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Title: Liquid-phase sintering of lead halide perovskites and metal-organic framework glasses

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Abstract: Lead halide perovskite (LHP) semiconductors show exceptional optoelectronic properties. Important barriers for their applications, however, lie in their polymorphism, instability to polar solvents, phase segregation and susceptibility to the leaching of lead ions. We report a family of scalable composites fabricated through liquid-phase sintering of LHPs and metal-organic framework glasses. The glass acts as a matrix for LHPs, effectively stabilizing non-equilibrium perovskite phases by interfacial interactions. These interactions also passivate LHP surface defects and impart bright, narrow-band photoluminescence with a wide-gamut for creating white LEDs. The processable composites show high stability against immersion in water and organic solvents, alongside exposure to heat, light, air, and ambient humidity. These properties, together with their lead self-sequestration capability, can enable breakthrough applications for LHPs.

One-Sentence Summary: Ultrastable and highly luminescent lead halide perovskite and metal-organic framework glass composites

Main Text:

Lead halide perovskites (LHPs) exhibit tunable bandgaps, high charge carrier mobilities, and bright, narrow-band photoluminescence (PL) that could offer advantages for optoelectronic applications over conventional Si-based and binary II-VI, III-V and IV-VI semiconducting materials (1). However, for successful technological integration, LHPs must overcome their inherent polymorphism, decomposition upon exposure to polar solvents, oxygen, heat and light, the presence of trap states, and the phase segregation and leaching of toxic heavy metal ions (2, 3). Targeted high optical absorptivity and direct band gaps optimal for photovoltaics and red-light LEDs, for example, are found in the CsPbI₃ pseudo-cubic ‘black’ phases (α -, β - and γ -phases), but thermodynamic factors promote their conversion to the inactive nonperovskite ‘yellow’ δ -phase under ambient conditions (Fig. 1A) (4). LHP materials for white light LEDs will critically depend on stabilization of this red emitter, ideally combined in a single broad-band luminescent material architecture.

The formation of LHP composites may offer solutions to some of these problems (5), but the ionic nature of LHPs is not entirely conducive to composite fabrication. Functional penalties incurred include LHP aggregation and decomposition, poor mechanical stability caused by weak interfacial interactions with the chosen matrix, and the formation of high concentrations of trap states (6). Research into a subfamily of metal-organic frameworks (MOFs) called zeolitic imidazolate frameworks (ZIFs) has enabled access to high-temperature ZIF liquids and microporous glasses after quenching (7). ZIF glasses have distinct physicochemical properties in terms of their porosity, reactivity, mechanical rigidity/ductility and optical response (8–10), and have been used as host matrices for crystalline MOFs (11, 12). Together, these properties make ZIF glasses prime candidates for addressing the multiple challenges for LHP composite formation.

We describe a new class of composites, fabricated by liquid phase sintering of crystalline LHPs and ZIF glass matrices, and show that industrial powder processing techniques used to form high-performance composites can be applied to chemically dissimilar LHPs and ZIF glasses. ZIF-62 ($\text{Zn}[(\text{Im})_{1.95}(\text{bIm})_{0.05}]$ (Im: imidazolate; bIm: benzimidazolate)) and CsPbI_3 were first synthesized mechanochemically and showed the expected phase transitions (Fig. 1A, fig. S1 to S3) (13). 25 wt% CsPbI_3 was then mixed with ZIF-62 glass (denoted as $\text{a}_g\text{ZIF-62}$, glass transition temperature T_g : $\sim 304^\circ\text{C}$, fig. S3B), and the mixtures are termed $(\text{CsPbI}_3)(\text{a}_g\text{ZIF-62})(25/75)$ (11). The ex situ synchrotron powder x-ray diffraction (XRD) pattern of $(\text{CsPbI}_3)(\text{a}_g\text{ZIF-62})(25/75)$ (mixture pattern in Fig. 1B) exhibited weak Bragg peaks, ascribed to the nonperovskite δ - CsPbI_3 phase. The mixture was sintered at different temperatures (up to 350°C) and then quenched with liquid nitrogen (referred to as cryogenic quenching) under flowing Ar. The resultant composites, termed $(\text{CsPbI}_3)_{0.25}(\text{a}_g\text{ZIF-62})_{0.75}$, showed XRD features consistent with the metastable γ - CsPbI_3 phase, with gradually increasing intensity with higher sintering temperatures (Fig. 1B, fig. S4). Negligible weight loss was observed during sintering (fig. S5).

