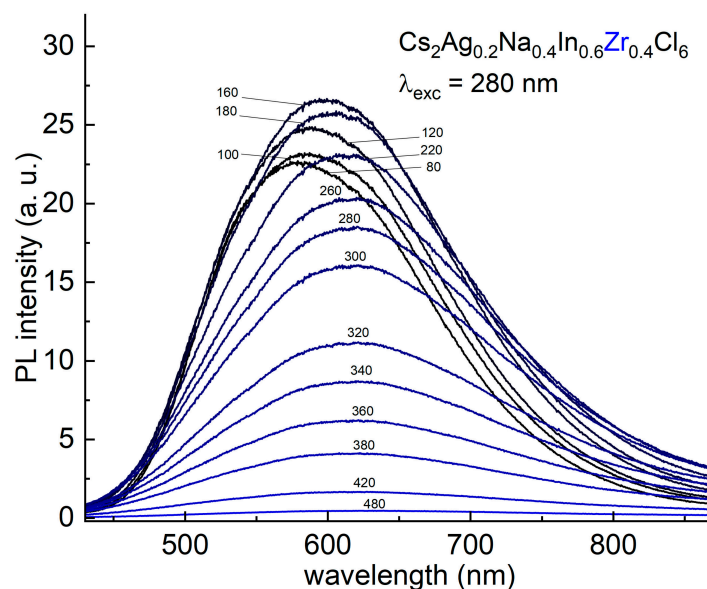


Figure 11. The PL of DHP doped with Zr.

The temperature dependent PL spectra show similar trends across all three samples, namely an initial increase in PL spectrum height with temperature in the cryogenic temperature range, followed by a decrease in PL intensity above some threshold temperature, which occurs in the 160 K–200 K range, depending on the sample. Additionally, an increase in FWHM is observed with increasing temperature as well as redshift in the luminescence peak. The decrease in PL intensity with increasing temperature is evidence of nonradiative quenching of luminescence. This is likely related to the binding energy of the exciton state. Increasing the temperature above a certain value will lead to the process of autoionization, where carriers trapped in the excitonic state are promoted to the valence and conduction bands, and ultimately recombine at luminescence quenching sites. Since this effect occurs along with the broadening and spectra shift of the PL spectra, one can conclude that the depth of the binding energy may be related to lattice expansion with simultaneous change in the bandgap of the system. In order to elucidate the actual PL intensity as a function of temperature, the total PL intensity was calculated as an integral of the temperature-dependent PL spectra in Figure 12.

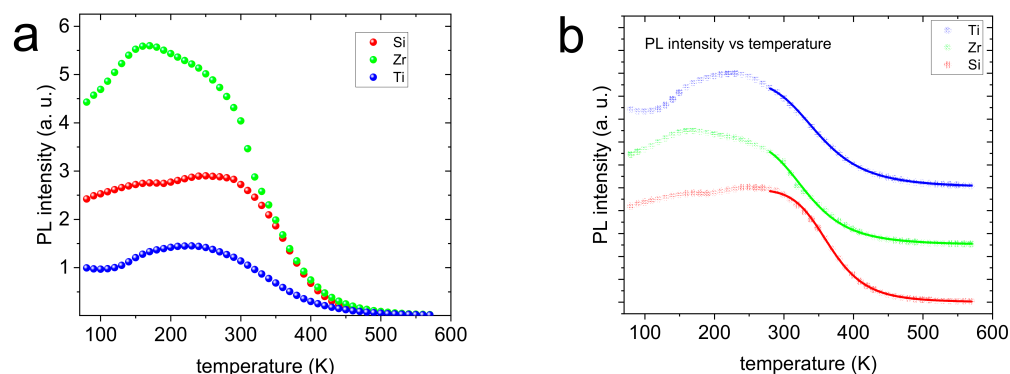


Figure 12. (a) Total PL intensity of the samples, (b) normalized PL intensity and fitting of the tail to Equation (1).

The total and normalized PL intensities with respect to temperature obtained by integrating the PL spectra in Figures 9–11 are presented in Figure 12a,b.

The temperature dependence of PL intensity is complicated, since some increase in PL intensity is observed in the cryogenic region, followed by a decrease beginning near room temperature. The decrease is attributed to nonradiative quenching and hence the tail of the data (starting from 300 K) was fitted to the standard model describing temperature-induced quenching with a single activation energy

$$I(T) = \frac{I_0}{1 + A \exp\left(-\frac{\Delta E}{kT}\right)}, \quad (1)$$

here, I_0 is the initial PL intensity, $A = \frac{p_{nr}}{p_r}$ is the ratio of the nonradiative and radiative decay rate, ΔE is the activation energy for the nonradiative quenching. The fitting result is presented in Figure 12b. The obtained activation energies ΔE are presented in Table 5.

