# Organic Cation Dynamics and Spectral Features in Hybrid Metal Halide Perovskites

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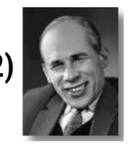
X International Voevodsky Conference "Physics and Chemistry of Elementary Chemical Processes" (VVV-2022)

2022 Novosibirsk 05-09 Sep 2022



## Introduction

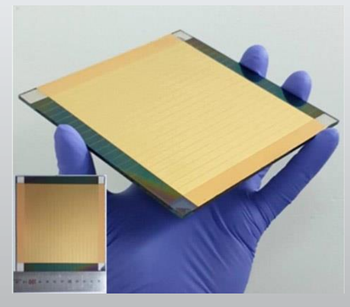
Over the past decade, hybrid perovskites have become one of the most efficient and cheapest materials for use in various photovoltaic devices such as solar cells, lasers, LEDs, and photodetectors [1]. Exceptional functionality of hybrid halide perovskites is due to useful physical properties such as tunable optical bandgap and absorption coefficient, long carrier lifetimes, high carrier mobility, large diffusion lengths [2], and low thermal conductivity. Many of these functional properties are closely related to the features of the phonon spectrum and the electron−phonon interaction.

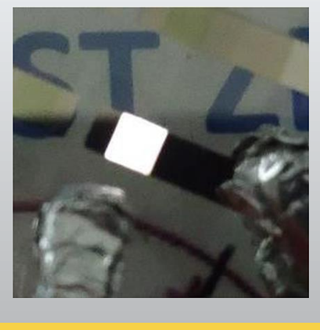
In this work, we present an infrared and terahertz spectra of methyl ammonia lead iodide/bromide in a wide temperature region (5–330 K).

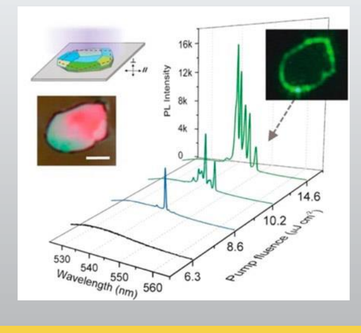
ACS Energy Lett. 2019: 4, 8, 1845-1851

Nat. Photonics 2021: 15, 238-244

Chem. Rev. 2019: 119, 12, 7444-7477



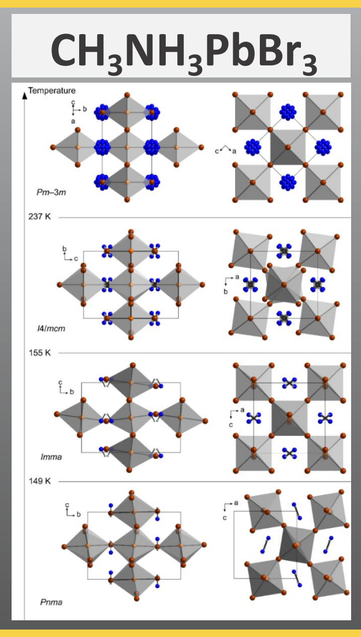





## Structural phase transitions

In hybrid organic–inorganic methylammonium lead iodide / bromide perovskite crystals, organic $CH_3NH^+_3$ molecular units reside in cages within the inorganic framework built by PbI6/PbBr6 octahedra sharing their corners.

Depending on the temperature, there are 3 structural phases for iodide perovskite and 4 structural phases for bromide perovskite.




**$CH_3NH_3PbBr_3$**

**Cubic**
> 327 K

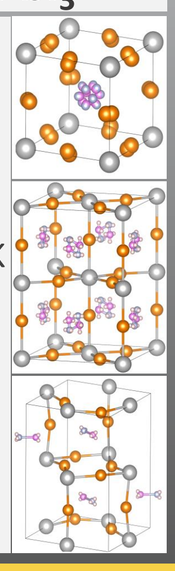
↓ $T_1$=327 K

**Tetragonal**
327 K < T < 161 K

↓ $T_2$=160 K

**Orthorhombic**
< 160 K

**$CH_3NH_3PbI_3$**



## Experimental setup and samples

The sample on a cryostat copper finger

Registration of reflection and absorption spectra: Bruker IFS 125HR Fourier Spectrometer

Range: 10 - 30000 $cm^{-1}$

Resolution: up to 0.2 $cm^{-1}$ (in this work)

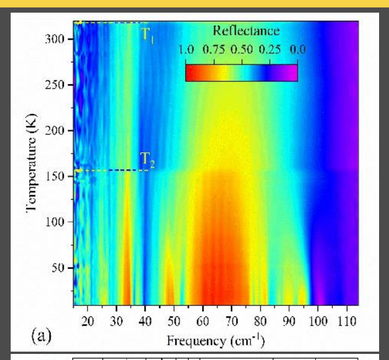
Sample cooling: CryoMech ST403 closed loop cryostat (Temperature range: 3.5-300 K)

