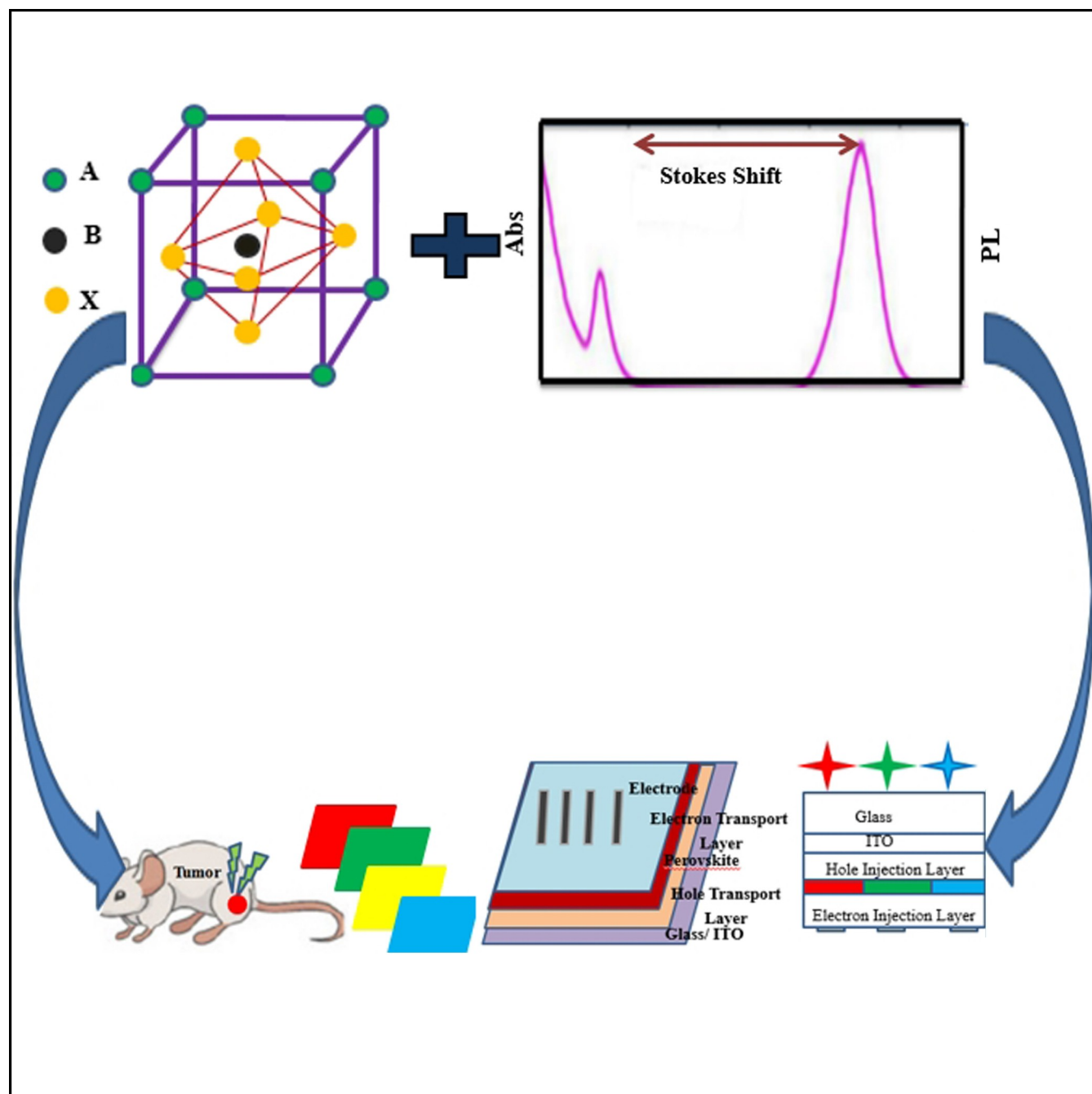


Stokes Shift in Inorganic Lead Halide Perovskites: Current Status and Perspective

Sehrish Gull,^[a] M. Haris Jamil,^[b] Xiuwen Zhang,^[a] Hoi-sing Kwok,^[c] and Guijun Li^{*,[a]}



Inorganic metal halide perovskite system is considered as a promising candidate for applications from display to biomedical industry. Intrinsic inorganic lead halides possess small Stokes shift or self-absorption, providing negative impact for both photo voltaic and biomedical applications. Therefore, the development of an inorganic halide perovskite system with large Stokes shift is a significant venture. This review aims to provide an updated survey of the Stokes shift phenomena in

the inorganic lead halide perovskites. The first section focuses about the mechanism, the second section gives different approaches in preparing inorganic perovskites with distinct Stokes shift, while the third section highlights the potential applications in both photovoltaic and biomedical areas. This review provides deep insight about the importance and usefulness of such phenomena in inorganic lead halides, essential for various applications.

