Hot Carrier redistribution, electron-phonon interaction, and their role in carrier relaxation in thin film halide perovskites

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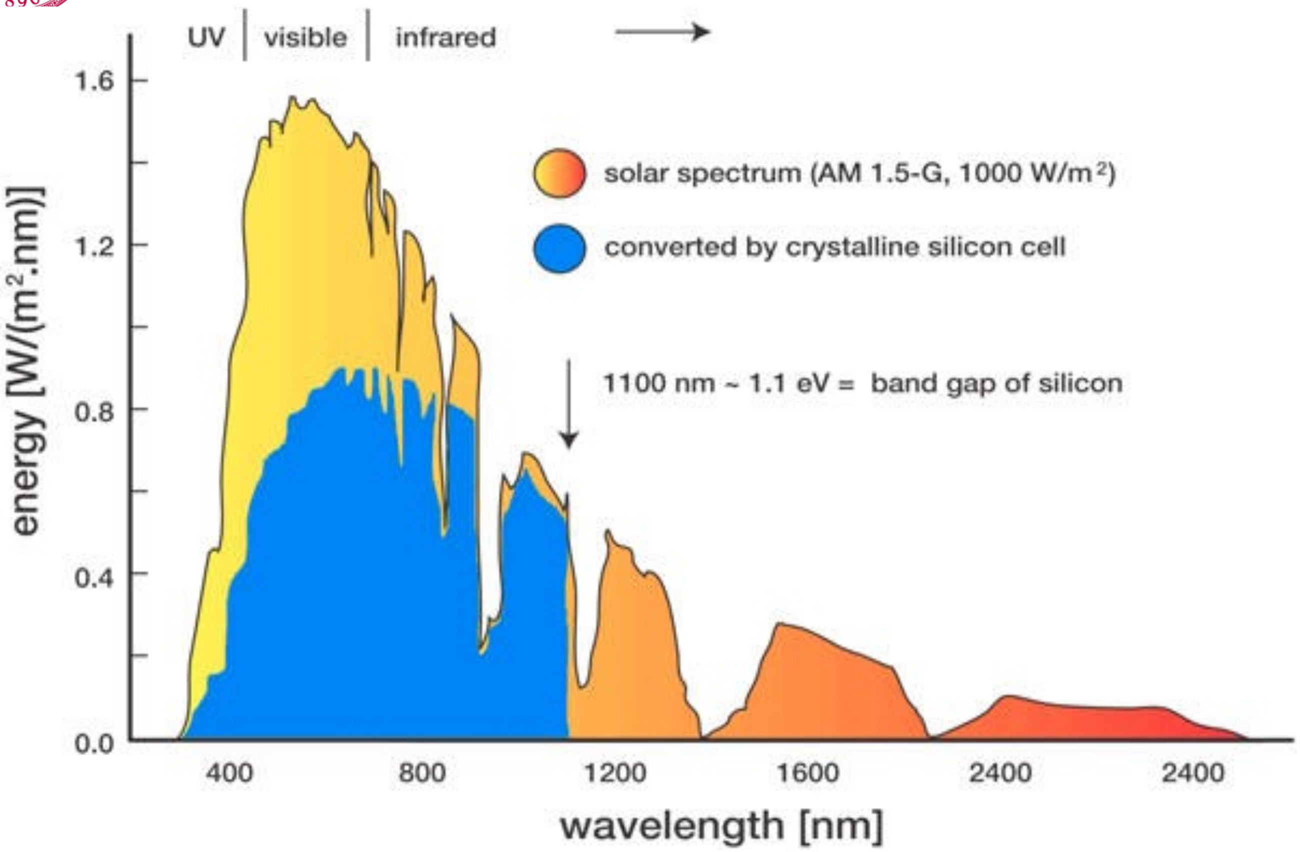
OUTLINE

