Redshifting the Absorption Edge of Double Perovskite Nanocrystals by Cu- and Fe-alloying

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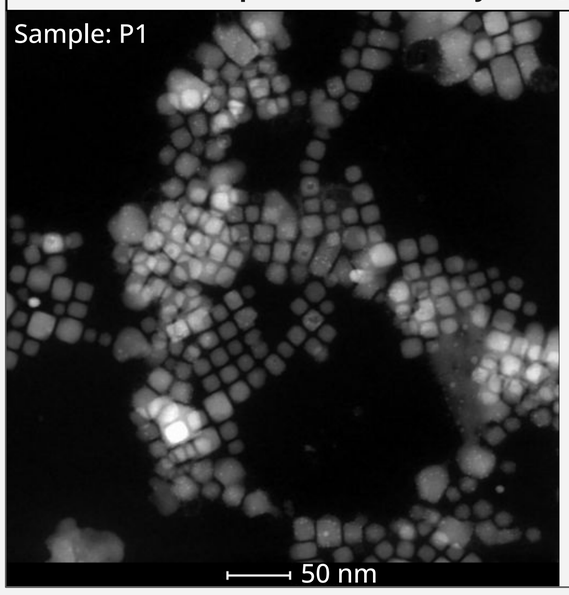
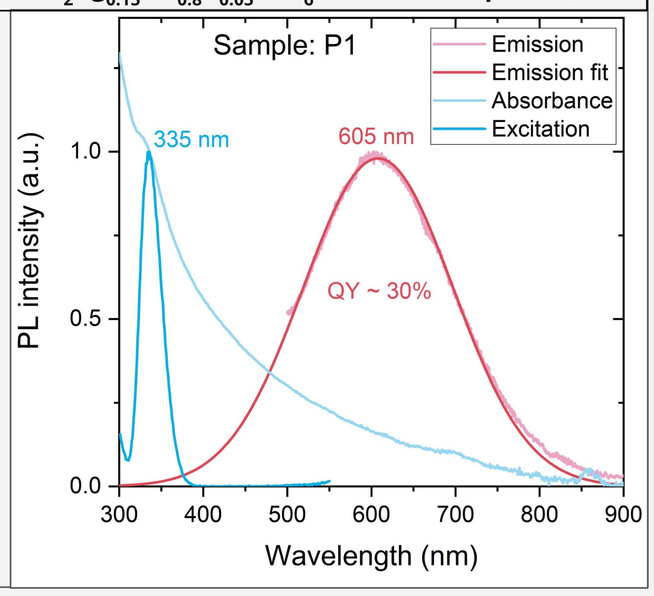
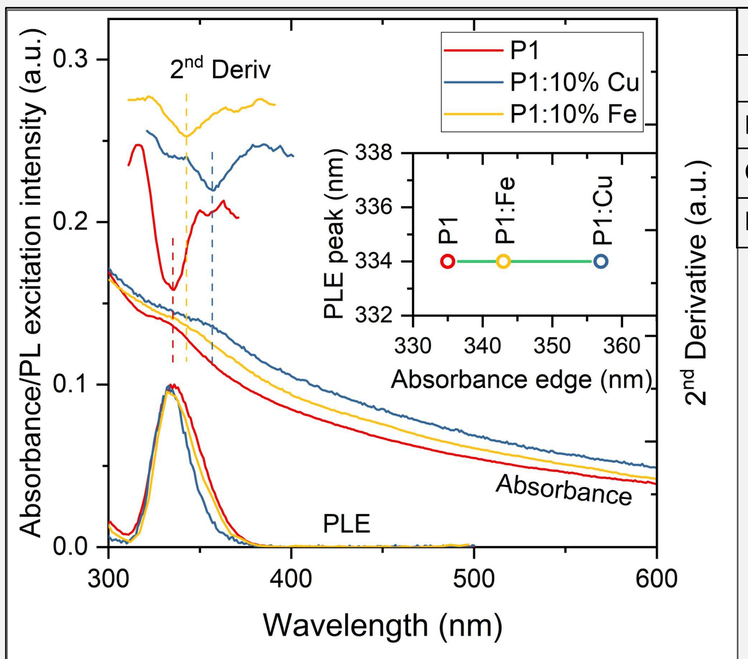
Synopsis