Table 5. Nonradiative quenching parameters for the total PL intensity.

Ion	A	ΔE (cm ^{−1})
Si	$(9.7 \pm 2.3) \times 10^5$	3500 ± 60
Zr	$(4.3 \pm 1.3) \times 10^4$	2470 ± 80
Ti	$(2.3 \pm 0.2) \times 10^4$	2438 ± 26

As can be seen from Table 5, silicon has the highest activation energy indicating higher thermal stability of the luminescence. The lowest activation energy observed for the Ti-containing sample suggests rapid luminescence quenching upon moderate thermal activation.

To further characterize the luminescent properties of the DHPs, decay profiles of the samples were acquired under 325 nm excitation and are presented in Figure 13.

The decay profiles are multicomponent in nature, comprising a nanosecond (ns) component followed by an intense microsecond (μs) afterglow.

The figures show that the silicon-doped sample exhibits the slowest relaxation, while the titanium-doped sample is attributed to non-radiative losses in the Ti-containing sample. This result is consistent with the lowest activation energy for the titanium-doped sample, as shown in Table 5.

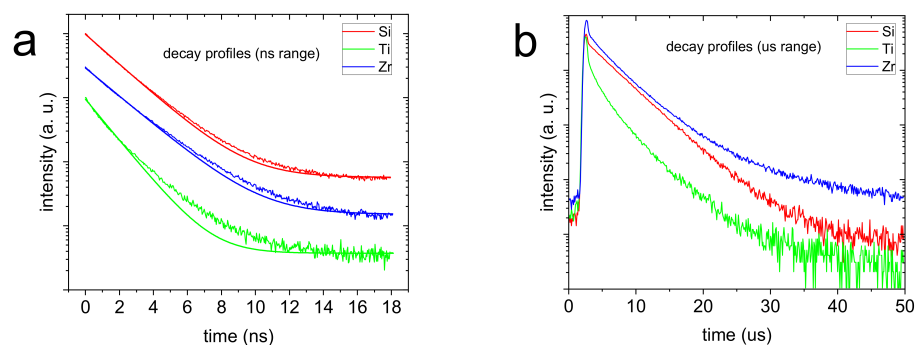


Figure 13. Luminescence kinetics of the samples in (a) ns range, (b) us range.

Complicated nature of the luminescence decay makes it difficult to perform quantitative analysis; however, the temperature-dependent decay kinetics in the ns range were further investigated with respect to temperature. Figure 14a–c presents the decay profiles of the samples under 325 nm excitation.

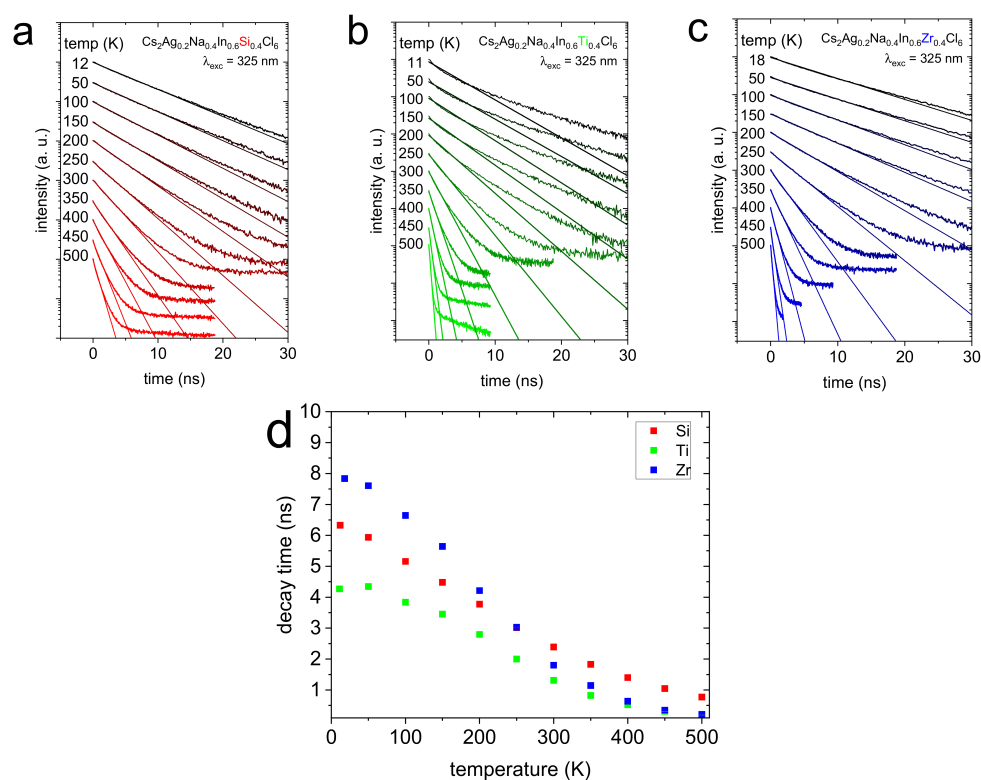


Figure 14. (a–c) Temperature-dependent ns range decay profiles of the samples along with single-exponential fitting. (d) Decay times as a function of temperature obtained from data (a–c).