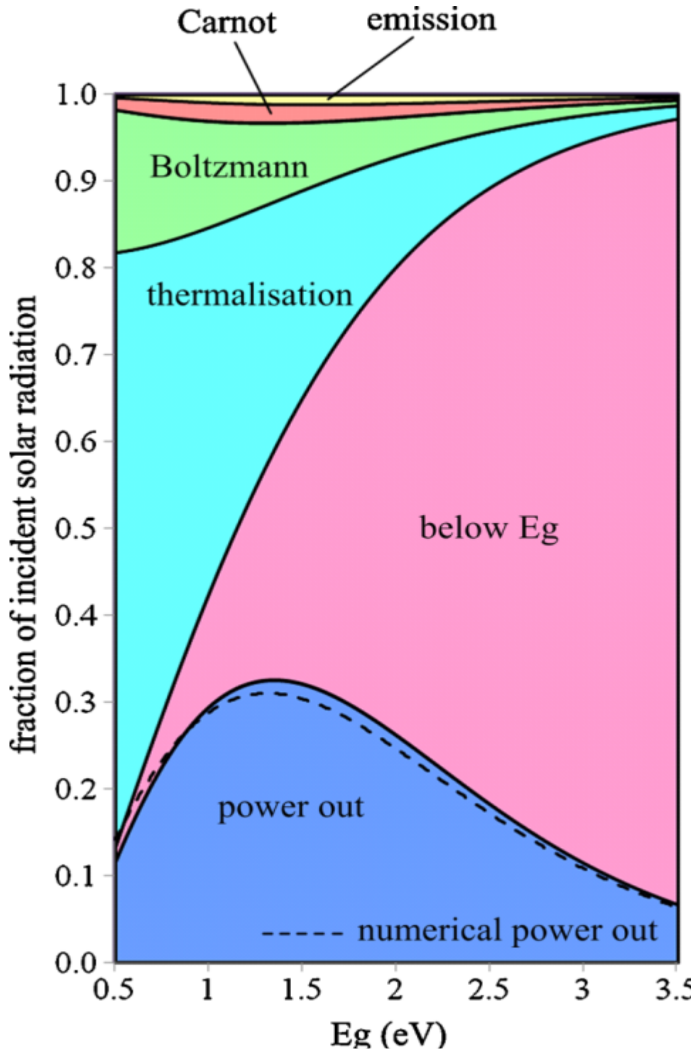
- Limitation of Photovoltaics
- Hybrid Organic Metal Halide Perovskites
- Temperature Dependent Photoluminescence (TDPL)
- Effect of Temperature: Phonons
- Temperature dependence: Emission vs Absorption
- Hot Carrier Dynamics: Transient Absorption
- Origin of Hot Carrier Thermalization
- Conclusion

Limitations of photovoltaics



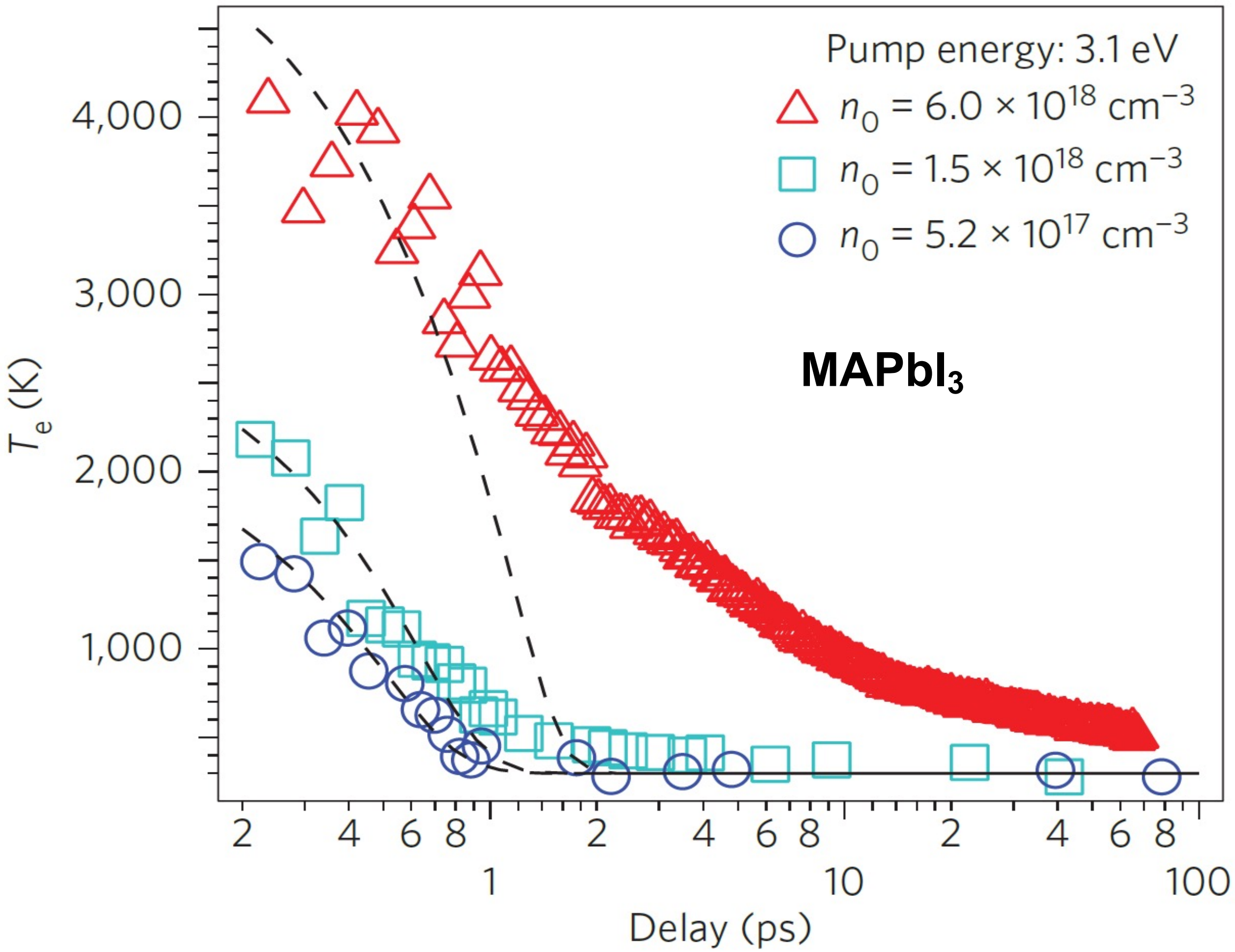
Portion of solar spectrum utilized by silicon cell: Source Wikipedia commons; Find paper and cite it.