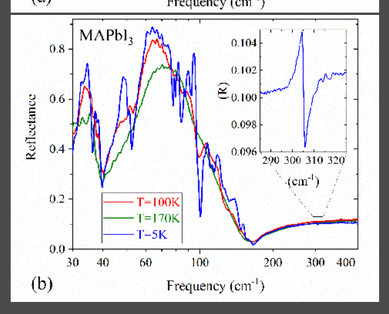
## Features in optical spectra at structural phase transition temperature

### $CH_3NH_3PbI_3$

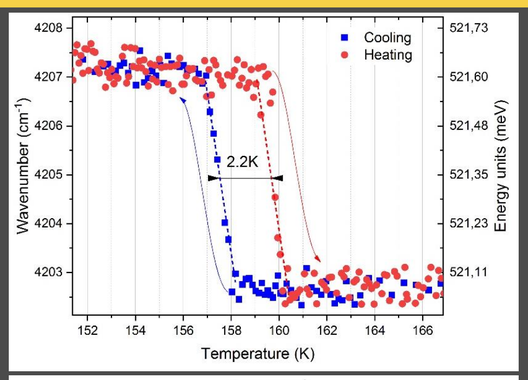
1)$CH_3NH_3I$ synthesis
2)$PbI_2$ synthesis
} Two precursors
3)$CH_3NH_3I + PbI_2 \rightarrow CH_3NH_3PbI_3$ [3]

Synthesized single crystals $CH_3NH_3PbI_3$

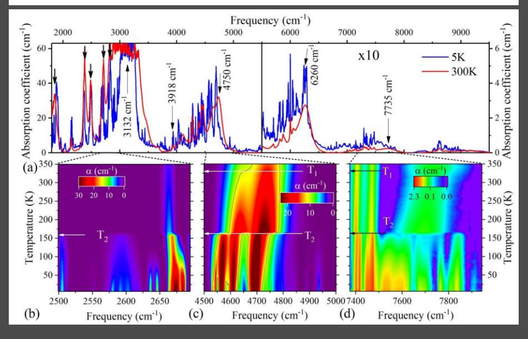


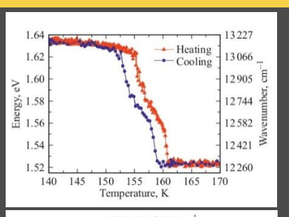

Reflection spectra of a $CH_3NH_3PbI_3$ single crystal (a) presented as the intensity map in the wave number – temperature axes and (b) at several selected temperatures.

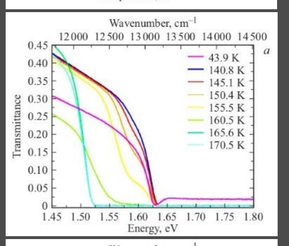


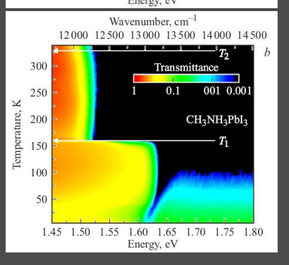

A hysteresis for the line position near 4000 $cm^{-1}$ at cooling and heating a $CH_3NH_3PbI_3$ single crystal.




Absorption spectra of a $CH_3NH_3PbI_3$ single crystal (a) at the temperatures of 300 and 5 K (b–d) Color intensity maps in the frequency–temperature axes for selected frequency regions.



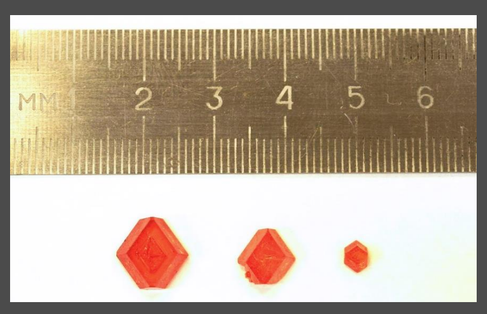

2.5 meV — 24.8 meV | 0.22 eV — 1.24 eV | 2.1 eV — 2.3 eV

20 $cm^{-1}$ — 200 $cm^{-1}$ | 1800 $cm^{-1}$ — 10000 $cm^{-1}$ | 17000 $cm^{-1}$ — 18500 $cm^{-1}$

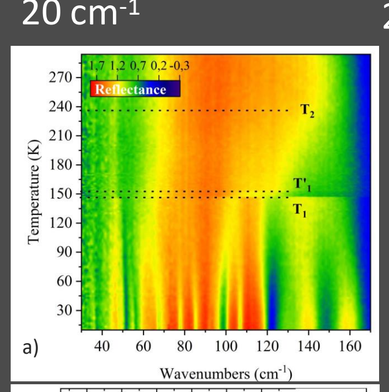
Designed by A. Anikeeva

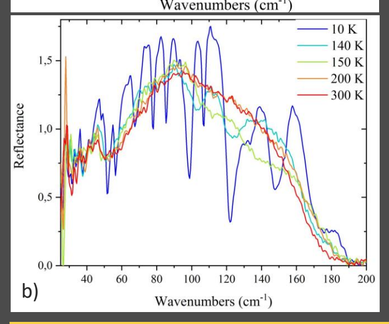
### $CH_3NH_3PbBr_3$

1)$CH_3NH_3Br$ synthesis
2)$PbBr_2$ synthesis
} Two precursors
3)$CH_3NH_3Br + PbBr_2 \rightarrow CH_3NH_3PbBr_3$ [4]

