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Real-time dynamic evolution monitoring of laser-induced exciton phase flips in 2D hybrid semiconductor $(\text{C}_{12}\text{H}_{25}\text{NH}_3)_2\text{PbI}_4$

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ABSTRACT

Real-time monitoring of room-temperature exciton photoluminescence (PL) while irradiated with ultrafast laser excitations (UV and infrared) in long alkyl-chain based $(\text{C}_{12}\text{H}_{25}\text{NH}_3)_2\text{PbI}_4$ inorganic–organic hybrid semiconductors is presented. These naturally self-assembled 2D hybrid structures show strong room-temperature Mott-type excitons confined within the lowest inorganic bandgap, which are highly sensitive to structural phase flips. Under both one-photon ($E_{1\text{PA}} \geq E_g$) and two-photon ($2E_{2\text{PA}} \geq E_g$) laser excitations, the exciton PL of unstable phase-II appears initially, and with prolonged laser exposure, the PL peak switches to a new stable blueshifted phase-I peak position. This exciton phase flip demonstrates different laser-induced structural deformations in inorganic quantum wells (PbI_6 extended network) associated with orthorhombic (phase-I) and monoclinic (phase-II) unit cells. One-photon absorption induced PL shows the various time dynamics of laser exposure depending on laser characteristics (continuous wave and ultrashort pulsed lasers), mostly influenced by localized heating, ablation effects, and third-order nonlinear effects such as saturation of linear absorption and exciton–exciton annihilation. However, in two-photon absorption induced PL, the near infrared laser excitation reveals the redshifted crumpled excitons from the deeper depth of the sample, which are induced by multiphoton absorption and avalanche ionization. A series of systematic linear and nonlinear steady-state and time-resolved PL studies are presented. A simplified kinetic model further provides an understanding of the real-time evolution of laser-induced excitons and their related phase flips. These laser-induced exciton phase flips and linear and nonlinear optical probing open a new avenue for novel functional properties and nonlinear absorption–based optoelectronic devices.

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I. INTRODUCTION

During the last few decades, researchers have extensively investigated the structural and optical properties of low dimensional inorganic–organic (IO) hybrid semiconductor systems. Depending upon the R-NH_3^+ type organic moiety conformation within two-dimensional inorganic semiconductors (MX_2 ; $\text{M} = \text{Pb}^{2+}$ and Sn^{2+} and $\text{X} = \text{Cl}^-$, Br^- , and I^-), they show various dimensionalities, resembling natural self-assembled quantum dots (0D), quantum wires (1D), and quantum wells (2D).¹ Crystallographically two-dimensional (2D) van der Waals materials represented by the general formula $(\text{R-NH}_3)_2\text{PbX}_4$, where R is a long alkyl-chain hydrocarbon $[(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4$ ($n > 3$)] and X is a halogen ($\text{X} = \text{Cl}^-$, Br^- , and I^-), have alternative stacking of corner-shared PbI_6 octahedral network, separated by wider bandgap alkylammonium moieties

forming natural multiple quantum well (MQW) structures.^{2–5} Having quantum confinement and dielectric screening effects, these systems show remarkable room-temperature Mott-type exciton binding energies up to 200–300 meV.^{6–10} In addition, these MQWs show strong reversible phase transitions, which directly influence the exciton energy phase flips.^{11,12} During such phase transitions, corner-shared PbI_6 octahedra can be either in staggered or in eclipsed arrangements, which often adopt orthorhombic and monoclinic crystal packing, respectively.¹³ These phase transitions are pronounced with temperature, thickness, and aging effects.^{11,14} It is also suggested that the conformed alkylammonium chains within the PbI_6 network changes undergo a flip from *trans* to *gauche* (or vice versa) arrangement during phase transition, which dictates the PbI_6 structural staggering.^{4,11,14} Since the exciton energies are strongly dependent on

structural packing, the phase-induced optical exciton switching is further helpful in various optoelectronic and advanced photonic devices.^{15–17}

