Low-Temperature Structural Change In $CH_3NH_3PbI_3$ Perovskite Single Crystals

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Vasilisa Anikeeva, [1,2] Kirill Boldyrev [1] and Olga Semenova [3]

[1] Institute of Spectroscopy RAS, Troitsk, Moscow, 108840, Russia

[2] Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141701, Russia

[3] Rzhanov Institute of Semiconductor Physics SB RAS, Novosibirsk, 630090, Russia

The growing interest in the study of organometallic perovskites $MAPbX_3$ ($MA = CH_3NH_3^+$, X = I, Br, Cl) as new materials for use in solar cells and photovoltaic devices is due to such excellent optoelectronic properties [1] as:

- extremely high luminescence efficiency;
- optimal band gap: *1.55 eV*;
- high value of the diffusion length of charge carriers: *175 μm*;
- absorption coefficient: *10^5 cm^{-1}* ;
- the cheapness and simplicity of obtaining material without the use of rare elements.

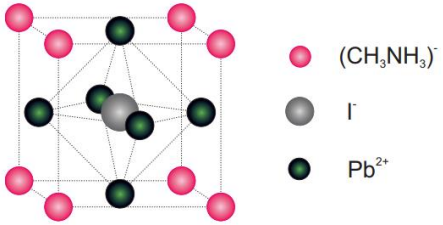
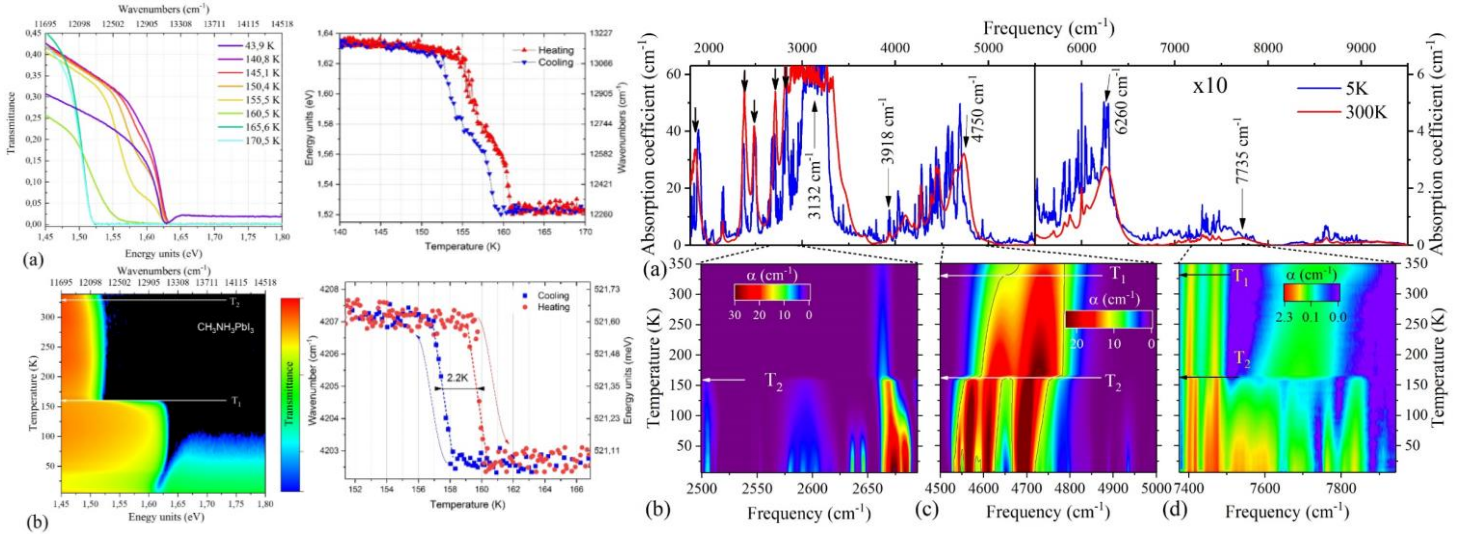


Fig. 1. Structure of organometallic perovskite $CH_3NH_3PbI_3$.

In this work, we studied the transmission spectra of $CH_3NH_3PbI_3$ single crystals in a wide temperature range (5 - 330 K). Near a temperature of 160 K, an abrupt shift in the edge of the absorption zone was observed, associated with the structural phase transition from the tetragonal phase to the orthorhombic phase, known from the literature [2]. The temperature dependences of the optical spectra of the $CH_3NH_3PbI_3$ single crystal allow us to clarify unresolved issues related to the band structure and the specific features of the electron-phonon interaction for this material, which is significant for practical using in photovoltaics.