- Transmission loss
- Thermalization loss
- Radiative-Recombination loss

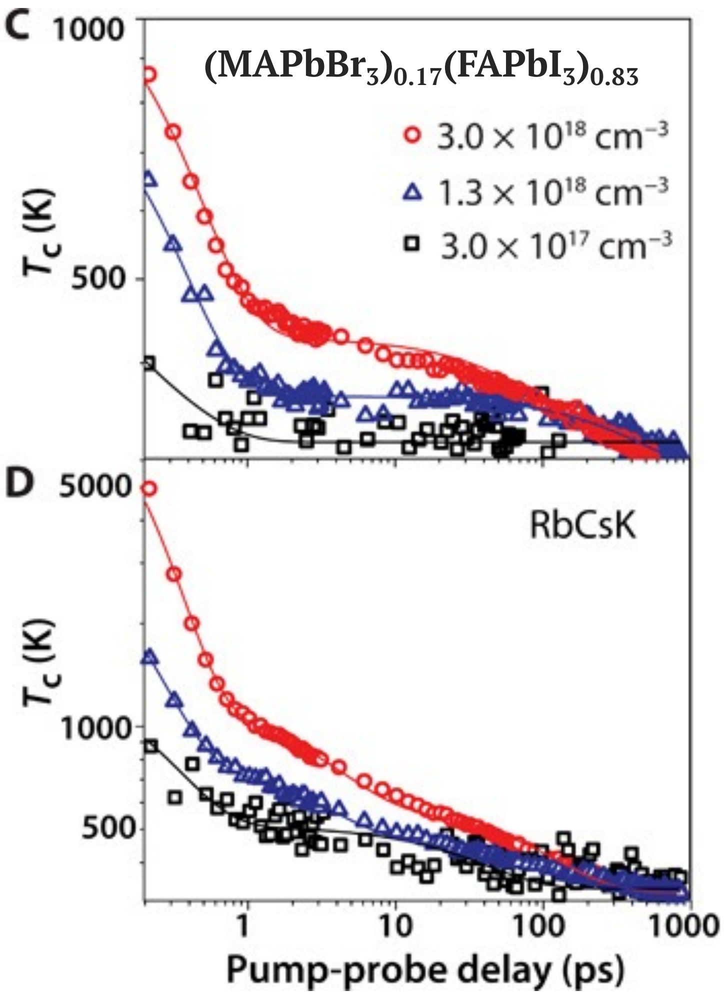


Contribution of different loss mechanisms for a range of band gap energies[Reproduced from: Hirst, Louise C., et al. "Fundamental losses in solar cells." Progress in Photovoltaics: Research and Applications 19, no. 3 (2011): 286-293.]