Figure 14 demonstrates the temperature dependent ns range decay profiles.

The temperature-dependent decay times show a gradual shortening with increasing temperature. The decays are roughly single-exponential at low temperatures; however, with increasing temperature a long component becomes visible, interpreted as the μ s range afterglow as seen in Figure 14b. A single exponential fitting was performed, excluding the afterglow component to assess the possible mechanism for shortening of the decay time. The obtained decay time values are presented in Figure 14d. It is seen that the decay time shortening occurs gradually over the whole temperature range without a clear onset, consistent with the behavior of the PL intensity. Therefore, the shortening cannot be ascribed simply to the nonradiative quenching, which has its onset around room temperature.

At low temperatures, down to approximately 200 K, the decay time decreases in the order $Zr > Si > Ti$; at higher temperatures, the order changes to $Si > Zr > Ti$. For the zirconium-containing sample near room temperature, Zr's non-radiative quenching begins to increase more strongly compared to the Si-containing system, which exhibits thermal stability. The titanium-containing DHP sample exhibits the shortest luminescence lifetime throughout the entire temperature range.

4. Conclusions

This paper presents the results of the synthesis and study of the luminescence characteristics of double halide perovskite (DHP) crystals alloyed with Si, Ti, and Zr ions. The synthesized double perovskite samples were comprehensively characterized using XRD, Rietveld analysis, SEM-EDS, ICP-OES. The results confirm the formation of the target phase and show that the experimental elemental composition is in close agreement with the target stoichiometry. The photoluminescence spectra demonstrate a gradual shift in the emission bands toward lower energies with the transition from Si to Zr, which corresponds to the trend of increasing ionic radius. This trend is consistent with the strengthening of crystal lattice distortions and the formation of deeper localized states, which leads to a decrease in emission energy. It is important to note that the luminescence color is tuned by cation substitution without changing the structure of the main crystal matrix, which demonstrates an effective approach to controlling the optical response of the material.

Temperature-dependent photoluminescence measurements in the range of 80–480 K showed that the emission intensity of all samples decreases with increasing temperature. The maximum intensity is observed at approximately 160 K for Si- and Zr-doped samples and at approximately 200 K for Ti-doped crystals. At low temperatures (80–100 K), PL intensity is lower compared to the intermediate temperature range, indicating the presence of temperature-dependent localization effects. With increasing temperature, the emission bands shift to longer wavelengths, and this effect is particularly pronounced for $Cs_2Ag_{0.2}Na_{0.4}In_{0.6}Ti_{0.4}Cl_6$. An analysis of the activation energy for thermal luminescence quenching in the crystals under study revealed the lowest value for the last sample, indicating rapid luminescence quenching upon slight heating. The sample containing silicon exhibited the highest thermal stability.

Time-resolved luminescence measurements reveal a multi-component decay character, including a fast nanosecond decay and a pronounced microsecond afterglow, indicating the coexistence of fast and delayed recombination channels. The Ti-doped sample exhibits the fastest decay due to dominant non-radiative losses, whereas the Si system is characterized by the highest thermal stability and the longest lifetimes. The temperature dependence, including the cross-correlation of decay times, confirms that the luminescence dynamics are determined by competing thermoactivated processes rather than a single quenching mechanism.

Overall, the photoluminescence characteristics and their temperature dependence highlight the potential of these materials for devices with tunable emission colors, including light-emitting diodes (LEDs) and phosphors for white light generation, where tunable emission and thermal stability are essential.

Author Contributions: Conceptualization, N.Z. and T.L.; methodology, Z.A. and T.L.; software, Z.A.; validation, G.B.; formal analysis, Z.A.; investigation, N.Z. and N.G.; resources, K.S. and G.B.; data curation, Z.A. and G.B.; writing—original draft preparation, N.Z. and G.B.; writing—review and editing, T.L. and K.S.; visualization, K.S. and N.G.; supervision, N.Z.; project administration, G.B.; funding acquisition, N.Z. All authors have read and agreed to the published version of the manuscript.

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