References

[1] M. R. Filip, Handbook of Materials Modeling (Springer, Cham, 2018), 1.

[2] P. S. Whitfield, N. Herron, W. E. Guise, et al, Sci Rep 6, 35685 (2016).

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Importance of researching a single crystal form

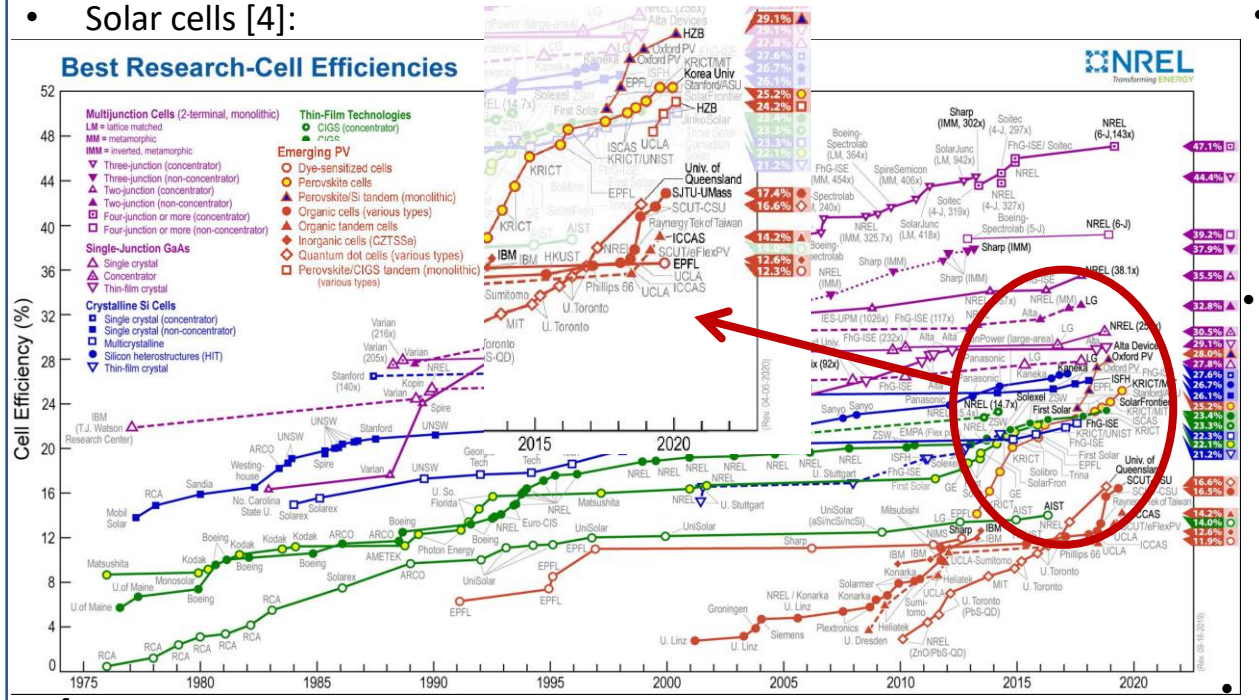
Currently, perovskite thin films are being intensively studied, and most of the claimed applications are focused specifically on polycrystalline thin films. Accordingly, many recent reviews regarding progress in perovskites focus on their form of polycrystalline film. However, the study of the fundamental properties of organometallic perovskites should be carried out precisely on single crystals because of their low density of traps and the absence of grain boundaries. In addition, recent studies have shown that perovskite single crystals have much better optoelectronic properties than their polycrystalline film analogues [3].

References

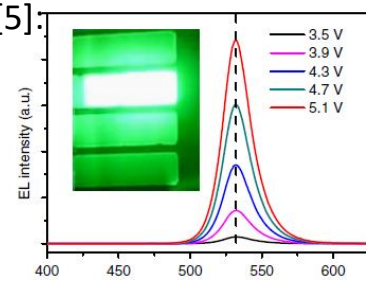
[3] J. Ding, Q. Yan, Sci. China Mater. **60**, 1063–1078 (2017).

Hybrid organometallic perovskites applications

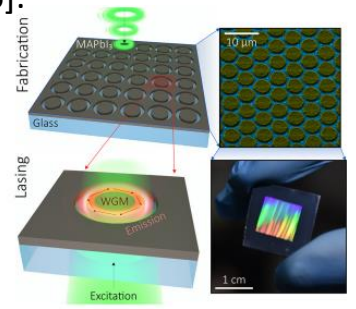
- Solar cells [4]:



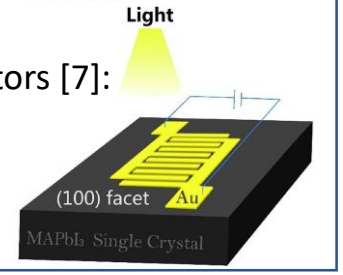
- LEDs [5]:



- Lasers [6]:



- Photodetectors [7]:



References

[4] NREL https://www.nrel.gov/pv/cell-efficiency.html.