When laser light interacts with such 2D van der Waals IO hybrids, the optical processes undergo a simple linear process (optical excitation, etc.) to a wide range of nonlinear processes depending upon various laser parameters such as wavelength and incident laser intensities.^{18,19} Upon continuous wave (CW) resonant excitation (in the absorbing region, $\hbar\omega \geq E_g$), along with typical linear band-to-band electron excitation, the irradiation further causes local heating and ablation effects,²⁰ whereas in the case of pulsed laser excitation, per pulse energy/intensity is extremely high enough to produce various nonlinear absorption effects such as saturation of absorption and exciton–exciton annihilation.^{18,19} In such cases, the absorption coefficient of the medium follows a nonlinear expression $\alpha = \alpha_0 + \beta I$, where β is the third-order nonlinear absorption coefficient.^{18,19} At relatively higher intensities, the laser-induced localized temperatures rapidly increase, thus causing structural deformation as well.^{21–24} On the other hand, with infrared high intensity laser excitation (nonresonant condition), two-photon induced absorption (2PA) is the dominant observed third-order nonlinear process, in which electrons in the valence band can absorb two (or more) low energy photons ($2\hbar\omega \geq E_g$) simultaneously and make an electronic transition to the conduction band and subsequently the relaxation of the electron resulting in the emission of a photon with a frequency greater than that of absorbed photons.^{15,18} Such two-photon probing by high intensity ultrashort pulses reveals information from the deeper depth of the sample of lattice defects and misaligned layers.¹⁸ During high intensity infrared pulse interactions, structural modifications can also take place through nonlinear optical processes via multiphoton absorption, tunneling, and avalanche ionization.^{19,21}

In this work, we demonstrate *in situ* laser-induced exciton photoluminescence (PL) changes in the naturally self-assembled $[(C_{12}H_{25}NH_3)_2PbI_4]$ ($n=12$, hereafter C12PI) IO hybrids. A series of linear and nonlinear steady-state and time-resolved PL studies of exciton phase-induced flip are presented in a systematic fashion. A diverse range of laser excitations are used to reveal many interesting facts about the origin of exciton PL and related structural phase-induced changes upon prolonged laser exposure.

II. EXPERIMENTAL DETAILS

The synthesis of dodecylammonium tetra iodoplumbate $[(C_{12}H_{25}NH_3)_2PbI_4]$, C12PI was carried out by mixing a stoichiometric amount of dodecylamine ($C_{12}H_{25}NH_2$) and lead iodide (PbI_2) in hydroiodic acid (HI; 57%) under constant stirring at room temperature.^{5,11,12} The resultant yellow color precipitate was filtered, washed, and dried for several days. The synthesized compound was dissolved in organic solvents such as tetrahydrofuran (THF) and the thin films (~ 150 nm) were obtained by spin coating the homogeneous solution on a pre-cleaned glass substrate and used for further experiments.

Various lasers were utilized to study the (i) 400 nm excited 1PA-PL and (ii) 800 nm excited 2PA-PL properties of C12PI. For 1PA-PL, the sources are (a) 400 nm CW laser (power, $P = 5$ mW,

intensity, $I = 2 \times 10^4$ W/cm²), (b) 400 nm fs1 [average power (P_{avg}) = 150 μ W, peak power (P_{pp}) = 15 W, $I = 0.6$ GW/cm²], and (c) 400 nm fs2 [P_{avg} = 40 μ W, peak power (P_{pp}) = 3×10^5 W, $I = 1 \times 10^3$ GW/cm²]. A BBO (Beta Barium Borate) nonlinear crystal is used to generate 400 nm from the fundamental 800 nm of fs1 and fs2 lasers. The 2PA-PL measurements were carried out by utilizing (a) 800 nm fs1 (P_{avg} = 150 mW, P_{pp} = 15×10^3 W, $I = 12$ GW/cm²) and (b) 800 nm fs2 (P_{avg} = 1 mW, P_{pp} = 8×10^6 W, $I = 7 \times 10^3$ GW/cm²) lasers. fs1 laser is an oscillator laser (Spectra-Physics, MaiTai, 690–1040 nm, 84 MHz, and 120 fs), and fs2 laser is a Ti:sapphire amplifier (Spectra-Physics, Spitfire Ace, 800 nm, 1 kHz, and 120 fs). A fiber optic coupled spectrometer, attached with a computer, is used to collect the spectra through appropriate high- and low-pass filters.¹⁸ 1PA- and 2PA-PL decay measurements on thin films were carried out using a Time Correlated Single Photon Counting (TCSPC, Becker & Hickl; SPC-130) detector (up to 10 ns) using (i) 400 nm and (ii) 800 nm fs1 excitation sources separately.