The broad PL emission of $\text{a}_g\text{ZIF-62}$ was reduced after mixing with CsPbI_3 , which we attribute to photon absorption by CsPbI_3 (fig. S6) (14). The $(\text{CsPbI}_3)_{0.25}(\text{a}_g\text{ZIF-62})_{0.75}$ composites started to show red PL emission after sintering-quenching at 175°C , with the strongest PL obtained with 275°C (Fig. 1C). Higher sintering temperatures red-shifted the PL maxima (fig. S7), concomitant with an observed decrease in the optical band gaps (Fig. 1D, fig. S6C). They also led to a lower defect density and enhanced homogeneity for the CsPbI_3 component, as indicated by the reduced PL full-widths at half-maximum (FWHM) and the longer excited-state lifetimes (fig. S8, Table S1) (15). Compared to a slower quenching, rapid, cryogenic quenching formed materials with optimal PL lifetimes and PL quantum yields (PLQY, $>50\%$) (fig. S9 and S10, Table S1).

Temperature-resolved high-resolution in situ synchrotron powder XRD was collected for $(\text{CsPbI}_3)(\text{a}_g\text{ZIF-62})(25/75)$ (Fig. 2A, fig. S11). The emerging peaks from $\sim 170^\circ\text{C}$ indicate the formation of α - CsPbI_3 ($Pm-3m$). These peaks intensified at higher sintering temperatures. During the quenching stage, the gradual emergence of β - CsPbI_3 ($P4/mbm$) (from $\sim 250^\circ\text{C}$) and γ - CsPbI_3 ($Pbnm$) (from $\sim 150^\circ\text{C}$) was evidenced (16). The deconvoluted α - CsPbI_3 crystallite size increased during sintering (Fig. 2B), consistent with the changes in band gap caused by quantum-confinement effects (5).

The evolution of α - CsPbI_3 crystallite size can be attributed to coarsening of CsPbI_3 grains and the phase transition from bulkier δ - CsPbI_3 crystallites, a cascade confirmed by synchrotron in situ small-angle x-ray scattering (SAXS). Coarsening of CsPbI_3 grains mainly occurred in the size range smaller than the XRD deconvoluted crystallite size at <10 nm, starting from 165°C (Fig. 2C, fig. S12 to S14). Upon sintering, atoms in CsPbI_3 grains became mobile from the Tamman temperature ($T_{\text{Tamman}} \sim 103^\circ\text{C}$) as approximated by $0.5 T_{\text{melt}}$ in degrees K (16, 17). A similar response could also be expected for $\text{a}_g\text{ZIF-62}$. Characteristic of liquid-phase sintering, CsPbI_3 grain coarsening and composite densification were observed at a temperature lower than the inherent T_g of $\text{a}_g\text{ZIF-62}$ ($\sim 304^\circ\text{C}$) (fig. S15) (18). The emergence of an interface resulting from densification occurs analogously to surface energy-controlled transitions from δ - to α -phase in solvent-modulated or ligand-capped CsPbI_3 quantum dots (19, 20), with the interfacial energy dominant for smaller grains resulting in phase transitions at lower temperatures. To examine our hypothesis that intimate interfacial contact is critical for phase control, we synthesized $[\text{Zn}(\text{Im})_{1.75}(\text{bIm})_{0.25}] \text{a}_g\text{ZIF-62}$ with a higher T_{melt} and higher viscosity caused by bulkier bIm

ligands and subsequently demonstrated the expected higher residual δ -CsPbI₃ content in the composite (fig. S16).