1. Introduction

The class of perovskite has long roots, originating from mineral calcium titanate (CaTiO_3) founded by German mineralogist Gustav Rose in 1839 with the crystal structure having a cation, a bivalent metal and a halide anion. Later on, Russian scientist Lev. A. Perovski, named and characterized this structure. Numerous compounds are formed with this structure including oxides, carbides, nitrides, hydrides and halides.^[1] In 1958, Moller explored perovskite structure in inorganic caesium (Cs) lead halide and it was analysed that spectral response of this material can be tuned by varying the halide content.^[2]

Similarly, organic cation methyl ammonium (MA) halide perovskite has been observed in 1978 by Weber, and significant advancement was made in 90s and 2000s by Mitzi and his co-workers, leading to the incorporation into the device for the first time.^[3] The halide perovskite class possesses a general formula of ABX_3 where A is cation (organic/inorganic), B can be divalent metal (Pb^{2+} , Sn^{2+} , Ge^{2+}), and X (Cl^- , Br^- , I^- or mixture) is an anion. A is much larger than B and X.^[4-6] Family of halide perovskite materials offer a number of benefits including size controlled tuneable emission covering full spectrum, narrow full width at half maximum (FWHM), high photo luminescent quantum yield (PLQY), long range electron hole diffusion, high carrier mobility, tuneable bandgap for different (photovoltaic, opto-electronic, and biomedical) applications and the existence of Stokes shift.^[7-9]

Stokes shift is the spectral difference in the position of the band maximum of the emission and absorbance, which greatly reduces the overlap between emission and absorption to suppress the problem of FRET/re-absorption losses.^[10,11] This

phenomena has been immensely studied and investigated in different systems including Cadmium,^[12] Copper,^[13] Indium^[14] and Zinc,^[15] etc, but recently it was observed in the system of inorganic lead halides (CsPbX_3 ; X=Cl, Br, I).^[16] The underlined mechanism of achieving this phenomenon is still controversial but some details are unpinned. In case of previous systems, different factors have been studied, including the size of the nanocrystal, type of solvent used at various stages, and also the excitation-deexcitation from the different energy levels, all of which are found to govern the mechanism of Stokes shift.^[17]

Hybrid organic-inorganic metal halides constitute a big family of materials. Alteration in their properties due to compositional and structural flexibility offers wide range of applications.^[18] Phenomena of Stokes shift is regarded as one of the most useful and peculiar characteristic for the halide perovskite system by providing solution to the problem of re-absorption and enhancing the applications to the broader.^[19]

Understanding the mechanism of Stokes shift in perovskite is quite helpful in attaining enhanced benefits from this vast class of materials. Various ways have been opted to engineer the Stokes shift in hybrid perovskites, including the optimization of particle size, reaction temperature,^[20] core shell formation,^[21] doping by transition and rare earth metals,^[22] and addition of organic ligands.^[23]


Inorganic metal halide perovskites have been regarded as fascinating class of materials forming multi-dimensional structures retaining the same chemical formula, carries vast number of applications.^[24,25] The presence of Stokes shift is highly desirable in different display and biomedical systems to achieve the better output performance. However, not even a single study is available to summarize about the importance and uniqueness of Stokes shift in the inorganic lead halide system. Regarding the usefulness of this phenomena, it is essential to summarize the progress of inorganic perovskites with the mechanism of Stokes shift at this stage. Through this review we targeted to discuss about the development of inorganic caesium lead halide system by focusing on the mechanism of Stokes shift.

Herein, we analysed the existence of Stokes shift in the inorganic lead halides, and gathered comprehensive details about the progress in this area including how the various factors influence its dependence. First part explains the existence of Stokes shift by describing the detailed mechanism along with the role of different dimensions and phases in the inorganic halides and reliance of Stokes shift on those phases. Second part highlights about the various approaches together with various reaction conditions useful for attaining the

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phenomena. In the third part, we gathered the effectiveness of Stokes shift for different applications. Finally, we sum up all the available details along with future perspective of Stokes shift in the inorganic lead halides.

2. Mechanism of Stokes Shift in CsPbX₃ System

Stokes shift is regarded as the distinctive feature of the organic and inorganic lead halide system. In principle, Stokes shift less than 35 nm may cause serious issues in different systems.^[26] When a system absorb photons with high energy, it gains energy and is pushed to an excited state, followed by the rapid relaxation to state (S_1). The system would come back to the ground state (S_0) with the loss of energy due to internal conversion including vibrational relaxation and dissipation, which results in red shift of the emission spectrum compared with the absorption spectrum. Energy absorbed by the system to reach from the ground state to the excited state is more considerable than the energy of emitted photon. Generally, the energy of a photon is given as following [Eq. (1)]:

$$E = h\gamma = hc/\lambda \quad (1)$$

Where h , γ , c , and λ are Plank's constant, frequency of the excitation source, speed of light, and wavelength, respectively. For the absorption energy, $E_a = hc/\lambda_a$, the emission energy is $E_{em} = hc/\lambda_{em}$. While, $E_{em} < E_a$ and $\lambda_{em} > \lambda_a$. The Above expression states that the emission wavelength is greater than the absorption wavelength that is, emission spectra maximum shows red shift as compared to the absorption spectra maximum, as described by the Jablonski energy diagram depicted in Figure 1.^[27–29]