Hot Carriers in Perovskites

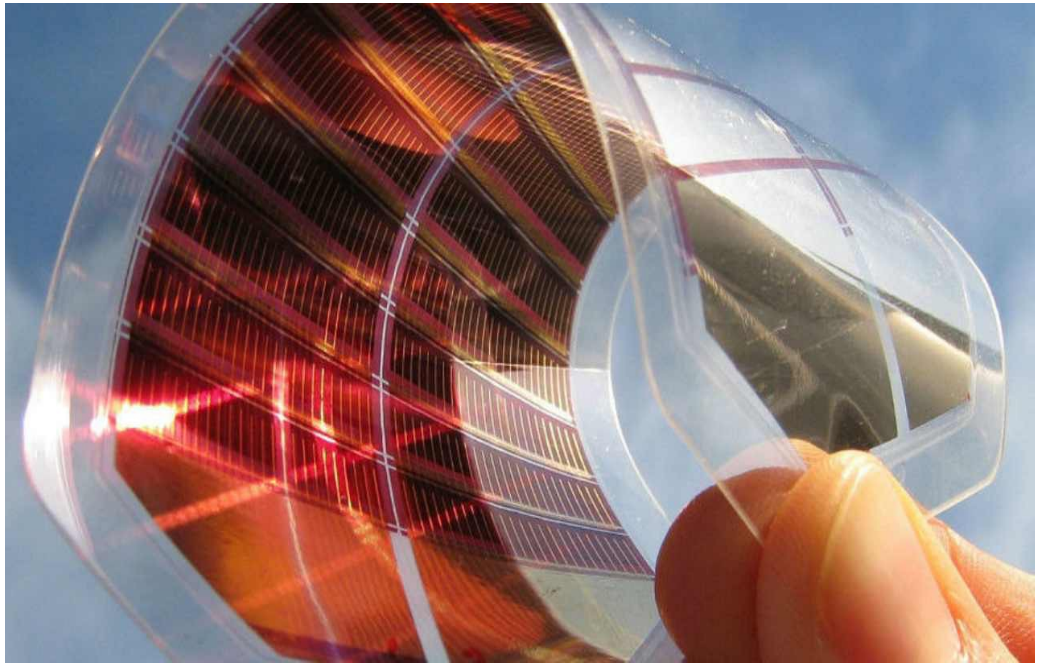


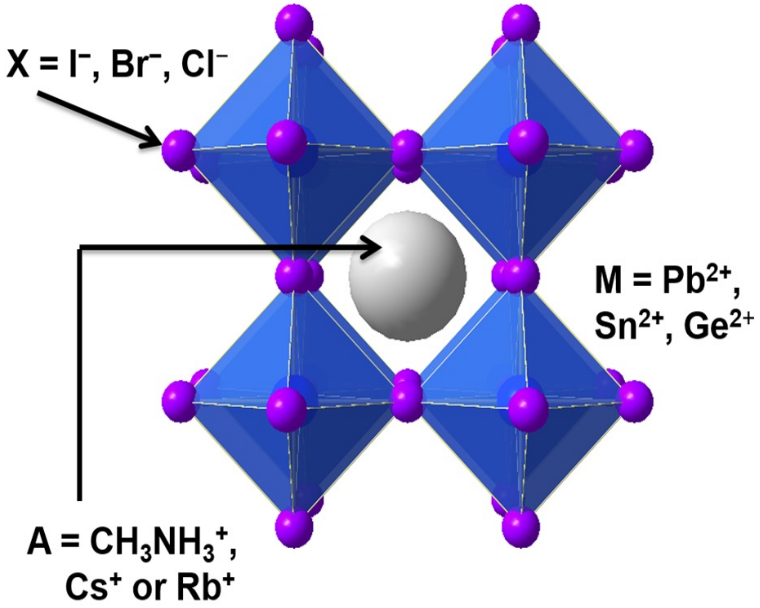
Y. Yang, M.C. Beard et al., Nature Photonics, 2015, 10.1038/nphoton.2015.213



Ti Wang et al.; Science Advances, 2020, vol 6 issue 43; DOI: 10.1126/sciadv.abb1336

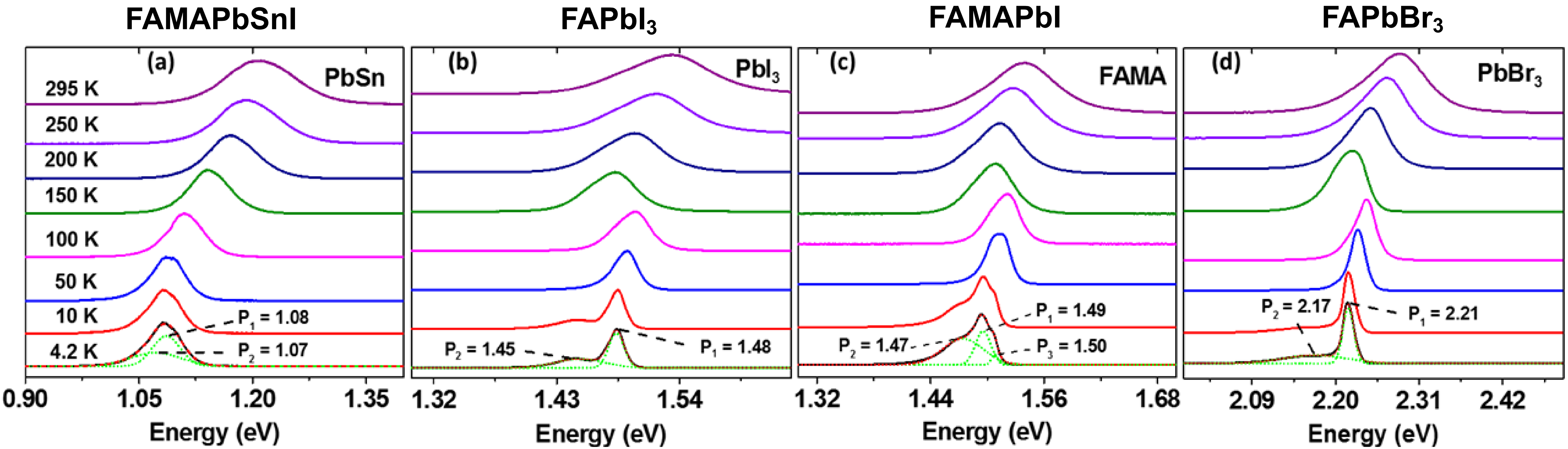
Hybrid Organic Perovskites





1) Halide perovskites are AMX_3 structured solution processible semiconductor, so the prospective cost of production is cheap.
2) These perovskites properties can be tuned -- changing composition.
3) Interesting properties depending on Ionicity, Polaronic effect, etc.