We further probed the changes in interfacial bonding within (CsPbI₃)_{0.25}(a_gZIF-62)_{0.75} by temperature-resolved synchrotron terahertz (THz) radiation and far-infrared (FarIR) vibrational spectroscopy. The 2nd-derivative spectra revealed the fine vibrational modes of Zn tetrahedra (Fig. 2D, fig. S17 and S18) (9). The modes assigned to Zn-N vibrations (~ 287 cm⁻¹) and Zn-I stretching (~ 135 cm⁻¹) within Zn(Im)₂(bIm)I tetrahedra by density functional theory (fig. S19) began to intensify with increasing temperature from $\sim 140^\circ\text{C}$. These changes were consistent with the endothermic response at $\sim 140^\circ\text{C}$ in the first heating ramp of differential scanning calorimetry (DSC) measurements, concomitant with changes in CsPbI₃ binding observed in phonon signatures and in ex situ spectroscopy (fig. S20 to S23).

Magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy provided insights into the different species complementary to vibrational spectroscopy. The broader signals from composite ¹³C and ¹⁵N spectra indicated additional disorder of ZIF component over the powder mixture (fig. S24). The ¹³³Cs MAS NMR spectra of (CsPbI₃)(a_gZIF-62)(25/75) exhibited narrow signals of δ -CsPbI₃ [260 parts per million (ppm)] (21) and CsI (~ 280 ppm). Broad, low signals extending between 0 and ~ 350 ppm can be ascribed to poorly crystalline, highly defective CsPbI₃ (Fig. 2E, fig. S25). After sintering, the broad contributions and CsI peaks diminished, and the major signals stemmed from γ -CsPbI₃. These signals exhibited notable shoulders (160 to 80 ppm), with shoulder intensities highly dependent on the sintering conditions. They could be assigned to Cs nuclei on or near the surface of CsPbI₃ grains where structural defects, sites of the interaction between the γ -CsPbI₃ and a_gZIF-62, or both are abundant. We also noted that the signals of the δ -CsPbI₃ of the same sample exhibited no shoulder, consistent with less interfacial contact between δ -CsPbI₃ and a_gZIF-62.

These observations allowed us to propose a mechanism for γ -CsPbI₃ stabilization within composites (22, 23). The α -, β - and γ -phases of CsPbI₃ have double-well phonon modes at the center of the Brillouin zone, driving the phase transition to δ -CsPbI₃ in a concerted phonon manner (24). The interfacial bonding disrupts the local Pb-I sublattice phonon modes and therefore avoids the harmonic order-disorder entropy (25, 26). Together with the physical confinement effect offered by the matrices, these factors counter the strong thermodynamic driving force to form δ -CsPbI₃.

We evaluated this mechanism further and verified embedded nanocrystals of γ -CsPbI₃ as the source of luminescence using microscopic measurements. After sintering the mixture of particles became a monolith with a smooth surface observed in scanning electron microscopy (SEM) (fig. S26 and S27). Annular dark-field scanning transmission electron microscopy (ADF-STEM) of (CsPbI₃)_{0.25}(a_gZIF-62)_{0.75} showed pronounced atomic number contrast between the two phases, further corroborated by energy-dispersive x-ray spectroscopy (STEM-EDS) elemental distribution mapping (Fig. 3A, fig. S28). The crystalline and amorphous regions were identified by scanning electron diffraction (SED) (27) with regions exhibiting Bragg diffraction corresponding to crystalline CsPbI₃ grains (Fig. 3B). Convolutional neural network (CNN) classification identified γ -CsPbI₃ as the major phase within the composite fragment. Individual grains were single-crystalline, whereas the speckle in the classification map arose from inherent ambiguities due to overlap in the diffraction peaks expected from δ - and γ -CsPbI₃ (Fig. 3C, fig. S29 and S30). The average size of CsPbI₃ from STEM was ~ 30 nm (fig. S31), readily modulated by extended ball milling before sintering, which further enhanced the composite PLQY to $>65\%$ due to a more pronounced quantum confinement effect (fig. S32) (5).