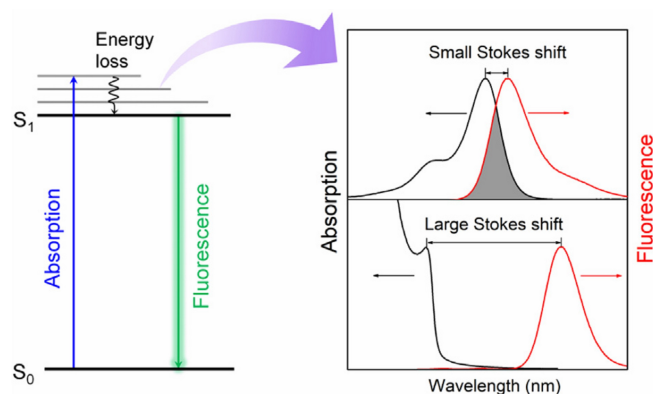


Figure 1. Representation of Stokes shift by Jablonski energy diagram. Reproduced with permission from Ref. [27]. Copyright 2021, Elsevier.

Two different mechanisms have been explained for the Stokes shift previously. In the first case, absorption takes place from S-state, which is deeper than the P-state in valence band to create exciton in the singlet state of electron and hole. In P-state de-excitation takes place with the help of phonons giving rise to the Stokes shift which is equal to the energy difference between exciton states formed with S and P hole states.^[30,31] While in the second mechanism, exciton in the singlet state first thermalizes into the triplet state where it de-excites with the help of phonons either to the deep lying original S-state or to the P-state at the top of the valence band. Also, this red shift is observed if final excited state has the same atomic configuration as the initial ground state, and it is known as the Frank-Condon shift, mostly related to the ultra-small nanoparticles.^[32,33]



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It is considered that the combination of parameters effectively control Stokes shift in colloidal systems including the type of synthesized material, size of the nanocrystals, reaction temperature, time, and type of surface coating ligands.^[34,35] Moreover, it may arise due to the band edge fine structure Splitting,^[36] phonon assisted emission and extrinsic effects like poly dispersity,^[37] and phonon self-absorption.^[38]

2.1. Phases and Dimensionalities of Cs-Pb-X System

Inorganic lead halides exist in different dimensions and phases. This class of materials are categorized into different structures including three dimensional (3D), two dimensional (2D), one dimensional (1D) and zero dimensional (0D) structures. Dimensionality of this material is defined by the linkage of the octahedral units $[\text{PbX}_6]^{4-}$ forming layers, chains and isolated units for CsPbX_3 and Cs_4PbX_6 while in case of Cs_2PbX_5 breaking of corner sharing $[\text{PbX}_6]^{4-}$ take place forming $[\text{PbX}_6]^{6-}$.^[39] Connectivity of the $[\text{PbX}_6]^{4-}$ octahedra is of manifolds, varying from corner-sharing to face-sharing to edge-sharing. If the octahedral units are isolated, it would correspond to 0D, while an arrangement of complete corner sharing octahedral would be a 3D perovskite. Figure 2 depicts the various dimensions of perovskite.^[40,41]

Caesium lead halide system having different phases including CsPbX_3 , Cs_2PbX_5 , and Cs_4PbX_6 ^[40] which can transform from one to the other under specific conditions. However, the complete mechanism is still under cover. Low dimension derivative emerged as better performer having large exciton binding energies, enhanced optical features and high structural stability.^[42]

Mechanism of Stokes shift is directly linked to the presence of Cs_4PbX_6 phase also known as “zero-dimensional perovskite”, although it possesses no structural similarity with the perovskite. This phase is considered as the sister material of CsPbX_3 .

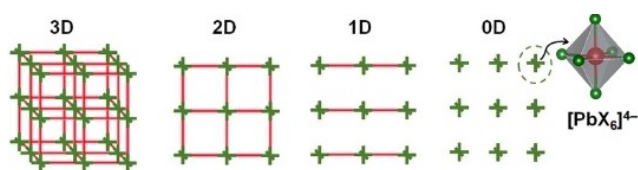


Figure 2. Representation of various dimensions of perovskite including 3D, 2D, 1D and 0D. Reproduced from Ref. [40]. Copyright 2019, Elsevier.

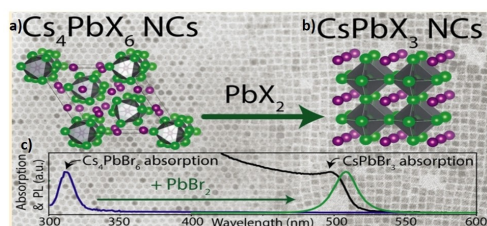


Figure 3. Structural orientation of a) Cs_4PbX_6 b) CsPbX_3 c) absorbance of Cs_4PbBr_6 , emission and absorbance for CsPbBr_3 . Reproduced from Ref. [44]. Copyright 2017, American Chemical Society.