[5] Z.-K. Tan, R. S. Moghaddam, M. L. Lai, et al., Nature Nanotech 9, 687–692 (2014).

[6] A. Zhizhchenko, S. Syubaev, A. Berestennikov, et al., ACS Nano 13, 4, 4140-4147 (2019).

[7] Z. Lian, Q. Yan, Q. Lv, et al., Scientific Reports, 5, 16563 (2015).

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Sample preparation

1) CH_3NH_3I synthesis
2) PbI_2 synthesis

} Two precursors

3) $CH_3NH_3I + PbI_2 \longrightarrow CH_3NH_3PbI_3$

Fig. 2. Synthesized single crystals.

References

[6] V. E. Anikeeva, O. I. Semenova and O. E. Tereshchenko, J. Phys.: Conf. Ser. 1124, 041008 (2018).

[7] O.I. Semenova, E.S. Yudanova, N.A. Yeryukov, et. al. Journal of Crystal Growth. 462, 45-49 (2017).

[8] E. S. Yudanova, T. A. Duda, O. E. Tereshchenko, O. I. Semenova, Journal of Structural Chemistry. 58, 8, 1567-1572 (2017).

Composition and structure

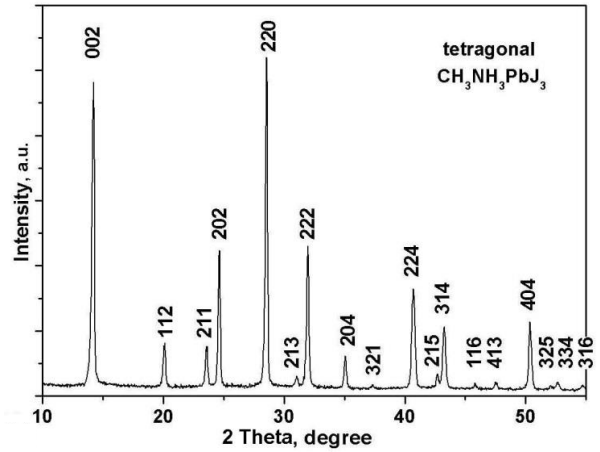

Fig. 3. XRD pattern of the $CH_3NH_3PbI_3$ crystals.

Space group:

I4/mcm

Lattice constant:

a = 8.8743 Å, c = 12.6708 Å

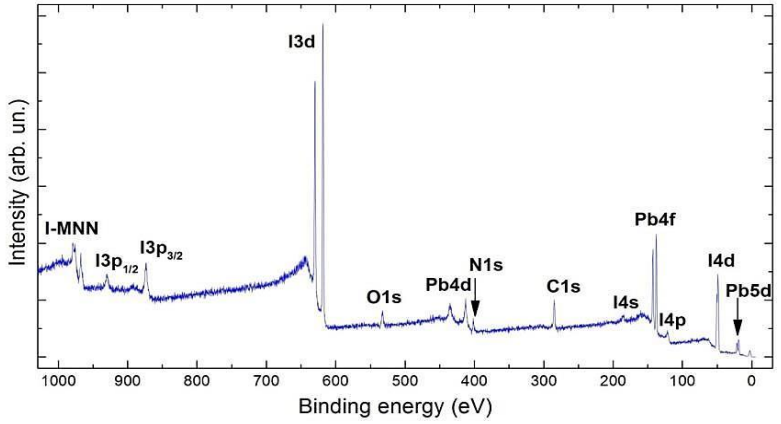

Fig. 4. Survey XPS spectrum of the $CH_3NH_3PbI_3$ single crystal surface.

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Experimental setup

Registration of absorption spectra:

Bruker IFS 125HR Fourier Spectrometer

Range: *10 - 30000 cm-1*

Resolution: *up to 0.2 cm-1*

Sample cooling:

CryoMech ST403 closed loop cryostat

(Temperature range: 3.5-300 K).

Fig. 5. The sample on a cryostat copper finger.

Fig. 6. Bruker IFS 125HR Fourier Spectrometer.