To probe the internal structure, we performed ADF-STEM tomography on a shard ($>1\ \mu\text{m}$) of $(\text{CsPbI}_3)_{0.25}(\text{a}_g\text{ZIF-62})_{0.75}$ (Fig. 3D). The voids in cross-sections of the volume are characteristic of densification processes in liquid phase sintering (18). Point diffraction data identified both δ - CsPbI_3 and γ - CsPbI_3 within the particle. A high degree of interfacial contact was correlated with γ - CsPbI_3 , consistent with the hypothesized phase control through interfacial stabilization (fig. S33). STEM-based cathodoluminescence (CL) detected strong, narrow luminescence from isolated grains ($<40\ \text{nm}$), with minor interparticle emission wavelength shifts (Fig. 3E-F, fig. S34). The variation of CL intensity is complex in origin, highly sensitive to the crystal quality and exposure to unpassivated surface states and particle size effects (28). Despite this, the CL spectra from individual grains provided incontrovertible evidence of luminescence from glass-bound nanocrystals of γ - CsPbI_3 .

Returning to the aim of achieving long device lifetimes, we evaluated the composites in diverse environmental and operational settings. The rigid, hydrophobic $\text{a}_g\text{ZIF-62}$ provided protection for CsPbI_3 (fig. S35 and S36), leading to stable PL emission for $(\text{CsPbI}_3)_{0.25}(\text{a}_g\text{ZIF-62})_{0.75}$ after extended ($\sim 20\ \text{h}$) sonication in various nonpolar, polar protic, and polar aprotic organic solvents (fig. S37). The composite also exhibited stability against 10,000 hours immersion in water, storage under ambient conditions for 650 days, mild heating and continuous laser excitation ($\sim 57\ \text{mW}/\text{cm}^2$) for $>5000\ \text{s}$ (Fig. 4A, fig. S38 to S40). The microporous composite design presents a key route to sequestration of toxic components (fig. S41 and S42), or to potential photochemical platforms where the CsPbI_3 crystals are not electronically insulated (fig. S43). $(\text{CsPbI}_3)_{0.25}(\text{a}_g\text{ZIF-62})_{0.75}$ made from mechanochemical precursors have similar performance compared with the solvothermal precursors, making the composite promising for up-scaling (fig. S44). Collectively, $(\text{CsPbI}_3)_{0.25}(\text{a}_g\text{ZIF-62})_{0.75}$ offers significant advantages over LHP composites with other substrates (fig. S45, Table S2).

Finally, an array of composites were formed from CsPbX_3 ($\text{X}=\text{Cl}$, Br and mixed halide ions) and $\text{a}_g\text{ZIF-62}$, showing a wide color gamut with narrow PL peaks (Fig. 4B and C, Table S3). For all the CsPbX_3 composites, their absolute PL intensities were at least two orders of magnitude higher than those of the corresponding pure CsPbX_3 samples, either as-synthesized or after being treated with identical sintering (fig. S46). These properties, together with the high processability (Fig. 4D), render these monolithic materials ideal candidates for downshifting white LEDs (fig. S47).

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Supplementary Materials

Materials and Methods

Supplementary Text

Figs. S1 to S47

Tables S1 to S3

References (30–61)