III. RESULTS AND DISCUSSION

Long alkylammonium based IO hybrids $[(C_nH_{2n+1}NH_3)_2PbI_4]$; $n = 12, 16$, and 18] are having special characteristic features of dual phase with stable orthorhombic (phase-I) and metastable monoclinic (phase-II) crystal packing, which are highly sensitive to temperature, aging, and heaviness due to thickness.¹¹ In these naturally assembled MQWs, the strong room-temperature Mott-type excitons are confined within the lowest inorganic (PbI_4^{2-} network) bandgap with substantially enhanced binding energies.¹¹ The typical absorption spectra for C12PI $[(C_{12}H_{25}NH_3)_2PbI_4]$ for both phase-I and phase-II are shown in Fig. 1(a). The narrow exciton absorption peaks are found to be at 490 nm and 505 nm corresponding to phase-I and phase-II, respectively. Both phases are having slightly different structural packing with Pb–I–Pb bond angle crumpling of PbI_6 network between phase-I and phase-II being 150.19° and 157.42°, respectively [Fig. 1(c)]. The schematic energy level diagrams for phase-I and phase-II in Figs. 1(b) and 1(d) represent various optical processes such as linear absorption and one- and two-photon radiative (1PA-PL and 2PA-PL) processes within the lowest inorganic bandgap.

Figure 1(a) shows one-photon and two-photon absorption induced PL excited by 400 nm (fs1 laser, where $E_{1PA} > E_g$, $I \sim 0.6$ GW/cm²) and 800 nm laser (fs1 laser, where $2E_{2PA} > E_g$, $I \sim 12$ GW/cm²). The conventional one-photon PL (1PA-PL) is essentially induced by direct excitation of the conduction band, where $E_{1PA} \geq E_g$ and the excitation involves the band-to-band transition followed by eventual radiative deactivation via exciton states. In the present case, both exciton PL peaks corresponding to phase-II and phase-I are observed. At the initial states of laser irradiation, the PL is dominated by phase-II (~ 517 nm) and upon longer duration, the emission is dominated by phase-I peak (~ 496 nm). The effect of laser irradiation will be discussed in the Secs. IV and V.

On the other hand, the two-photon excitation (2PA) is a third-order nonlinear excitation process where two photons ($2E_{2PA} \geq E_g$) are required to achieve a population of the conduction band and eventual radiative transition from the exciton states. When we compare both 1PA- and 2PA-PL, they show similar distinctly different phase-I and phase-II emissions but 2PA-PL

FIG. 1. (a) Exciton absorption and PL spectra of phase-I and phase-II of the C12PI thin film. The linear (one-photon induced PL, 1PA-PL) and nonlinear (two-photon induced PL, 2PA-PL) excited PL are shown by downshifting along the y axis scale. The phase-II (red) and phase-I (blue) contributions are indicated with dotted lines and double headed arrows, respectively. Schematic energy level diagram for (b) phase-I and (d) phase-II showing various optical processes: linear absorption and one-photon (1PA) and two-photon (2PA) absorption induced photoluminescence processes within lowest inorganic (PbI_4^{2-} network) bandgap. (c) Schematic crystal packings of $(\text{C}_{12}\text{H}_{25}\text{NH}_3)_2\text{PbI}_4$ (C12PI) phases, wherein the Pb–I–Pb extended network Pb–I–Pb bond angle variations are projected.

emission peaks are redshifted by about 50 meV energy difference, compared to 1PA-PL [Fig. 1(a)]. In our recent communication,¹⁸ it was extensively discussed that the origins of 1PA-PL and 2PA-PL are different: 1PA excitation essentially invokes only the free-excitons from the top few layers and 2PA excitation probes the deep-level crumpled-excitons due to the larger penetration depth. Thus, our study clearly demonstrates the two types of excitons in each phase (phase-I and phase-II) involved by linear and nonlinear excitations. Both these characteristic excitons show entirely different radiative properties and crystal packing dependence which will be discussed in Secs. IV and V.

The laser-induced room-temperature phase-II to phase-I flips are complex to understand. In particular, the nonlinear excited excitons, wherein due to higher laser intensities of short-pulse lasers, the induced third-order nonlinearities may cause several higher-order processes such as saturation of absorption, exciton–exciton annihilation, and excited state absorption.¹⁸ To explore the exciton switching behavior in both linear and nonlinear excitation, the PL spectra are monitored in the real-time spectral domain for longer duration laser exposure.