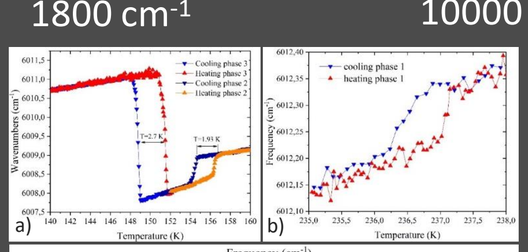


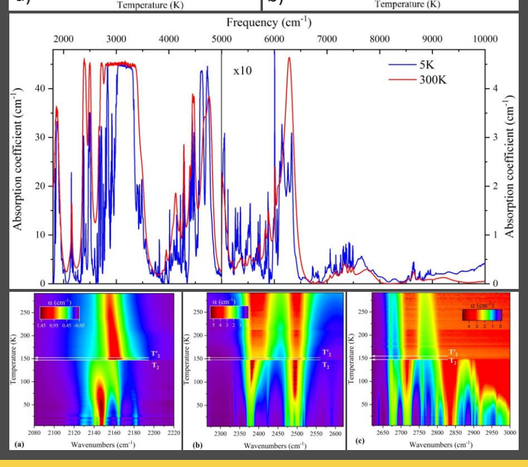
Synthesized single crystals $CH_3NH_3PbBr_3$



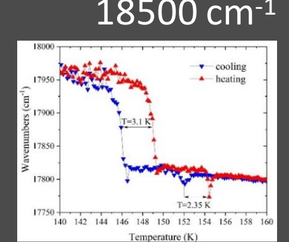

Reflection spectra of a $CH_3NH_3PbBr_3$ single crystal (a) presented as the intensity map in the wave number – temperature axes and (b) at several selected temperatures.

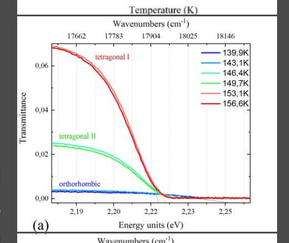


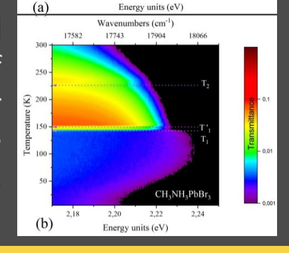




A hysteresis for the line position near 6000 $cm^{-1}$ at cooling and heating a $CH_3NH_3PbBr_3$ single crystal at the temperature regions of tetragonal to orthorhombic phase transition (a) and for cubic to tetragonal phase transition (b).

Absorption spectra of a $CH_3NH_3PbBr_3$ single crystal near the band edge presented as selected spectra near the temperatures of phase transitions (a), as the color intensity map in the frequency–temperature axes (b).




## Acknowledgments

RSF Russian Science Foundation

This work was supported by the Russian Science Foundation (Grant No.19-72-10132).

## Conclusions

- A high sensitivity to the structural phase transitions and to changes in the rotational dynamics of the $CH_3NH_3^+$ molecular cation is demonstrated by the multiphonon spectra.
- Splitting of selected multiphonon lines observed below the temperature of ~70 K is tentatively assigned to the tunneling splitting.
- A complete melting of the orientational order above the temperature of the orthorhombic to tetragonal phase transition leads to a noticeable broadening of vibrational lines.
- The temperature dependence of peak positions in spectra is a hysteretic dependence, which means that the phase transitions mentioned above are first-order phase transitions.
- At the temperature 100 K we observed the phonon line narrowing and appearance of visible dips in the reststrahlen band which correspond to a glassy slowing of the rotational dynamics of the $CH_3NH_3^+$ molecular cation [5].

## References

1. Z. Lian, Q. Yan, et al., Sci Rep., 5, 16563 (2015).
2. T. Brenner, D. Egger, L. Kronik, et al., Nat. Rev. Mater., 1, 15007 (2016).
3. O. Semenova, E.Yudanova, N.Yeryukov, et al., J. Cryst. Growth 462, 45 (2017).
4. A. Melnikov, V. Anikeeva, O. Semenova, S. Chekalin Phys. Rev. B 105, 174304 (2022).
5. K. Boldyrev, V. Anikeeva, O. Semenova, M. Popova, J. Phys. Chem. C, 124, 42, 23307 (2020).