Temperature Dependent Photoluminescence



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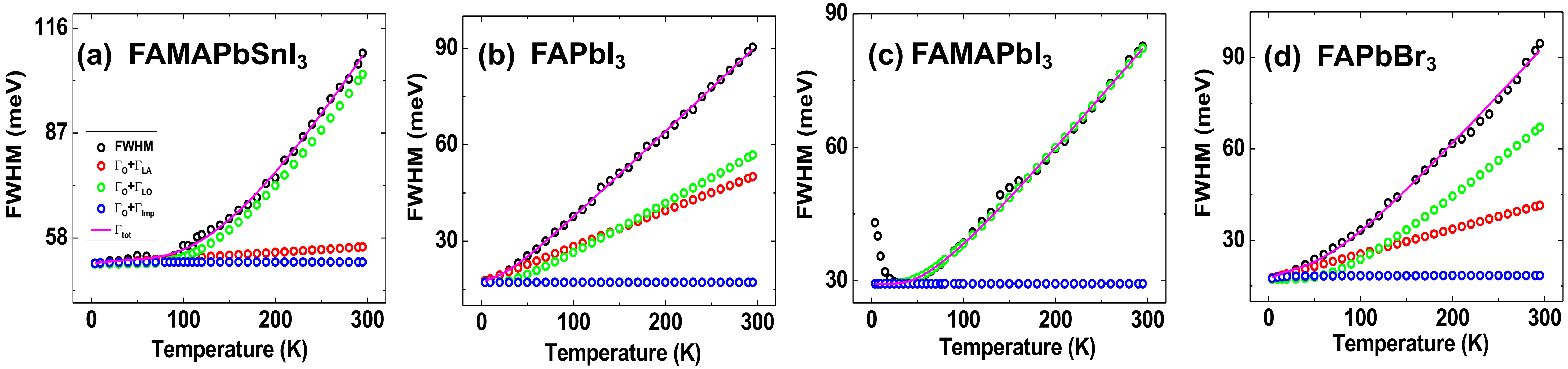
1) All shown increasing bandgap with increasing temperature – property of perovskites.
2) Phase change in pure ‘Pb’ at around 150 K – ‘Pb’ dictates the phase stability.
3) Combination of ‘Pb’ + ‘Sn’ – improved stability.

Effect of temperature: Phonons



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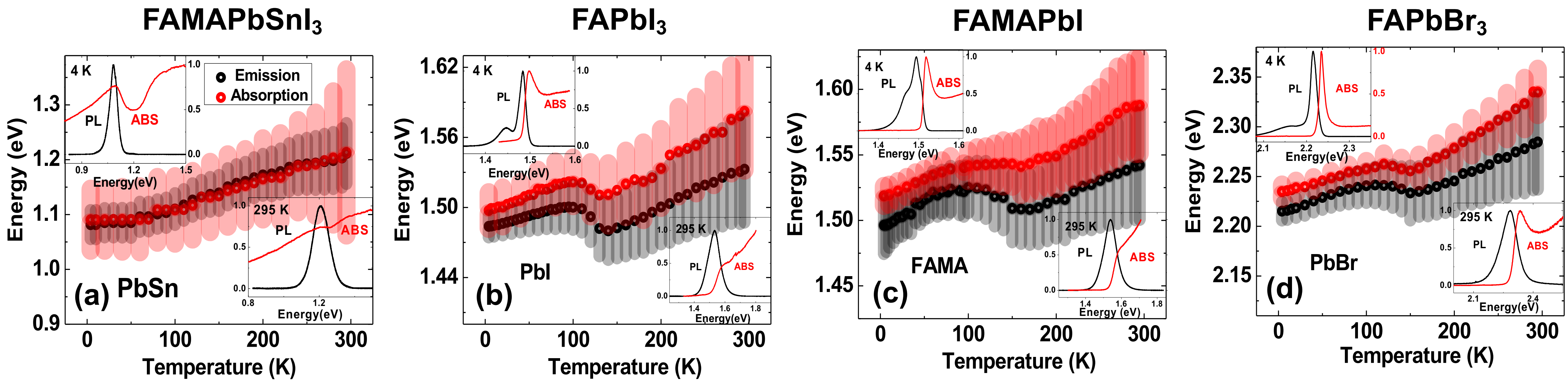
$$\Gamma_{tot}(T) = \Gamma_0 + \Gamma_{LA}T + \frac{\Gamma_{LO}}{\left[exp\left(\frac{E_{LO}}{k_B T}\right) - 1\right]} + \Gamma_{imp}exp\left(\frac{E_B}{k_B T}\right)$$

J.V.D. Veliadis, *et al., Phys Rev B*, **50** (1994) 4463-4469.