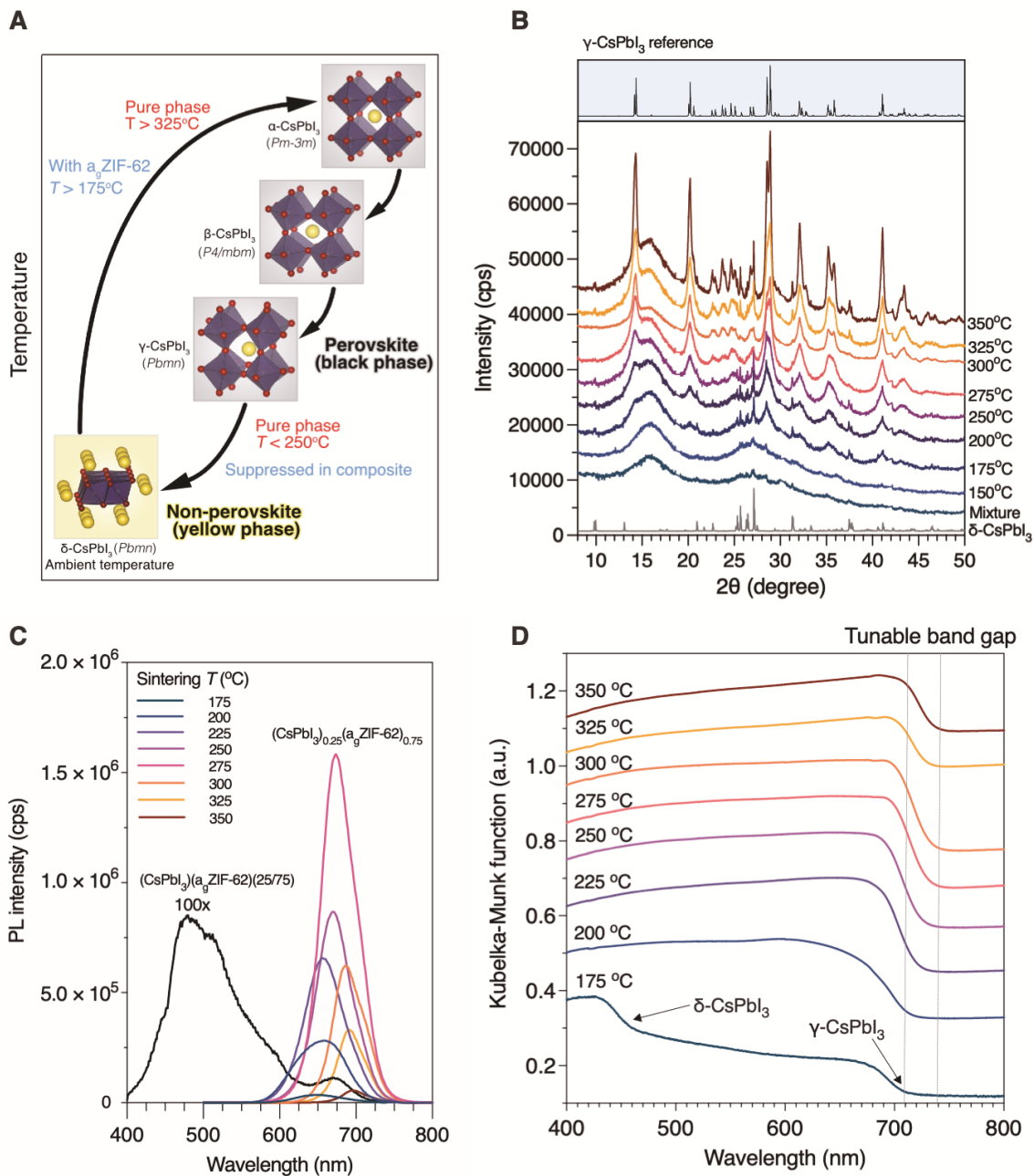


Fig. 1. Fabrication of $(\text{CsPbI}_3)_{0.25}(\text{a}_9\text{ZIF-62})_{0.75}$ composites at various sintering temperatures. (A) Phase transition of CsPbI_3 in its pure phase and within the composites. (B) Ex situ room-temperature synchrotron powder XRD for $(\text{CsPbI}_3)(\text{a}_9\text{ZIF-62})(25/75)$ (marked as Mixture) and $(\text{CsPbI}_3)_{0.25}(\text{a}_9\text{ZIF-62})_{0.75}$ composites fabricated with different sintering temperatures. (C) PL spectra and (D) Ultraviolet-visible (UV-Vis) absorption spectra for $(\text{CsPbI}_3)_{0.25}(\text{a}_9\text{ZIF-62})_{0.75}$ composites fabricated at different sintering temperatures. Arrows mark two band edges attributed to δ - and γ - CsPbI_3 observed for the sample prepared at 175°C.