Trigonal Cs_4PbX_6 is considered as wide bandgap material, with unique optical characteristics. From the structural point of view, in CsPbX_3 octahedron is connected with the nearby octahedron through halogen ion sharing at the edges, while in Cs_4PbX_6 each octahedron is totally separated from the closest by the intermediate caesium ions.^[6,43] Structural representation of Cs_4PbX_6 and CsPbX_3 is shown in Figure 3(a,b) along with highlighted absorbance wavelengths of Cs_4PbBr_6 and CsPbBr_3 in Figure 3(c).^[44]

Optical characteristics of Cs_4PbX_6 is a grand topic of debate. Here, we refer some most common reasons for the optical characteristics of Cs_4PbX_6 . Nikel et al., showed that Cs_4PbBr_6 possesses an emission wavelength of 545 nm, ascribed due to the CsPbBr_3 -like impurity.^[45] A very recent report by Chen et al., also suggested that during the formation of Cs_4PbBr_6 , CsPbBr_3 nano structures grows parasitically, which are actually responsible for the emission.^[46] Afterwards, Akkerman et al., reported optical properties and they concluded that Cs_4PbBr_6 exhibits no luminescence but after minor doping of CsPbBr_3 , nano crystals show strong green emission.^[44,47] Similarly, Kondo and his co-workers reported series of experiments concluding that Cs_4PbX_6 , CsX and CsPbX_3 coexist and emission arises due to small portion of CsPbX_3 while absorption is totally dependent on the Cs_4PbX_6 .^[48,49]

Zou et al., also reported no emission with strong absorbance characteristic from Cs_4PbBr_6 .^[50,51] According to one more report by Jia et al., it was observed that in the core/shell formation of $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$, CsPbBr_3 used as seed possessing strong emission while after the coating absorbance intensity magnified and further enhanced by increasing the thickness of the shell, while the emission remain unaltered.^[52] Similarly, a recent report by Bao et al., stated that the strong infra-red fluorescence observed from the alpha phase of CsPbI_3 embedded in Cs_4PbI_6 .^[53]

It is also considered that luminescence may arise due to the quasi self-trapped Frenkel excitons, system possessing the phenomena of Stokes shift arises due to the lattice relaxation. Structural variation results in various distributions of the carrier/exciton wave functions of these crystals governing the property of luminescence. CsPbX_3 is a direct bandgap phase, with the delocalized Wannier-type excitons and the luminescence originates from free Wannier excitons at room temperature. In comparison, Cs_4PbX_6 possess Frenkel type excitons captured the octahedron, carrying luminescence from self trapped excitons at room temperature.^[54,55]

3. Various Approaches Governing the Stokes Shift in CsPbX_3 System

The mechanism of Stokes shift depends on various factors starting from the synthesizing methodologies controlling the optical structural and morphological characteristics of the product. Inorganic lead halides exist in different orientations depending on the type of synthesis method used. Numerous approaches have been used and modified for achieving the

best and required characteristics from this class of materials, hot injection method is considered as the most commonly used synthesizing technique for the synthesis of inorganic lead halides due to easy synthesizing approach, allowing mono disperse, size controlled formation of nanocrystals, and cost effectiveness.^[56,57] The key factors controlling the overall process depend on the (i) ratio of surfactant (ii) reaction temperature (iii) reaction time (iv) amount and reactivity of the precursors reacting, and the (v) type of ligands used during the reaction.^[7,58] Stokes shift in the class of inorganic halide perovskites has been maximally reported through the colloidal synthesis of hot injection (HI) synthesizing strategy. In 2015, Loredana Protesescu et al., introduced synthesis of CsPbX₃ by using hot injection strategy for the first time with outstanding characteristics by utilizing inexpensive precursors. Typically, synthesis involved the preparation of caesium precursor and lead halide precursor separately at elevated temperature. Frequently, using ligands include oleic acid (OA) and oleylamine (OAm) were introduced, and then caesium precursor was directly injected into the lead precursor. All the process was carried out at elevated temperature and under inert environment.^[57]

Although not much reports are available about the inorganic lead halides with the Stokes shift because of the inadequate information about the mechanism, scientists are trying hard to dig about it in deep. Yi Yuan et al., synthesized CsPbBr₃ by hot injection strategy as previously developed with the modification of the ligand from OAm to octylamine (OTAm) and cetylamine (CTAm), enhancing the reaction time and temperature effecting the overall properties of product along with the origin of small Stokes shift of 10–15 nm.^[59] Fan Fang et al., also reported about the Stokes shift of 15 nm in CsPbBr₃ nanocrystals by typical HI method and they related the existence with the morphology.^[60] Brennan et al., reported existence of size dependent Stokes shift of ~100 to 30 meV in CsPbBr₃ nanocrystals through standard HI method.^[61] Similarly, recently, Taizu Masuda et al., reported about the existence of Stokes shift of approx. 44 meV in mixed halides by HI method.^[62] Also, a single report about the existence of large Stokes shift of about 290 nm in CsPbI₃ has been reported by S. Gull et al., by modifying the reaction temperature and the amount of injected caesium precursor.^[63] Moreover, by doping with manganese, large Stokes shift in the inorganic halide has also been reported. Qian Wang and co-workers reported about more than 200 nm Stokes shift for CsPbCl₃:Mn²⁺ with yellow emission synthesized by HI strategy.^[64] System of inorganic halides are considered as an ideal candidate from medical to the photovoltaic industry. Stokes shift is highly desirable to achieve the enhanced benefits from this class of materials, but it is quite challenging to inscribe the Stokes shift in the inorganic lead halides.