The real-time PL monitoring of various 400 nm (CW and pulsed) laser excitations are shown in Fig. 2. Here, three types of 400 nm excitations are used: (a) CW laser, (b) femtosecond high repetition (84 MHz, fs1) laser, and (c) femtosecond low repetition (1 kHz, fs2) laser. In all studies, at the initial stages, the phase-II PL at ~517 nm is dominating with PL contribution at ~496 nm (of

phase-I) either appears as a shoulder or low intense emission. After continuous exposure of laser irradiation, the phase-I PL intensity gradually dominates at the expense of phase-II PL. These studies are close to the temperature-dependent PL changes, where the phase transformation occurs from low-temperature to high-temperature.^{11,14} However, it is to be noted that the laser average power (P_{avg}) levels of these three different excitation sources are substantially different; therefore, the eventual PL transformation rate is also different. In general, in all cases, the increasing trend of PL intensity phase-I gradually stabilizes and reaches to a threshold. In CW excitation, the decrease/bleaching of PL at a longer duration is due to local heating and ablation effects [Fig. 2(a3); marked in the shaded region],²⁰ whereas in the case of 400 nm femtosecond laser excitation, per pulse intensity is extremely high enough (15 W and 3×10^5 W for fs1 and fs2) to produce nonlinear effects such as changes in the excited state population and nonlinear absorption effects. Thus, the incubated absorption and eventually radiative deactivation induced by prolonged laser exposure substantially vary with time, according to the characteristics of the laser. At the same time, the 1PA-PL spectral profiles are the same for all excitations. Upon optical excitation using a femtosecond laser, the radiative processes are dominated by several nonlinear optical effects, including absorption saturation and exciton–exciton annihilation.¹⁸ A detailed discussion on nonlinear 1PA-PL can be found in our previous communication.¹⁸ The transient behavior of these nonlinear 1PA-PL at different laser excitation intensities will give more details

FIG. 2. Laser-induced one-photon excited PL (1PA-PL) dynamic changes of C12PI: (a1)–(c1) show the time vs PL spectral mapping and phase switching behavior when excited with CW, fs1, and fs2 lasers of 400 nm. Corresponding spectra are depicted in (a2)–(c2). The phase-II and phase-I PL at 517 nm and 496 nm are marked with dotted lines as I and II. (a3)–(c3) represents PL peak intensities plotted along with laser exposure time. Dotted line curves are obtained from the JMAK model fits using Eq. (1).

of such nonlinearities, which will be discussed later. Furthermore, the dynamic evolution of both phase-I and phase-II PL intensities are explained through a growth model in Secs. IV and V.

The optical excitation in the below bandgap NIR region, two-photon (2PA) induced absorption ($2E_{2PA} \geq E_g$) and the consequent visible emission (2PA-PL), is an interesting third-order nonlinear process. Here, the absorption cross sections follow $\alpha = \alpha_0 + \beta I$, in which the laser excitation intensity-dependent nonlinear absorption (β) arises mainly from two- (or multi-) photon absorption, reverse saturation of absorption, etc. Due to the minimum absorption in the NIR region, the nonlinear two-photon absorption is more insightful of the deeper energy levels of the sample due to the larger penetration depth ($1/\alpha$), whereas conventional absorption accesses only the surface region (top few layers).^{18,25}

The real-time PL monitoring for longer laser exposure under 800 nm fs1 and fs2 excitation lasers are shown in Fig. 3. As discussed before, slightly redshifted 2PA-PL originated from crumpled-excitons states which are contributed from the deeper depths of the sample. The 2PA-PL phase flips from initial phase-II to longer exposure phase-I are the same as 1PA-PL results (Fig. 2). Since 2PA-PL occurs at relatively higher laser intensities (12 and 7000 GW/cm² for fs1 and fs2 lasers), the PL exciton switching due to structural modification involves various nonlinear processes such as multiphoton absorption, tunneling, and avalanche

ionization.^{19,23} Also the PL exciton switching from both fs1 and fs2 laser excitations occur at different time scales depending on laser parameters (pulse energy and repetition rate),² with the respective PL peak positions remaining the same. Thus, from both Figs. 2 and 3 results, it can be inferred that both free-excitons (1PA-PL) and redshifted crumpled-excitons (2PA-PL) show laser-induced phase flips with different dynamic evolutions.

Since the origins of 1PA-PL and 2PA-PL are completely different, the time-resolved photoluminescence measurements are carried out for a better understanding of surface related free-excitons and deep-level nonlinear crumpled-excitons. The laser excitation intensity-dependent 1PA-PL ($\lambda_{em} = 517$ nm) and 2PA-PL ($\lambda_{em} = 525$ nm) dynamics are recorded using time correlated single photon counting mode using 400 and 800 nm fs1 laser excitations, respectively (Fig. 4).