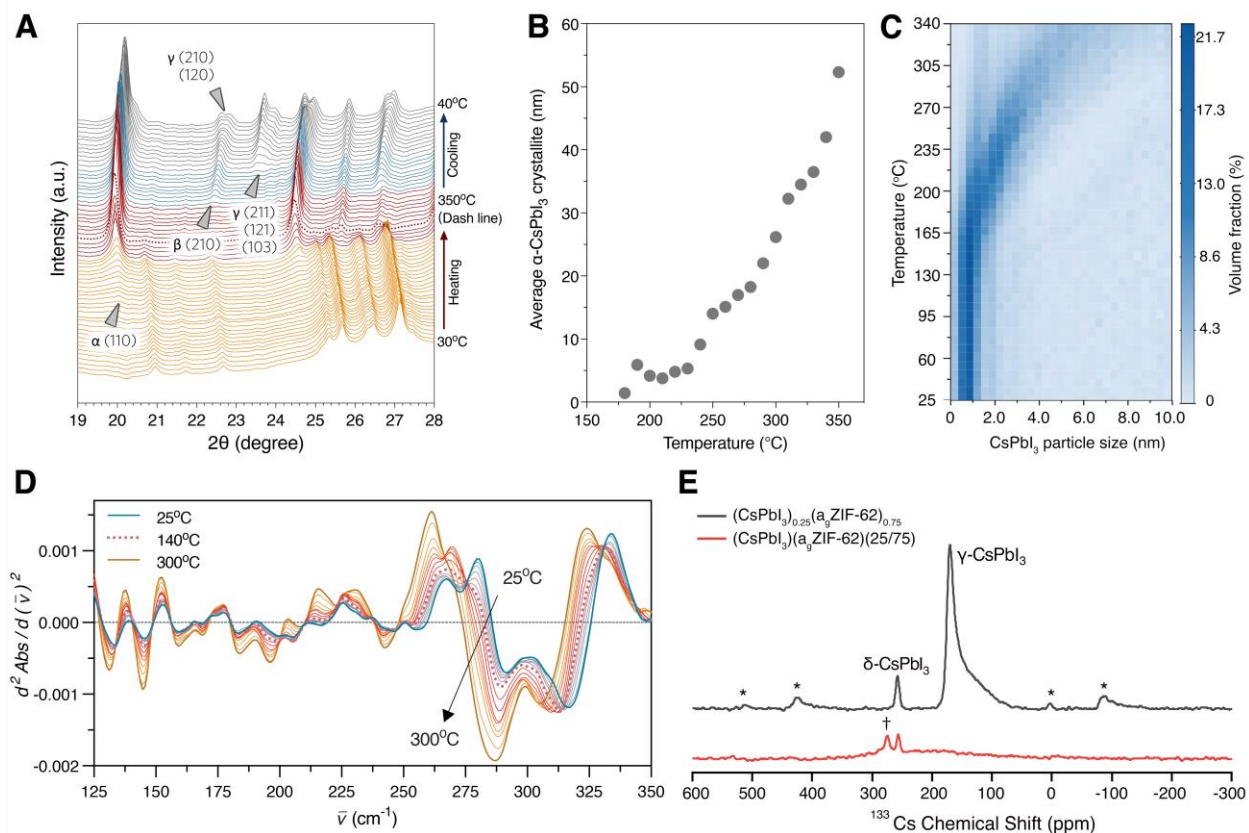


Fig. 2. Structure and bonding evolution during sintering. (A) Temperature-resolved, high-resolution in situ synchrotron powder XRD for $(\text{CsPbI}_3)(\text{a}_g\text{ZIF-62})(25/75)$, with the Bragg peak hkl indices marked for different CsPbI_3 phases. The dominating phases are color-coded as: δ (yellow), α (red), β (blue) and γ (gray). (B) Average sizes of α - CsPbI_3 deconvoluted from in situ powder XRD. (C) CsPbI_3 particle-size evolution during sintering fitted from in situ SAXS patterns. (D) Temperature-resolved 2nd derivative in situ THz FarIR spectra for $(\text{CsPbI}_3)(\text{a}_g\text{ZIF-62})(25/75)$ during the first heating ramp. (E) ^{133}Cs MAS NMR spectra of $(\text{CsPbI}_3)(\text{a}_g\text{ZIF-62})(25/75)$ and 275°C sintered $(\text{CsPbI}_3)_{0.25}(\text{a}_g\text{ZIF-62})_{0.75}$. (* denote spinning sidebands and † denotes the weak signal of CsI).