Stokes shift generally arises due to the rapid decay to the lowest vibrational level, resulting in the loss of energy by thermalization of the excessive vibrational energy. Stokes shift may further display due to solvent effects, excited state reaction complex formation, and energy transfer.^[65] Although, existence of Stokes shift and its causes in the system of inorganic halide is

at the developing phase. Here, we summarized the most common approaches responsible for achieving large Stokes shift in the system reported so far:

3.1. Size and Composition Strategy

Stokes shift is highly dependent on the size, composition and morphology. Size and morphology of the nanocrystal is mainly reliable on the synthesizing conditions.^[66] Intrinsic lead halides possess Stokes shift with size ranging from 4.1–11.7 nm has been reported by Michael C. Brennan and co-workers for the first time. Such Stokes shift of ~10 to 30 meV for CsPbBr₃ NCs has been observed as shown in Figure 4(a).^[16,61] Size dependent Stokes shift varies according to the type of halide used, in the order CsPbI₃ > CsPbBr₃ > CsPbCl₃.^[67] Previously, this size dependent Stokes shift has been reported in CdSe.^[68] It was observed that there exists inverse relation between size and Stokes shift that is, small nanocrystals possess large Stokes shift and vice versa. It is considered that size dependent Stokes shift is intrinsic to the electronic structure of the nanocrystals. In case of CsPbBr₃ nanocrystals, such Stokes shift existed due to the band edge emission and absorption as a consequence of transitions from conduction band edge states to confined hole state and valence band edge state to conduction band edge state respectively. Hence, magnitude of the Stokes shift is dependent on the energy difference between confined hole state and valence band edge state.^[16,67] Photon recycling also imparts size dependent Stokes shift. Actually, due to the quantum confinement effect (QCE), bandgap distribution enhances, when the size is quite small it results in reiteration of photon recycling and consequently red shifted emission.^[38] A similar report by Yi Yuan et al., also explained about the existence of small size dependent Stokes shift of 10–15 nm in CsPbBr₃ nanocrystal, which is attributed by the variation of reaction temperature arises due to the quantum size effect as shown in Figure 4(b).^[59]

Yinsheng Guo et al., reported about the temperature dependent Stokes shift in CsPbBr₃. They studied the mechanism with the temperature variation from 4–300 K, and it was found that below 50 K there exist no Stokes shift while after that with the increment in temperature Stokes shift appear. Until 50 K, Stokes shift decreases with the increment in the temperature because of potential fluctuations like defective sites, formational disorder and surface states that permit the relaxation and confinement into trap states before the radiative recombination as shown in Figure 4(c).^[70,72] S. Gull et al., also reported temperature dependent Stokes shift in CsPbI₃ system. From the synthesis temperature between 95 °C to 160 °C there exist large Stokes shift of 289 nm which reduces with the increment in reaction temperature and vanishes at 170 °C as shown in Figure 4(d).^[63]

Composition and morphology also contribute equally towards the occurrence of Stokes shift in the inorganic lead halide. Fan Fang et al., synthesized inorganic lead halide perovskites by different methods as shown in Figure 4(e–g). Reported Stokes shift is highly reliable on the type of halide

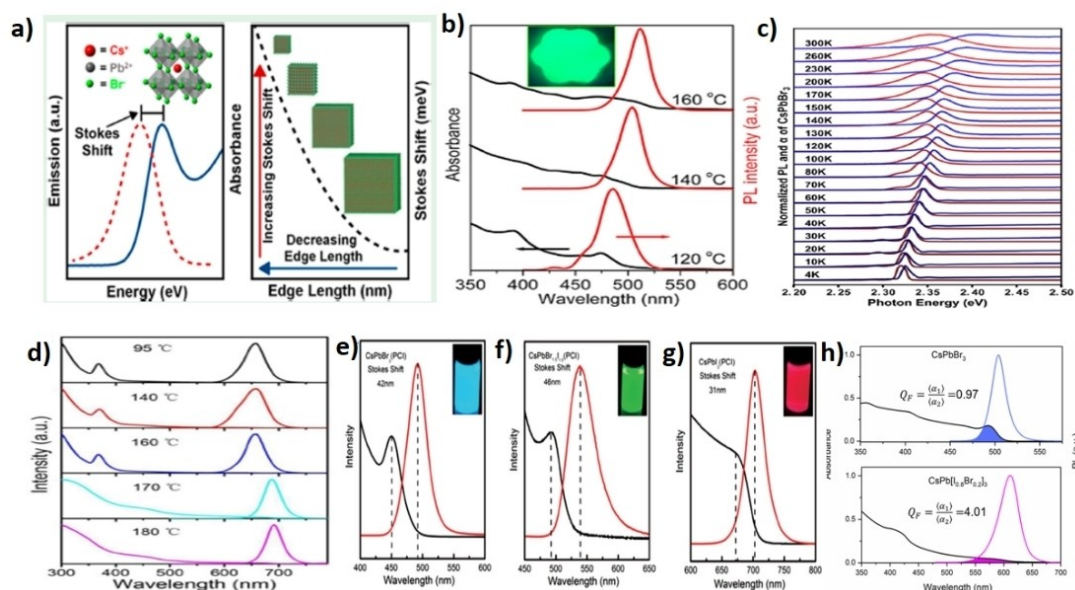


Figure 4. Size and composition dependent Stokes shift. (a) Size dependent Stokes shift. Reproduced from Ref. [61]. Copyright 2017, ACS Publications. (b–d) Temperature dependent Stokes shift. Reproduced from Ref. [69]. Copyright 2018, ACS Publications. Reproduced from Ref. [70]. Copyright 2019, Nature. (e–h) Composition dependent Stokes shift. Reproduced from Ref. [60]. Copyright 2018, Wiley-VCH. Reproduced from Ref. [71]. Copyright 2017, Elsevier.