Both PL dynamics show bi-exponential behavior $I(t) = I_0 + \sum_{x=1,2} A_x \exp(-\frac{t}{\tau_x})$ with two decay components (τ_1 and τ_2) and A_x is the relative amplitude contribution. These lifetime components are plotted against excitation intensities in Figs. 5(a) and 5(b), respectively. The dominant lifetimes (>70%) of 1PA-PL are in the range of 250–210 ps with a longer lifetime (τ_2) component in the range of 800–750 ps. The shorter lifetimes (τ_1) of 1PA-PL are attributed to the exciton lifetimes and the values are close to the reported literature for similar IO hybrids and other 2D

FIG. 3. Laser-induced two-photon excited PL (2PA-PL) dynamic changes of C12PI. (a1) and (b1) show the time vs PL spectral mappings when excited with fs1 and fs2, 800 nm lasers, respectively. The phase-II and phase-I PL peaks are marked as II and I. Corresponding spectra are shown in (a2) and (b2). (a3) and (b3) represents PL peak intensities plotted along with laser exposure time. Dotted line curves are obtained from the JMAK model fits using Eq. (1).

semiconductors.^{18,26,27,34,35} The longer lifetimes are attributed to defect-induced PL, born out of the structural defects of the thin film. Recently, we have reported intensity-dependent 1PA and 2PA exciton lifetimes in one of the cyclic based IO hybrid, $(C_6H_9C_2H_4NH_3)_2PbI_4$ (CHPI).¹⁸ These exciton lifetimes are strongly influenced by the one-photon induced saturation of absorption and exciton–exciton annihilation, whereas the 1PA-PL lifetimes monotonically decrease with the increase of laser intensity.^{18,26} Typically, in this laser intensity region, saturation of the absorption of the excited state is the dominating phenomena and the excited state hot electrons will follow the nonlinearity of exciton–exciton annihilation; therefore, exciton radiative lifetimes follow a decreasing trend. During the exciton–exciton annihilation process, the strong interaction of hot excitons results in

nonradiative deactivation followed by the energy transfer to other excitons which goes to the higher excited state and then radiatively relaxes to the lower energy states.¹⁸ Delport *et al.* reported the similar behavior in picosecond laser based PL decay kinetics study of $(C_2H_3NH_3)_2(CH_3-NH_3)_{n-1}Pb_{n-1}I_{3n+1}$ type IO hybrids.²⁶ Different research groups have reported laser intensity based exciton–exciton annihilation effects in PL dynamics for various 2D materials (MoS₂, black phosphorus, etc.).^{34,35}

In 2PA-PL decay dynamics (Figs 4 and 5), the dominant lifetimes (>80%) are from the longer component (τ_2) ranging between 1150 and 710 ps and the shorter lifetime (τ_1 , 400–200 ps) components are in minority with only about 20% contribution. Since two-photon excitation probes deeper inside the sample, the resulting radiative deactivation rates are composed of not only the crumpled

FIG. 4. (a) 1PA-PL dynamic decay curves of the C12PI thin film at various laser intensities. $\lambda_{ex} = 400$ nm (fs1 laser) monitored at $\lambda_{em} = 517$ nm. (b) 2PA-PL dynamic decay curves of the C12PI thin film at various laser intensities. $\lambda_{ex} = 800$ nm (fs1 laser) monitored at $\lambda_{em} = 525$ nm.

FIG. 5. (a) Laser intensity-dependent 1PA-PL exciton lifetimes of the C12PI thin film monitored at 517 nm (phase-II) ($\lambda_{\text{ex}} = 400$ nm, fs1 laser). (b) Laser intensity-dependent 2PA-PL exciton lifetimes of the C12PI thin film monitored at 525 nm (phase-II) ($\lambda_{\text{ex}} = 800$ nm, fs1 laser). (c) Plot of exciton PL energy vs Pb-I-Pb in-plane bond angle of various 2D IO hybrids.¹¹ PL maxima of C12PI phase-I and phase-II under 1PA-PL and 2PA-PL are shown in blue and red squares, respectively. Dashed lines are guide to the eye.

excitons but also the dominant structural deformation-related PL as well. At deepest thicknesses, the extended PbI_6 layers are expected to show disordered behavior in which the Pb-I-Pb in-plane bending becomes more strained.⁵ Such crumpled excitons show redshifted emission with increased broadness (Fig. 1). This is also reflected in the dominated defect-induced longer lifetimes (τ_2) compared to the exciton lifetimes (τ_1) of 2PA-PL [Fig. 5(b)]. In general, the free-exciton (1PA-PL, $\tau_1 = 250$ –210 ps) lifetimes are shorter than crumpled excitons (2PA-PL, $\tau_1 = 400$ –200 ps). Both these lifetimes show dominant intensity dependence suggesting the strong involvement of nonlinear effects related to excited state absorption mechanisms.¹⁸