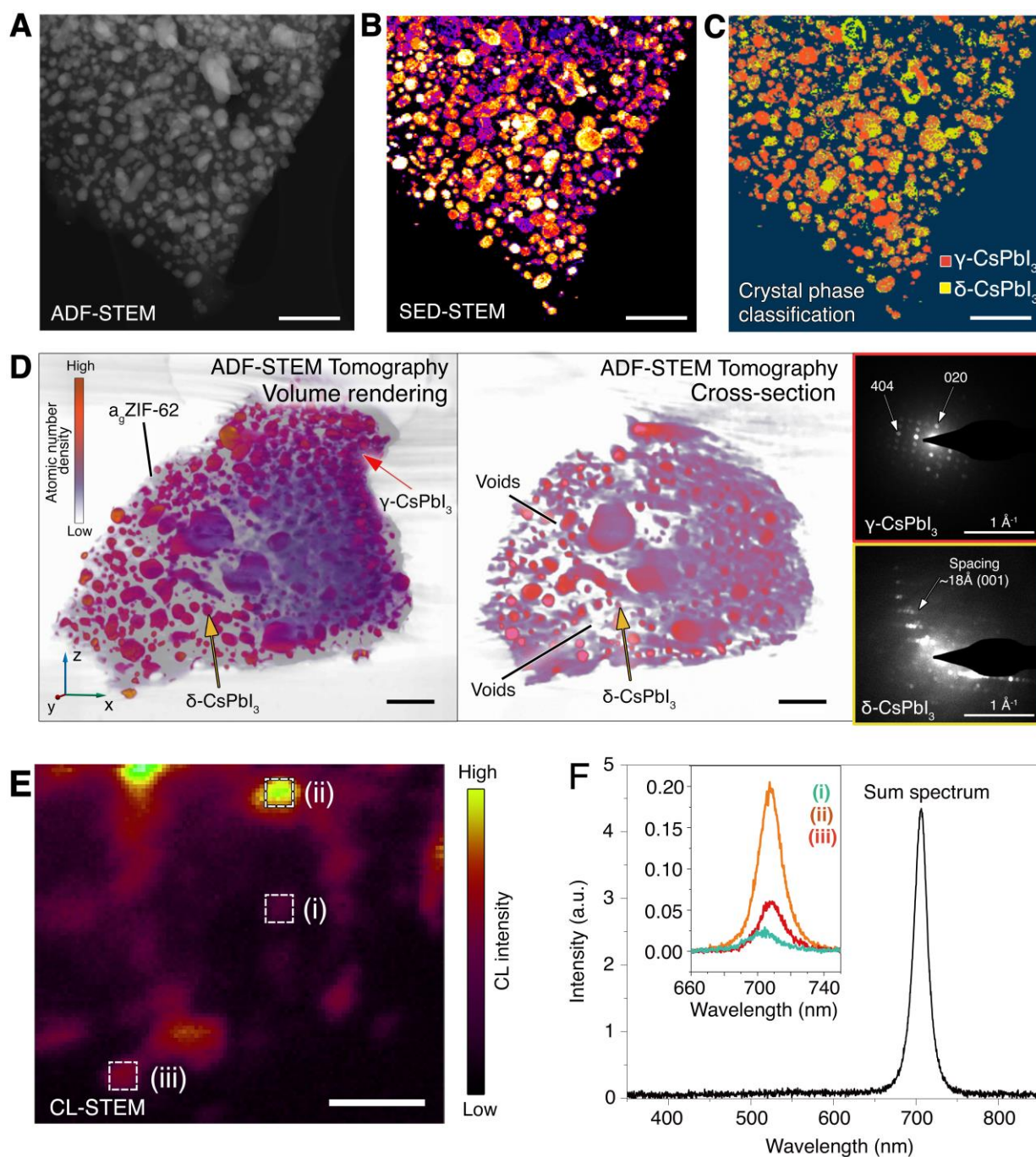


Fig. 3. Phase distribution for the $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ composite fabricated with 300°C sintering. (A) ADF-STEM image, (B) SED-STEM mapping and (C) CsPbI_3 crystal phase classification results for $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ composite. (D) Volume rendering of a tomographic reconstruction of $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ and a single cross-sectional plane extracted from the volume. Color-coded arrows highlight the regions where selected area electron diffraction data were collected. Scale bars in (A to D) are 250 nm. (E) CL-STEM mapping of the integrated CL intensity. The scale bar is 70 nm. (F) CL spectra acquired at each STEM probe position, and the sum CL spectrum of the whole region in (E).