Extracted broadening parameter

Perovskites	Γ_0 (HWHM) (meV)	E_{LO} (meV)	Γ_{LO} (meV)
$FAMAPbSnI_3$	51 ± 6	40 ± 4	204 ± 20
$FAPbI_3$	17.2 ± 2	8.5 ± 4	16 ± 4
$FAMAPbI_3$	29.3 ± 9	15 ± 3	43 ± 4
$FAPbBr_3$	17.3 ± 8	20 ± 10	59 ± 19

Temperature dependence: Emission vs Absorption



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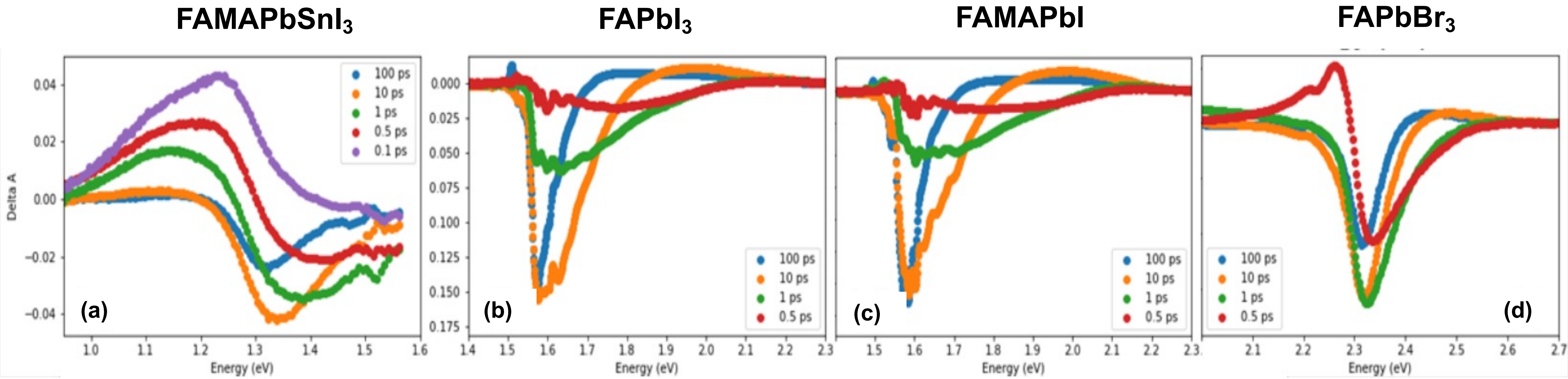
1) Stokes shift is the manifestation of Exciton B.E + Ionicity in these materials.
2) All films exhibits increasing polaronic trend with temperature except Sn.
3) ‘Sn’ system – Stokes shift screened due to sub bandgap states.