IV. DISCUSSION

Naturally self-assembled two-dimensional inorganic-organic hybrids $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4$ ($n > 3$) are known to show temperature-induced structural phase transitions, while retaining the 2D layered arrangement. Barman *et al.* have reported temperature-induced phase transitions in $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4$ (C_nPI ; $n = 12, 16$, and 18) using IR spectroscopy and claimed that the crystal packing changes are broadly associated with the changes

within the conformed alkylammonium chains.^{12,28,33} At this phase change, the conformed alkylammonium chains change from *trans* to *gauche* (or vice versa) arrangement which further results in the form of structural phase transitions.^{3,11,14} Billing *et al.* have reported temperature-dependent phase transition in C_nPI 2D layered materials from single-crystal XRD analysis, wherein the phase transitions are attributed to the conformational deformation of alkylammonium chains and the consequent relative shift in the inorganic PbI_6 extended network.²⁹ At the same time, Pradeesh *et al.* extensively investigated the Mott-type exciton absorption and PL reversible phase flips for C_nPI ($n = 12, 16$, and 18) at temperatures around 60 °C due to the structural crystal packing phase flip between orthorhombic to monoclinic.^{11,14} It has been shown that these exciton phase flips are also observable due to thickness and aging effects. Phase changes are also demonstrated from room-temperature exciton PL *in situ* monitoring, when dodecylammonium iodide $[(\text{C}_{12}\text{H}_{25}\text{NH}_3)\text{I}]$ are intercalated into parental 2D inorganic semiconductor PbI_2 thin film. During this intercalation process, the unstable phase-II excitons first observed, and the most stable phase-I excitons emerge slowly and saturate.¹⁷ Shahab *et al.* also reported temperature-induced reversible phase transition in mixed halide inorganic-organic hybrid $(\text{C}_{12}\text{H}_{25}\text{NH}_3)_2\text{PbI}_{4(1-y)}\text{Br}_{4y}$ ($y = 0$ –1).⁴

In this study, we demonstrate a real-time view of the exciton behavior during prolonged laser exposure. Here, we have observed distinctly different phases: initially, the unstable phase-II followed by the stable phase-I (Fig. 2). Generally, the laser-induced structural modifications in inorganic semiconductors occur due to covalent bond breakage and the eventual collapse of the electronic bandgap.²¹ With the advancement of high power and ultrafast lasers, the laser-matter interactions reveal several progressive linear and nonlinear processes depending on the laser parameters such as laser fluence, pulse characteristics, wavelength, and interaction time.¹⁹ At relatively higher intensities, the laser interaction induced localized temperature of the interaction zone rapidly increases and causes structural deformation. Such laser-induced structural modifications can also be explained by the plasma model where covalent bond destabilization may take place due to electronic excitation.^{21,23} In our present research, the laser-induced phase transitions (Figs. 2 and 3) are born out of laser-matter interactions, when the valence band electrons are rapidly excited (from both 1PA- and 2PA-excitations) to the conduction band and these hot electrons destabilize the covalent bonding in the inorganic (PbI_6 extended network) crystal packing resulting in lattice irregularities.²¹ Here, it is to be noted that the localized temperatures of 50–100 °C are enough to observe such structural modifications in these soft two-dimensional and weak van der Waals layered hybrid material.

Another interesting observation is the photoluminescence observed while exciting in the near infrared region. The 2PA-PL show distinctly different redshifted excitons (~505 and 525 nm) compared to their counterpart 1PA-PL free-excitations (496 nm and 517 nm). These two distinctly different 1PA and 2PA excitons show different radiative dynamics (Figs. 4 and 5).

In general, the deformation of the inorganic PbI_6 layers [Fig. 1(c)] in terms of disruption in Pb-I covalent bonding results in the variation of the crystal packing. The bandgap and the consequent exciton energies are strongly correlated to the Pb-I-Pb bond angle of the PbI_6 inorganic network.¹¹ The exciton PL energies

corresponding to phase-I and phase-II of 1PA-PL and 2PA-PL are plotted in Fig. 5(c) along with various experimental exciton energies reported for different $(\text{R-NH}_3)_2\text{PbI}_4$ IO hybrids.¹¹ One can see that 2PA-PL exciton energies are lower than 1PA-PL, which matches with the speculation that the exciton energies will be lower for more crumpled inorganic layers. This is also suggestive evidence that infrared excitation provides information from the low-lying crumpled layers, which cannot be probed by conventional 1PA excitation due to penetration depth constraints.