We synthesize **double perovskite nanocrystals** for application in transparent luminescent solar concentrators. However, their > 3 eV absorption edge hinders their photovoltaic applications. Bromide-based double perovskites exhibit redshifted absorption edges than chloride-based ones but emit no light. Here we present alternate approaches based on metal alloying to achieve absorption redshift without quenching emission. Moreover, we investigate **PL dynamics as a function of temperature and magnetic field**, which reveal the structure of the luminescent excited state. Namely, we show that PL lifetimes at 150 K become ~ 3X longer than at RT, indicative of **non-radiative recombination quenching**. The infinitely long PL decays below 20 K signify the **occupation of a dark excited state, which is brightened by magnetic field**.

Base double perovskite nanocrystals [1]: $Cs_2Ag_{0.15}Na_{0.8}K_{0.05}InCl_6$:0.5% Bi (Sample: P1)

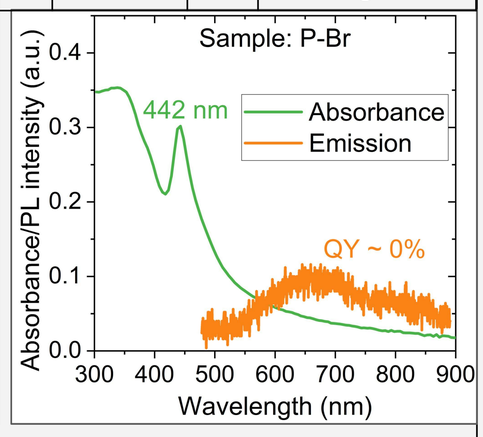






ABSORPTION REDSHIFT

	ABS edge	QY	Comments
Br	442 nm	~ 0	No emission
Cu	357 nm	13%	Unchanged PLE
Fe	343 nm	24%	Unchanged PLE



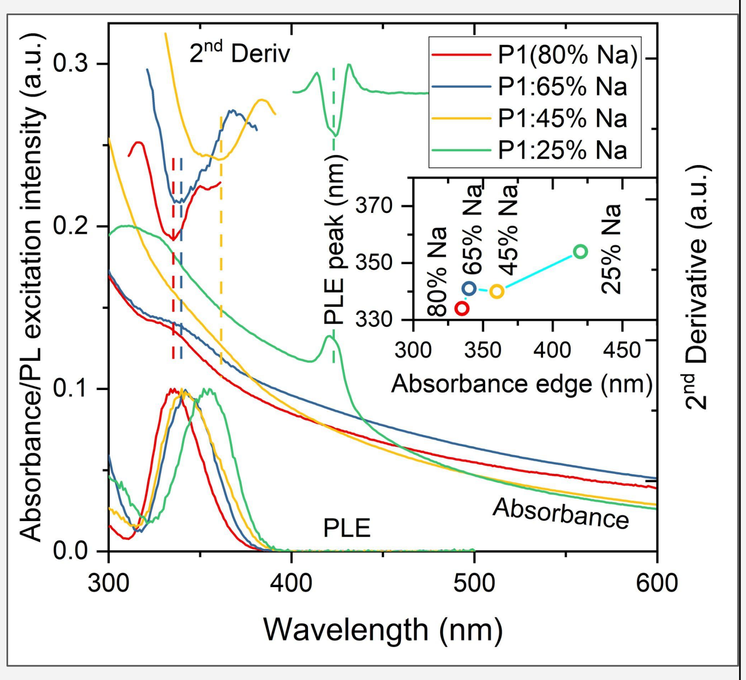
Weak ABS shoulders identified with 2nd-order derivative

Halide alloying and Cu/Fe-alloying are suboptimal for ABS redshift

Na-Ag alloying

Bulk $Cs_2NaInCl_6$ bandgap ~ 5.1 eV
Bulk $Cs_2AgInCl_6$ bandgap ~ 3.3 eV
%Na ↘ ⇒ absorbance redshift [2]