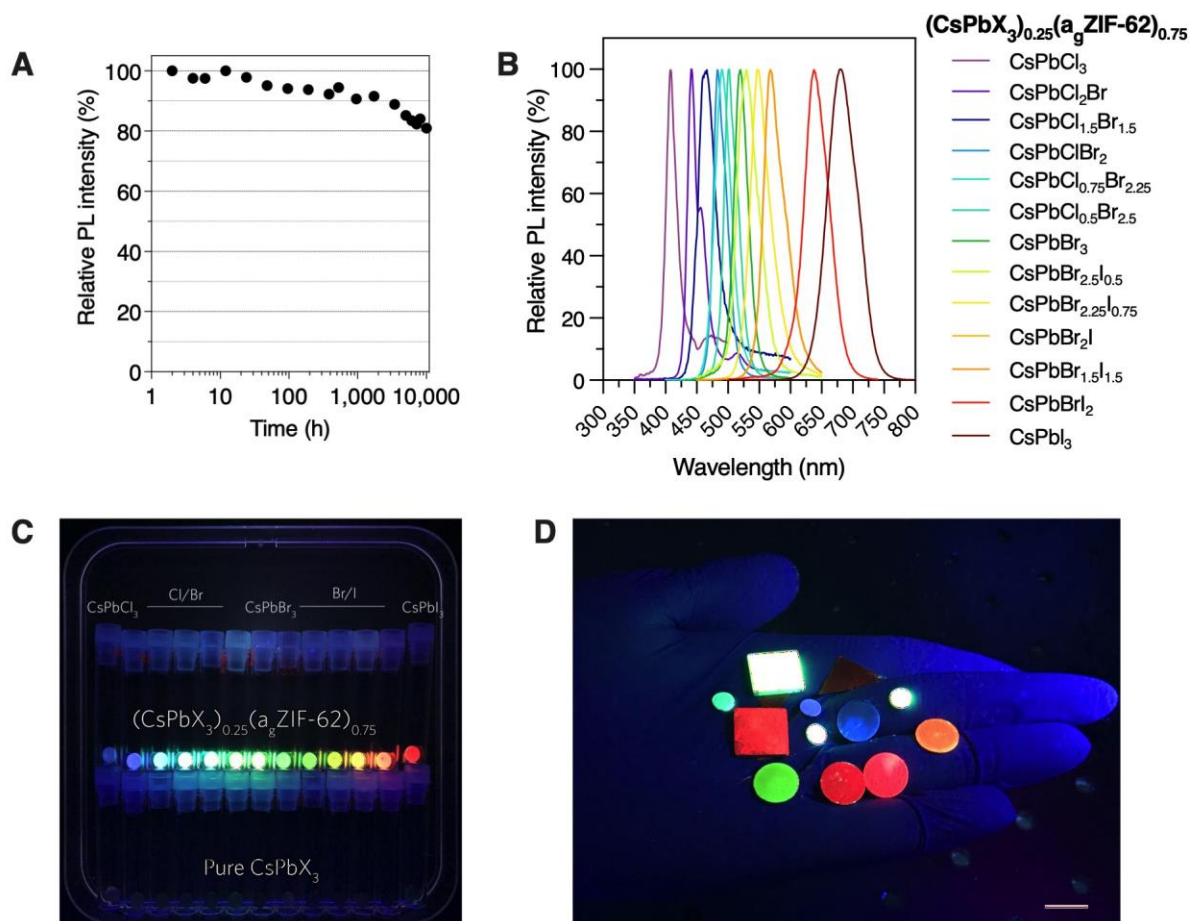


Fig. 4. Stability and optical performance of the composites. (A) Change of the relative PL intensity for $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ immersed in the Milli-Q water. Sample was sintered at 300°C. (B) Normalized PL intensities of the $(\text{CsPbX}_3)_{0.25}(\text{agZIF-62})_{0.75}$ composites (X=Cl, Br, I and mixed halide ions). (C-D) Optical photos of the composites and pure CsPbX_3 under 365 nm UV light. Composites for (B-D) were sintered at 275°C. Scale bar in (D) is 1 cm.