Hot carrier dynamics: Transient Absorption



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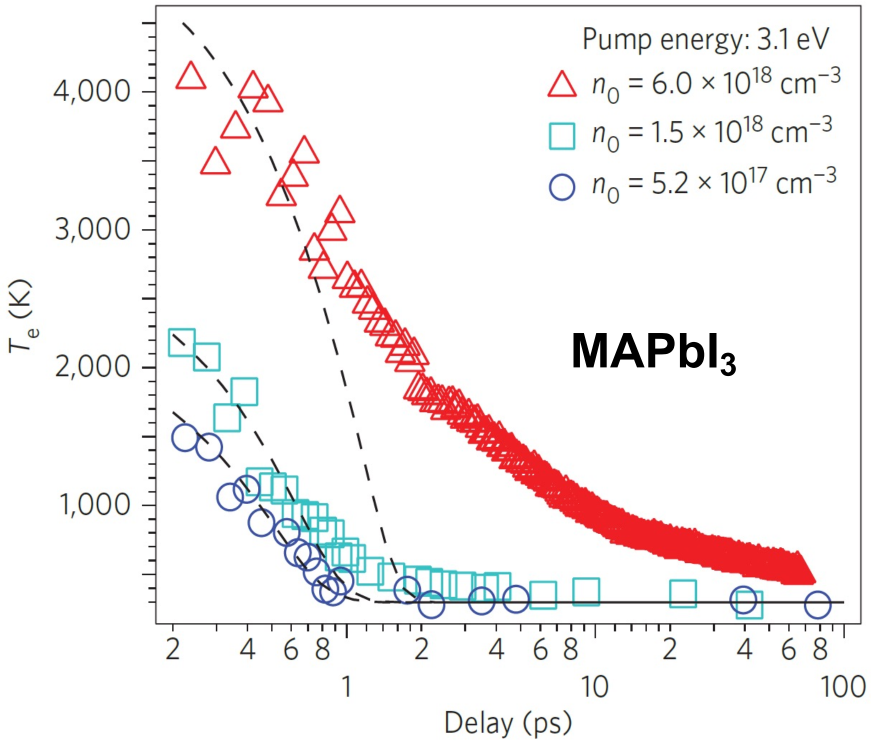
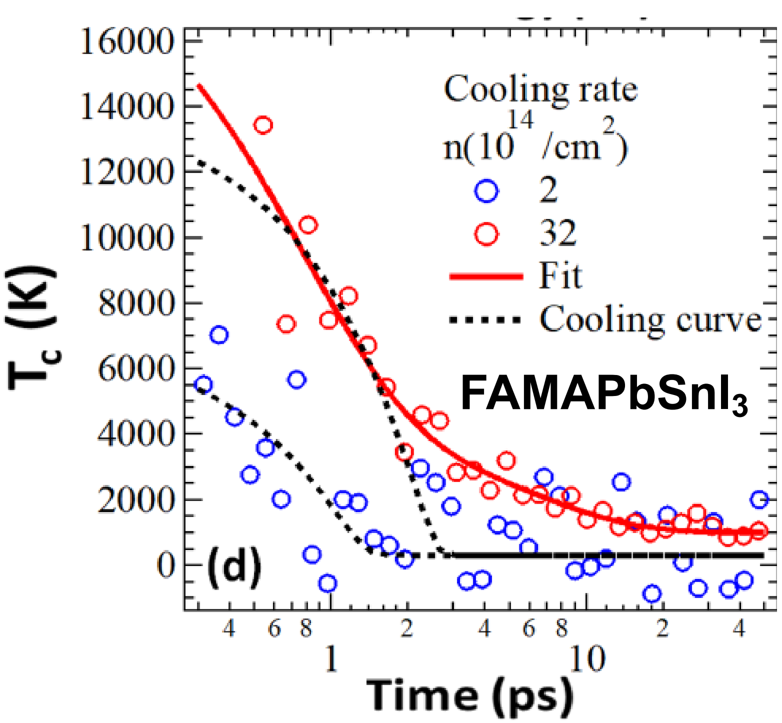
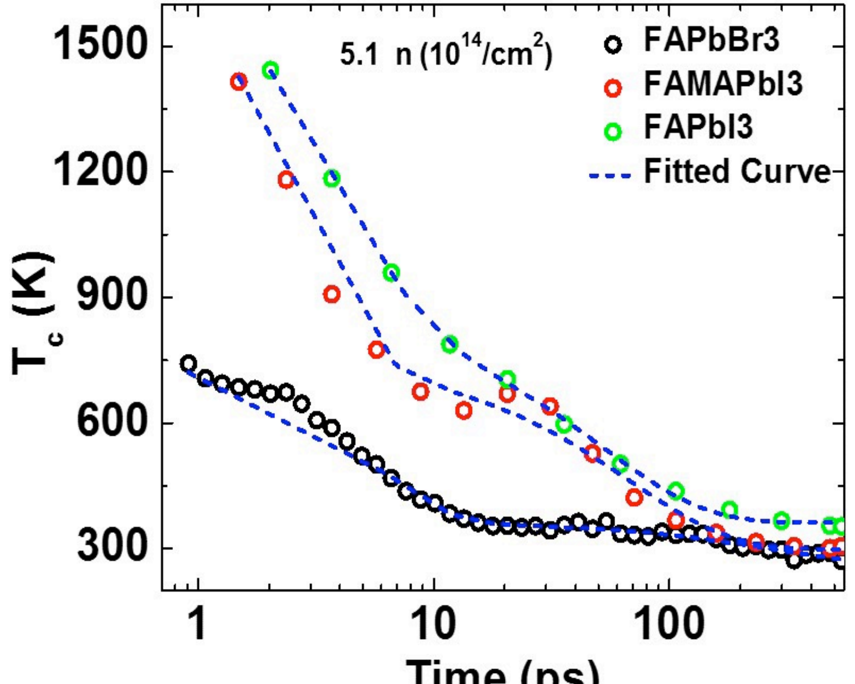
1) At short time – high energy tail - the manifestation of hot carriers.
2) Carrier temperatures extracted – high energy tail.
3) With time tail relaxes as carriers settle comes to conduction band edge.