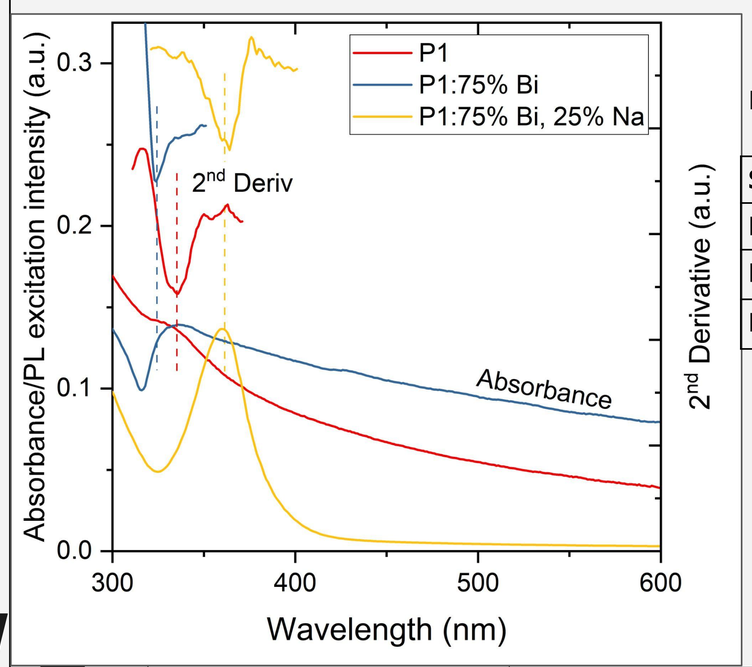
%Na	ABS edge	PLE peak
80	335 nm	334 nm
65	340 nm	341 nm
45	360 nm	340 nm
25	420 nm	360 nm



Bi-In alloying

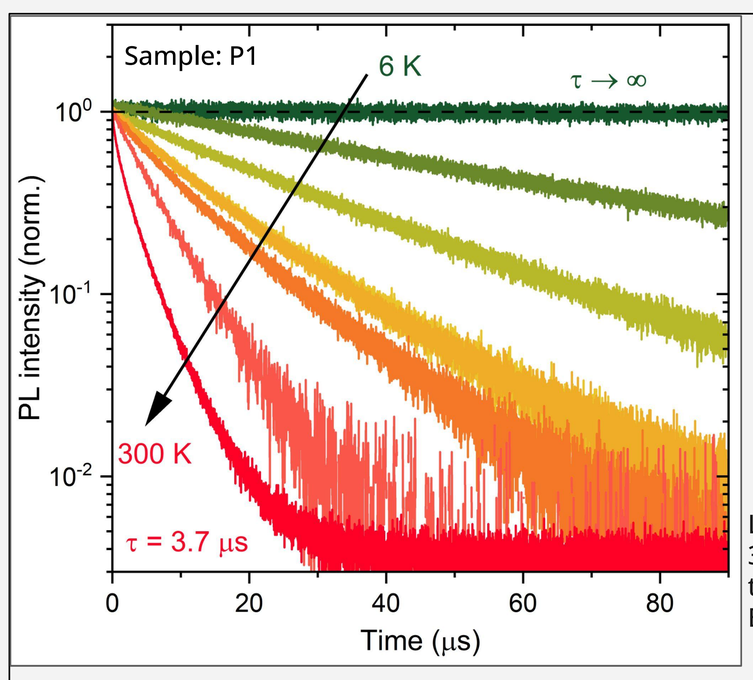
Bulk Bi-In alloying ⇒ ABS redshift [3]

Sample	ABS edge
P1	335 nm
P1:75% Bi	325 nm
P1:75% Bi, 25% Na	360 nm

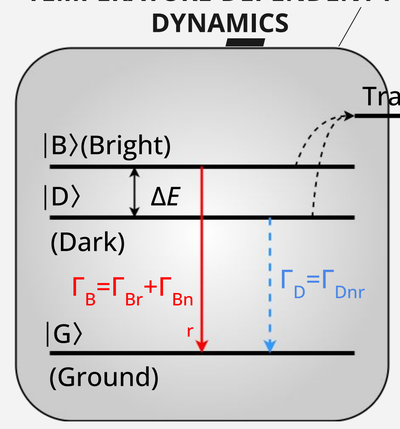


FUTURE PLANS

- Cl/Br-alloyed double perovskite nanoplatelets
- Fabrication of transparent luminescent solar concentrators