used and the morphology attained that is, 42 nm for CsPbBr₃ (nanowires), 46 nm for CsPbBr_{1.5}I_{1.5} (nanowires), and 31 nm for CsPbI₃ (hybrid of nanorods and nanoparticles). Moreover, Haiguang Zhao and co-workers reported small overlap between emission and absorbance spectra in CsPbBr₃ and mix halides CsPb(Br_xI_{1-x})₃ as shown in Figure 4(h). In mixed system overlap was four times higher than the single halide, and the Stokes shift arises due to large size distribution in the mixed system.^[60,71]

3.2. Phase Oriented Stokes shift in CsPbX₃ System

Phase is an important parameter for the existence of Stokes shift in the inorganic lead halide perovskite. Low dimensional Cs₄PbX₆ is considered as the most significant phase regarding the mechanism. Several reports are available declaring that it is the prominent feature for the occurrence of the Stokes shift. Attaining this phase requires excess of caesium oleate with the low synthesizing temperature.^[44] It is also observed that ratio of caesium and lead halide is an important factor in achieving this major phase. Origin of luminescence from such low dimensional phase is still under intense discussion. In some cases it is considered that the luminescence is not due to the exciton emission from Cs₄PbX₆ while small inclusions from CsPbX₃ act as emission centres in Cs₄PbX₆ which enclose excitons because of the bandgap variation among the two phases.^[18]

Existence of Stokes shift has been reported significantly in CsPbBr₃ and CsPbI₃. It is considered that such phenomena are directly attributed to the presence of large bandgap, 0D Cs₄PbX₆ phase, because of highly compact structure resulting in small exciton energy, consequently giving rise to the Stokes shift.^[73] A number of reports are available about the existence

of Stokes shift in CsPbBr₃, where it was clearly declared that the mechanism is highly dependent on the low dimensional phase.^[18,44,74]

Similarly, a single report is available about the existence of Stokes shift in CsPbI₃ due to the presence of multi-phases. It was found that there exist various phases with different percentage varying with the amount of injected caesium precursor as shown in Figure 5(a, b).

Table 1 shows the exact percentage of each phase along with the injected precursor and it was observed that with maximum amount of caesium precursor Cs₄PbI₆ exist about 69% with maximum Stokes shift.

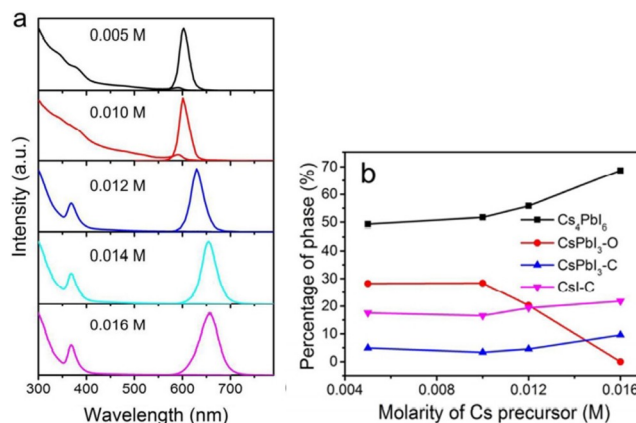


Figure 5. Variation of Stokes shift and phases along with the molarity of caesium precursor (a) Emission and absorbance at different caesium precursor (b) variation of phases with injected caesium precursor. Reproduced from Ref. [63]. Copyright 2020, Elsevier.

Caesium molarity (M)	CsPbI ₃ -C	CsPbI ₃ -O	Cs ₂ PbI ₆	CsI
0.005	4.91	28.24	49.3	17.55
0.010	3.33	28.4	51.71	16.56
0.012	4.57	20.26	55.8	19.37
0.016	9.56	/	68.68	21.76 ^[63]

3.3. Doping based Stokes shift in CsPbX₃ System

Doping is a way of intentionally inducing impurities to host system for getting changed and desired output characteristics. Doping introduce new energy bands providing new pathways for electron-hole recombination resulting in the narrow emission bandgap and thus red shifted emission. Therefore, doping helps in enhancing the Stokes shift effectively.^[75] In this regard, doping through transition and rare earth metals in the inorganic halide with large Stokes shift has been reported. For example, in the system of mixed halides (CsPbCl_{3-x}Br_x, x = 0,1,1.5,2,3) doped with Europium (Eu³⁺) has been reported with the Stokes shift of 5,10,9,10 and 11 nm, respectively. Existence of such Stokes shift in the doped system is related with the energy relaxation, occurred in the process of exciton transition from excited to the ground state as presented in Figure 6(a–c). The interaction between excitons and dopants in the host system is explained through energy transfer mechanism as shown in Figure 6d. Under the excitation wavelength of 365 nm, electrons excite from the conduction band of the perovskite host to form the bounded excitons. One portion of