From Figs. 2 and 3, the dynamic evolution of phase-I, at the expense of phase-II, is widely different for different excitations. This is due to the differences in the pulse characteristics and wavelength of excitation which strongly influence the linear and nonlinear properties. Such growth of phase transition/stability kinetics can be generally explained by kinetic models, including a widely accepted *Johnson-Mehl-Avrami-Kolmogorov* (JMAK) model (or *Avrami* model).^{17,30–32} With the assumption that multidynamic processes are involved during laser-induced exciton PL dynamics/transformation, the JMAK expression for exciton PL peak intensities $I(t)$ could be written as

$$I(t) = 1 - \sum_{j=1,2} \frac{1}{\exp(k_j t)^{m_j}} \quad (1)$$

where the *Avrami* exponent m depends on factors such as multiple growths, phase segregation, photobleaching, ablation or sample damage, etc. The rate constant k resembles the growth rate. For unidirectional (1D) growth/transformation, m is $\sim(+)$ 1, whereas for higher-order dimensionalities and growth saturation, its value is $>(+)$ 2. Any negative $(-)$ m value indicates the photobleaching or sample degradation. In our previous communication, we have successfully demonstrated the real-time monitoring of organic moiety $(\text{R-NH}_3)\text{I}$ intercalation into the parent 2D layered PbI_2 to obtain device-quality two-dimensional inorganic-organic perovskite $(\text{R-NH}_3)_2\text{PbI}_4$ thin films.¹⁷ This is with a motive to observe the initial nucleation followed by the desired *one-directional* intercalation and transformation of PbI_2 into an ordered 2D layered crystal packing. This was well explained by the JMAK model based on both *ideal* and *non-ideal* cases.¹⁷ Furthermore, the intercalation of long alkyl-chain halide moieties $(\text{C}_n\text{H}_{2n+1}\text{NH}_3\text{I}, n = 12)$

demonstrated the *non-ideal* phase-flip dynamics between two distinct low and high-energy excitons.

Here, we attempted to model the laser-induced phase transformation in longer alkyl-chain halide based 2D inorganic-organic hybrid material $[(\text{C}_{12}\text{H}_{25}\text{NH}_3)_2\text{PbI}_4, \text{C12PI}]$ using the JMAK model. The respective JMAK model fits for all 1PA-PL and 2PA-PL real-time PL intensity vs exposure time data are represented with dotted lines in Figs. 2 and 3. The fitted constants and m and k values are tabulated in Table I. Here, both phase-I and phase-II PL dynamic variations are fitted with double dynamic behavior ($j = 2$).

The general observations of PL dynamic evolution from JMAK modeling are as follows:

- i. Under continuous wave (CW, 5 mW) 400 nm (1PA) excitation, the unstable phase-II exciton appears from the initial exposure with a low intense phase-I exciton component [Fig. 2(a3)]. Upon prolonged laser exposure, the phase-I gradually increases at the expense of phase-II. The JMAK fitting of phase-II PL reveals a negative m value $(-)$ 0.84, indicating the decrease in the phase-II component, whereas, phase-I PL initially shows a positive value of $m = (+)$ 1.3 suggesting the unidirectional phase growth which is followed by a negative value of $m = (-)$ 1.26, indicative of laser-induced sample degradation that is shown in the shaded region. In similar IO hybrids, the ablation was observed at above 12 mW powered with 400 nm CW laser irradiation.²⁰
- ii. In the case of femtosecond laser (400 nm, fs1 and fs2) excitation, the peak powers (15 W and 3×10^5 W) are relatively high compared to CW excitation (5 mW). It is to be noted that the fs1 laser is a high repetition laser (84 MHz), compared to low repetition fs2 laser (1 kHz). Thus, with 400 nm fs1 laser, the sample degradation and phase flipping are relatively faster due to more number of laser pulses interacting with the sample [Fig. 2(b3)]. As a consequence, the phase-I growth curve is dominated by the sample degradation [$m = (-)$ 1.3], whereas, with the low repetition rate of the fs2 laser, phase-I follows a gradual unidirectional growth [$m = (+)$ 0.86] followed by photobleaching and/or sample degradation at relatively longer times [Fig. 2(c3)]. In both cases, the

TABLE I. Fitting parameters of the JMAK model for C12PI phase-I and phase-II under linear one-photon and nonlinear two-photon induced photoluminescence.