TEMPERATURE-DEPENDENT PL DYNAMICS



3-level model

Lifetime vs temperature fitted with a 3-level model [4] with higher bright triplet and lower dark singlet states. Excitonic model, fixed phonon energy

$$\tau_{PL} = \frac{1+\frac{1}{3}\exp\left(\frac{\Delta E}{k_B T}\right)}{\Gamma_B + \frac{1}{3}\Gamma_D \exp\left(\frac{\Delta E}{k_B T}\right)}$$

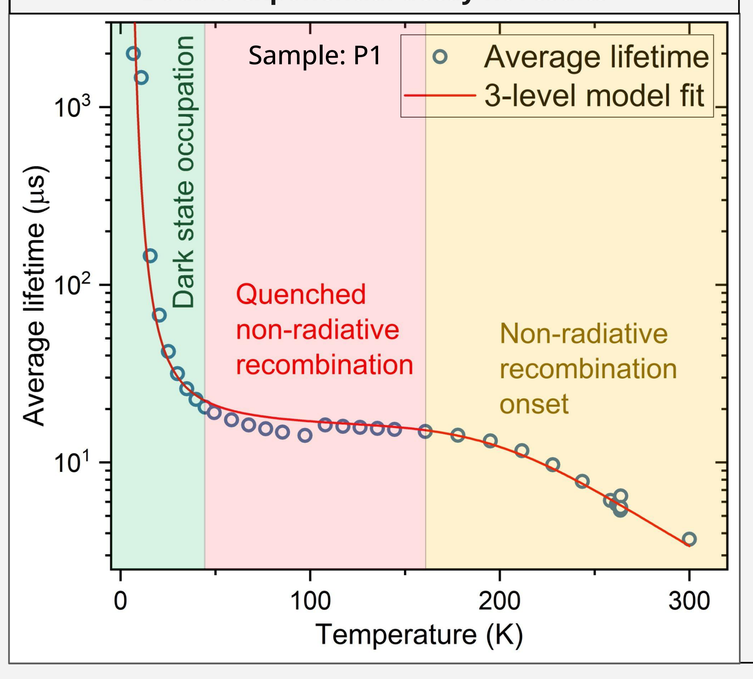
$$\Gamma_{B/D} = \Gamma_{Br/Dr} + \Gamma_{Bnr/Dnr}$$