electrons at the conduction band radiated photons to return the valence band, while other part relax to ⁵D₀ state of the Eu³⁺ and radiate to ⁷F_{0,6} state causing transfer of energy from excitons to Eu³⁺ to the perovskite host.^[76] According to another report, Qian Wang et al., used different Mn²⁺ ratios helpful in tuning the emission from ultraviolet to the yellow region along with Stokes shift due to the energy transfer from CsPbCl₃ host to Mn²⁺ ions. Similarly, co-doping by manganese (Mn²⁺) and Ytterbium (Yb³⁺) into the CsPbCl₃ system has also been proved as a useful strategy with multiple emissions along with the Stokes shift by providing re-absorption free system which arises due to energy transfer process from the host system to the dopants depicted in Figure 6(e, f, g).^[70] Although detailed process of energy transfer (ET) mechanism in Mn²⁺ and Yb³⁺ is still under research, but some details are discussed. Through excitation by ultraviolet light excitons first photogenerated in the perovskite host CsPbCl₃. At the band edge partial exciton recombination takes place giving rise to the bandgap photo luminescence (BG-PL). After Mn²⁺ doping, part of excited electrons, transfer energy to the excited state ⁴T_{1g} of the dopant through Dexter-type energy transfer,^[77] whereas, for the Yb³⁺

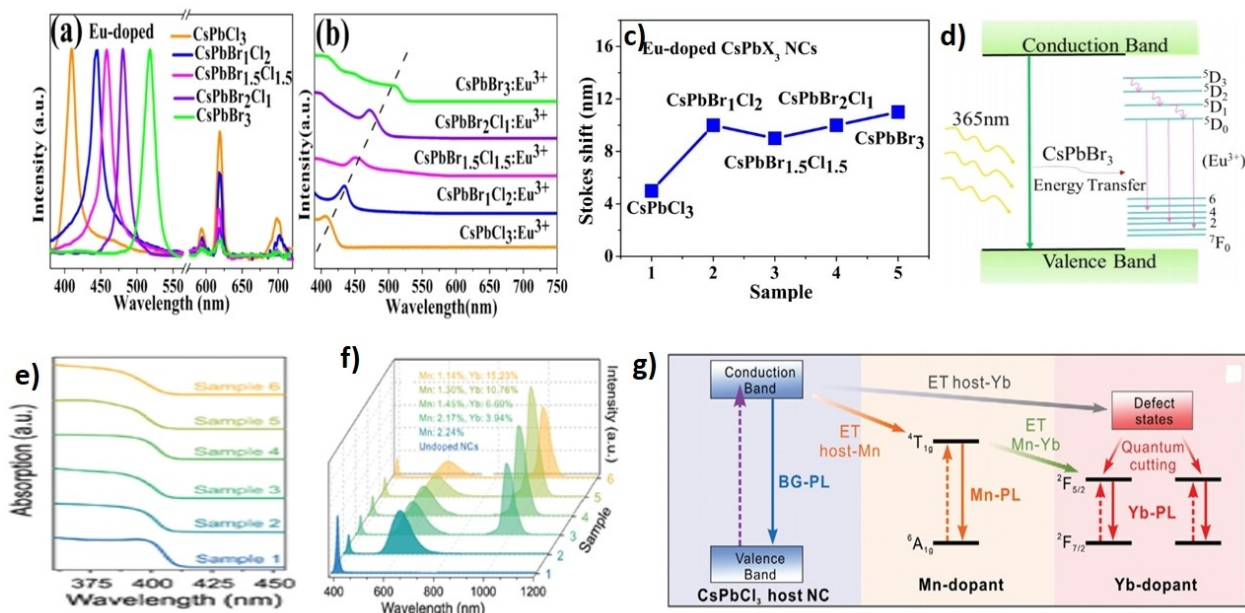


Figure 6. Doping dependent Stokes shift (a–d) Doped CsPbCl_{3-x}Br_x (x = 0,1,1.5,2,3) system with Stokes shift and ET mechanism. Reproduced from Ref. [76]. Copyright 2018, ACS Publications. (e–g) Mn²⁺/Yb³⁺ co-doped CsPbCl₃ perovskite with Stokes shift along with proposed ET process. Reproduced from Ref. [78]. Copyright 2020, Wiley-VCH.

dopants, internal lattice defects play part for the photo relaxation mechanism because of charge variation of Yb^{3+} ions in the host system. Energy transfer (ET) takes place from localized defects then to the proximate Yb^{3+} ions followed by quantum cutting process, also direct transfer of energy from the $^4\text{T}_{1g}$ state of Mn^{2+} dopant to the $^2\text{F}_{5/2}$ state of Yb^{3+} ions within the perovskite system takes place, causing population (depopulation) of the excitation states of the Yb^{3+} (Mn^{2+}) resulting in the increment (decrement) in the PLQY of the system also.^[78,79]