Origin of thermalization



Y. Yang, M.C. Beard et al., Nature Photonics, 2015, 10.1038/nphoton.2015.213





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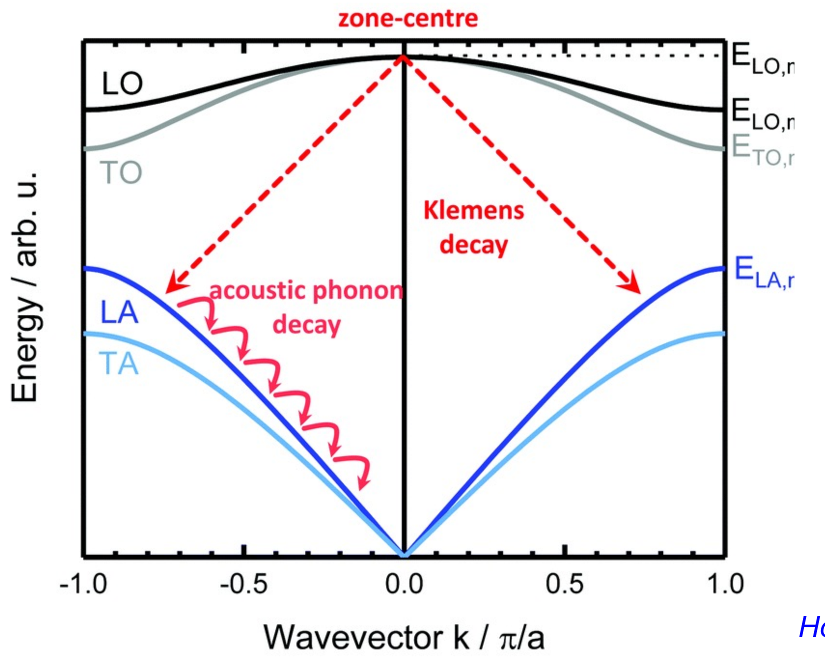
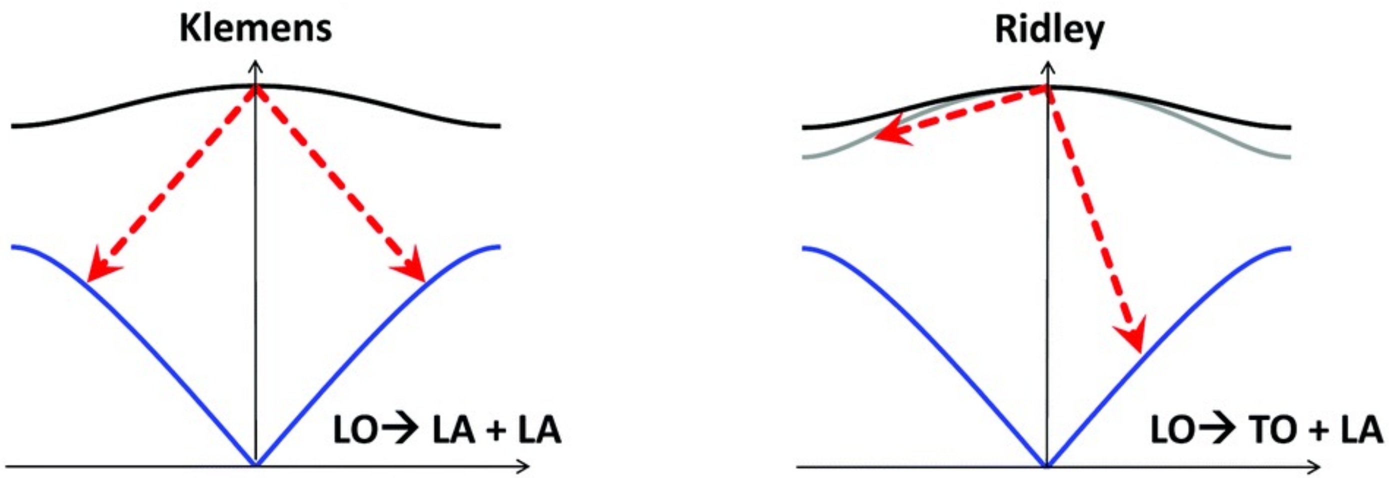
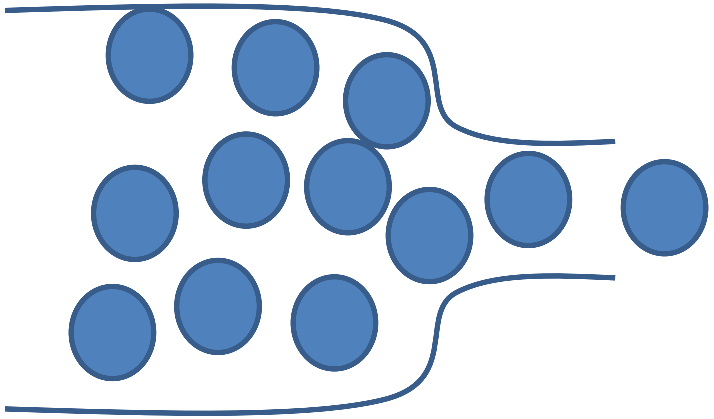
1) All perovskites independent of composition follow similar trends in terms of thermalization of photoexcited hot carriers.
2) Despite several clear differences in the Sn analysis, this trend is similar.
3) Thermalization effects in perovskites appear to be universal across systems.

Thermalization of Hot Carriers





Hot carrier solar cells and the potential of perovskites for breaking the Shockley–Queisser limit, S. Kahmann and M.A. Loi, J. Mater. Chem. C, 2019, 7, 2471-2486, DOI: 10.1039/C8TC04641G



1) Hot e^- + LO phonons : Decay- LA : Thermalizes via. Thermal conductivity
2) In polar semiconductors the LO phonon decay – Klemens and/or Ridley.
3) Klemens is inhibited in perovskites but not Ridley.
4) LA phonons + low thermal conductivity = slow thermalization.

Conclusion

- TDPL, Transmission spectra and Transient Absorption spectra are analyzed for different components.
- Despite having very different binding energy, phononic energy, ionicity across all 4 systems, the carrier thermalization trend is very similar.
- Slow cooling of carriers is attributed to phonon bottle neck associated with LA phonons and intrinsic low thermal conductivity in perovskites limiting the dissipation of acoustic phonons.

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