$$\Gamma_B = k_0\left[\exp\left(\frac{E_{ph}}{k_B T}\right) - 1\right]^{-n}$$

$$\Gamma_D = k_0\left[\exp\left(\frac{E_{ph}}{k_B T}\right) - 1\right]^{-m}$$

$$\Delta E = (m-n)E_{ph}$$

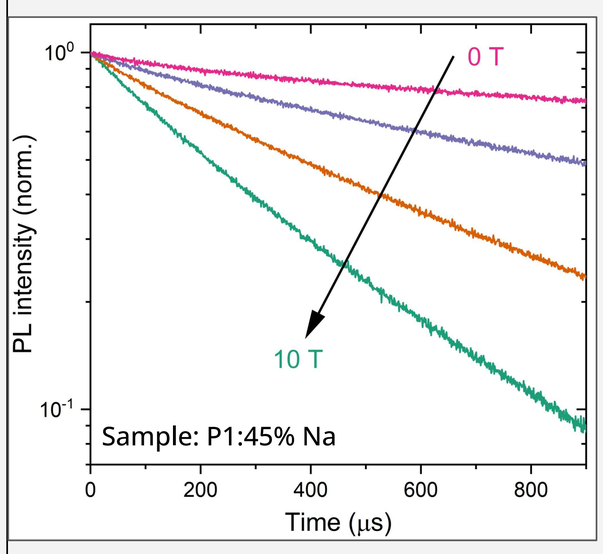
Double exponential decay fit results

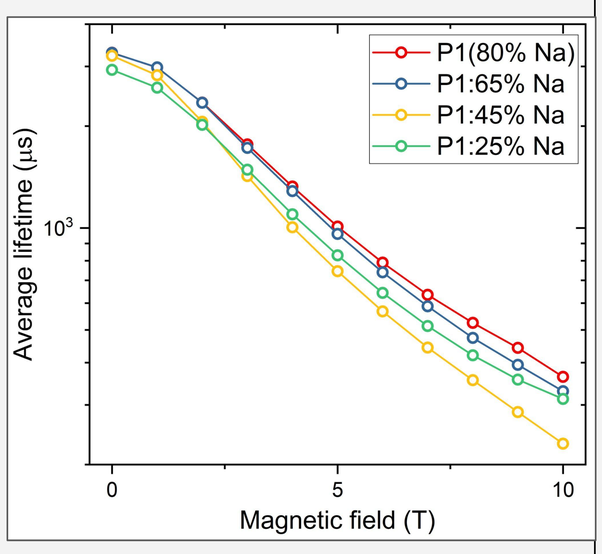


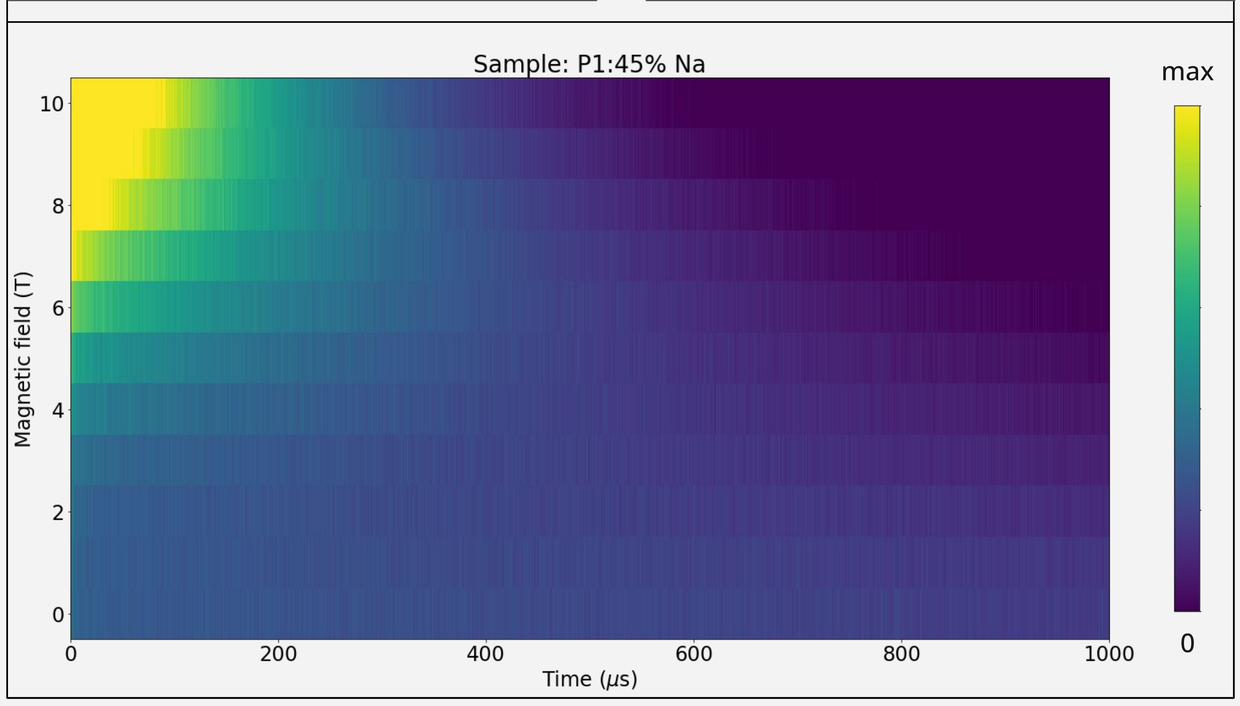
Fitting parameters				
%Na	**80**	**65**	**45**	**25**
ΔE (meV)	4.3	3.4	3.4	3.1
$1/\Gamma_{Br}$ (μs)	11	18	15	22
$1/k_0$ (μs)	0.22	1.5	1.5	3.9
n	3.1	1.6	1.1	1.0
E_{ph} (meV)	33 [5]	33	33	33

MAGNETIC FIELD-DEPENDENT PL DYNAMICS

- Subject to magnetic fields, PL decays become shorter ⇒ mixing of bright and dark states
- At 10 T, PL lifetimes 1/10th of RT lifetimes
- At 10 T, PL decays show absence of circular polarization ⇒ dark excited state is a singlet







References
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[3] O. Stroyuk et. al. 2022 Mater. Adv., 2022, 3, 7894
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[5] L. Zdrazil 2022 doctoral thesis, Palacky University Olomouc, Czechia

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