4. Applications of Stokes Shift

Class of inorganic lead halides has been considered as a suitable candidate for number of different applications including enhanced efficiency photovoltaic, optoelectronic, photonic and medical systems. Engineering of Stokes shift in the inorganic halide system is quite laborious. Presence of Stokes shift is highly desirable for different applications to get improved output. For photovoltaic devices, it is quite helpful in resolving the self-absorption problem, which arises due to the overlapping between the emission and absorbance of band edges where emitted photon is frequently absorbed. Similarly, for the medical systems it is quite suitable for increasing the detection sensitivity and accuracy of the system.^[80,81]

Different photovoltaic devices like large area luminescent solar concentrators (LSCs) are solar energy utilization device consisting of transparent or semi-transparent matrix materials and fluorescent active materials, where, self-absorption and fluorescence quenching are common issues that drastically limit the long optical pathways of LSCs. To solve this problem, material with suitable fluorescence along with the high photo luminescence quantum yield (PLQY) and large Stokes shift is demanded.^[82] In this regard, inorganic lead halides are considered as an appropriate material, by providing size/composition dependent PL and absorbance spectra, high PLQY along with the Stokes shift. So, to embed the required properties either mixing or doping has been applied to avoid the re-absorption problem in the LSCs.^[22,71,83]

Four times more Stokes shift in mixed halide $\text{CsPb}(\text{Br}_x\text{I}_{1-x})_3$ as compared to solo CsPbBr_3 providing less re-absorption losses and better optical efficiency has been attained and then used for LSCs.^[71] Strategy of inducing a dopant in the inorganic system also proved helpful for increasing the overlap between the optical spectra. Doping of Manganese (Mn^{2+}) into such system reported with nearly zero reabsorption emitters for LSCs has been achieved, while doping of manganese left the PL of the system almost completely unaffected.^[22] Co-doping by transition (Mn^{2+}) and rare earth (Yb^{3+}) metals into the inorganic CsPbCl_3 system provided multiple emissions and reduced re-absorption for the LSCs.^[78]

Similarly, solar cells having the ability to convert the sunlight directly into the electrical energy considered as an important entity in the renewable energy mix, where the trouble of overlapping in the optical spectra imply the energy transfer not only by diffusive charge transportation but by

repeated recycling among the photons and electron hole pairs (known as photon recycling).^[38] To overcome the obstacle of overlapping and the issue of self-absorption Stokes shift is engineered to get the better output. So, the strategy of doping,^[84] and passivation of the lead halides are quite noticeable.^[85] Moreover, such systems are also effective for photo detection and further use of such photo detector into visible light communication systems.^[86]

From a medical point of view inorganic halides proved themselves quite useful after the encapsulation by the protective layers of various polymers to cover the bio-toxicity. Inorganic metal halide based scintillators considered an auspicious approach due to fast response time without afterglow effect also having high spatial resolution providing better imaging and low cost radiographic opportunity with the presence of Stokes shift minimizing the signal cross talks along with enhancing the detection sensitivity.^[87,88] Through such system tumour detection by exosome imaging,^[89] multiplex cellular imaging and tumour targeting has been reported.^[90]

For display application, colour conversion materials with large Stokes shift are highly demanded, as the conventional luminescent materials without Stokes shift suffers from the poor contrast ratio exhibiting colourful appearance under environmental incident light. By making use of the Stokes shift, we may be able to improve the contrast ratio without additional filter for environmental light prevention.

5. Summary and Outlook

Inorganic lead halide system is regarded as the potential member with useful and interesting aspects, highly compatible for display to biomedical industry. Through this review we focused to highlight the various interesting features of inorganic caesium lead halide system, intrinsically inorganic metal halide system possess small Stokes shift. The existence of small Stokes shift imparts Förster resonance energy transfer (FRET) or re-absorption, providing negative impact on the applications. So, to address this issue the phenomenon of Stokes shift is in high demand, although not so many reports are available. We aimed to gather the updated progress in this area regarding inorganic caesium lead halide systems. Until now, various inquired reasons for the occurrence of Stokes shift include the existence due to different phase, size, morphology, halide composition, reaction temperature, and doping. Still enormous efforts are needed to dig about the actual mechanism in deep and make the system useful with enhanced benefits to the broader extent.

For the future perspective, it is needed to optimize the synthesis conditions including temperature, amount of injected precursor, inducing the combination of new ligands which is helpful in attaining the mechanism of Stokes shift. Similarly, addition of transition metal like chromium may have the ability to preserve the optical characteristic of the inorganic lead halides due to the similarity of ionic radius and valence states with lead and also been able to induce the mechanism of Stokes shift. Also, one more proposed approach is the formation

of hetero structure with the suitable material for example, a single report about the formation of CsPbI₃/PbSe has been published recently presenting the reduction in the Stokes shift caused due to the outer growth of PbSe recommending the involvement of few phonon states during the relaxation mechanism.^[91] Hence it can be concluded that the mechanism of Stokes shift in the inorganic system can be inscribed not only by variation of reaction conditions but also by the doping or growing outer shells by choosing the optimal materials.

Although, inorganic metal halide with the mechanism of Stokes shift is quite useful but the development and usage of such system is at the embryonic stage. Different applications have been reported through such system but not a single report is available about the usage of such concept as colour conversion system, where it can be helpful in controlling the Stokes loss arises due to the Stokes heat compromising the efficiency and colour quality of the product.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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