Phase-I, 496 nm					Phase-II, 517 nm			
One-photon (1PA)	k_1^{-1}	k_2^{-1}	m_1	m_2	k_1^{-1}	k_2^{-1}	m_1	m_2
400 nm, CW	26.7	57.8	(+)1.35	(-)1.26	38.46	109.9	(-)0.84	(-)0.16
400 nm, fs1	34.4	3.7×10^6	(-)1.30	(-)0.01	13.16	500.0	(-)1.17	(+)0.21
400 nm, fs2	40.0	142.8	(+)0.86	(-)0.31	30.30	169.9	(-)0.05	(-)0.80
Phase-I, 505 nm					Phase-II, 525 nm			
Two-photon (2PA)	k_1^{-1}	k_2^{-1}	m_1	m_2	k_1^{-1}	k_2^{-1}	m_1	m_2
800 nm, fs1	200	200	(+)0.21	(+)0.21	20.4	0.264	(-)0.70	(-)0.003
	62.5	41.7	(-)0.21	(-)0.04	24.39	24.39	(-)0.28	(-)0.28
800 nm, fs2	1.2	1.1	(+)0.09	(+)0.11	9.17	9.34	(-)0.39	(-)0.39
	1.8	0.3	(+)0.03	(+)0.03				

dominant laser–matter interaction phenomenon is the non-linear optical process of linear absorption saturation.¹⁸

- iii. With NIR (800 nm, 2PA) excitation, the observed phase flips [Figs. 3(a3) and 3(b3)] are dominated by the nonlinear processes (two-photon absorption and avalanche ionization) related population of conduction band and consequent exciton emission. Due to various nonlinearities involved, the JMAK model fits also follow different trends at various time zones of laser exposure. The resultant fitting parameters are given in Table I. In both fs1 and fs2 laser excitations, the phase-II conversion is dominated by fast decay [with (–) m] and the evolution of phase-I component is fast growth followed by photobleaching.

V. CONCLUSIONS

In conclusion, the laser-induced exciton PL dynamic phase flips in inorganic–organic hybrid $(\text{C}_{12}\text{H}_{25}\text{NH}_3)_2\text{PbI}_4$ (C12PI) thin film are reported. These IO hybrids show two different optical excitons that arise from the crumpling of the inorganic quantum well layers (PbI_6 extended network), which are sensitive to temperature, annealing, and thickness. These two room-temperature structural phases (orthorhombic and monoclinic) show similar two-dimensional alternative stacks of inorganic and organic networks but with differences in their PbI_6 extended network (Pb–I–Pb) crumpling. In this systematic study, we report laser-induced PL exciton phase flips from both one-photon ($E_{1\text{PA}} \geq E_g$, 400-nm excitation, 1PA-PL) and two-photon ($2E_{2\text{PA}} \geq E_g$, 800-nm excitation, 2PA-PL) prolonged laser excitations. One-photon excited (1PA) excitons are free-excitons that represent only the surface layer emissions, whereas 2PA excitons are crumpled-excitons that originated from lower-lying deeper energy levels and exhibit redshifted emission. With laser excitation in the absorbing region ($E_{1\text{PA}} \geq E_g$), distinct phase flips are observed: initial phase-II related PL shows a systematic decrease in the intensity with the evolution of a blueshifted phase-I related PL peak. These exciton PL dynamic evolutions are strongly influenced by the localized laser heating and ablation effects and third-order nonlinear effects such as saturation of linear absorption and exciton–exciton annihilation. The 1PA- and 2PA-transient PL lifetimes show strong laser intensity dependency, suggesting the involvement of third-order nonlinear processes such as exciton–exciton annihilation and multiphoton absorption. Simplified *Johnson–Mehl–Avrami–Kolmogorov* (JMAK) modeling of real-time PL dynamic processes further reveal many interesting insights, such as growth of phase-I and dissociation of phase-II components, photo-induced dissociation, and laser ablation effects. The detailed understanding of such laser-induced phase changes can be extended to many new materials such as $[(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MX}_4]$ ($n > 3$ –22) $\text{M} = \text{Pb}^{2+}$, Sn^{2+} , Ge^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , and Eu^{2+} and $\text{X} = \text{Cl}^-$, Br^- , and I^- and 3D perovskites $[(\text{C}_n\text{H}_{2n+1}\text{NH}_3)\text{MX}_3]$ ($n = 1, 2$) $\text{M} = \text{Pb}^{2+}$ and Sn^{2+} and $\text{X} = \text{Cl}^-$, Br^- , and I^- for potential applications in optoelectronics and advanced functional devices.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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