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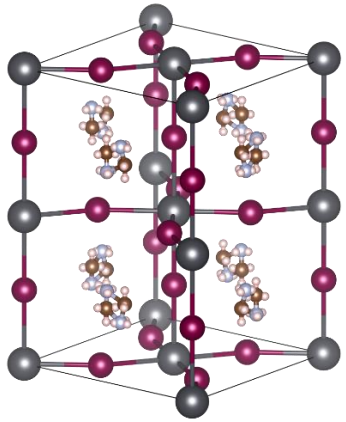
Structural phase transition

Tetragonal



160 K

Orthorombic

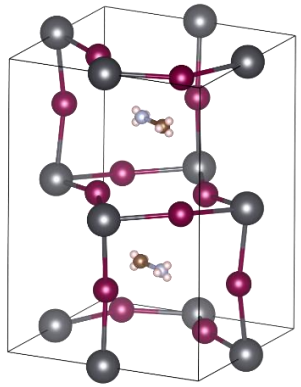


Fig. 7. Structural phase transition from orthorhombic phase (a) to tetragonal phase (b) [1].

References

[1] M. R. Filip, Handbook of Materials Modeling (Springer, Cham, 2018), 1.

Transmission spectra near the band edge

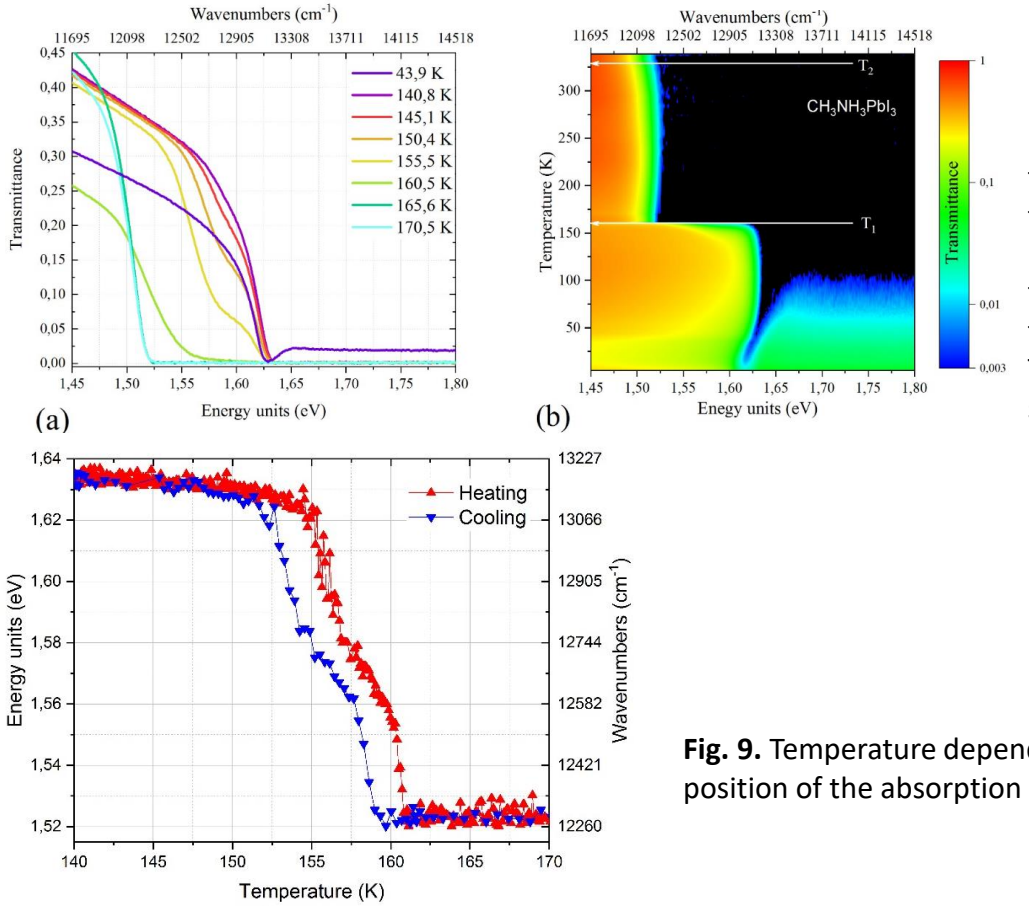


Fig. 8. The transmission spectra near the band edge of $CH_3NH_3PbI_3$ (a) at several temperatures close to the transition temperature from the rhombic to the tetragonal phase and (b) are presented in the form of an intensity map for a temperature range of 5 - 330 K. The temperatures T_1 and T_2 of the structural phase transitions are marked with horizontal arrows.

Fig. 9. Temperature dependences of the position of the absorption edge.

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Reflection spectra in the FIR region

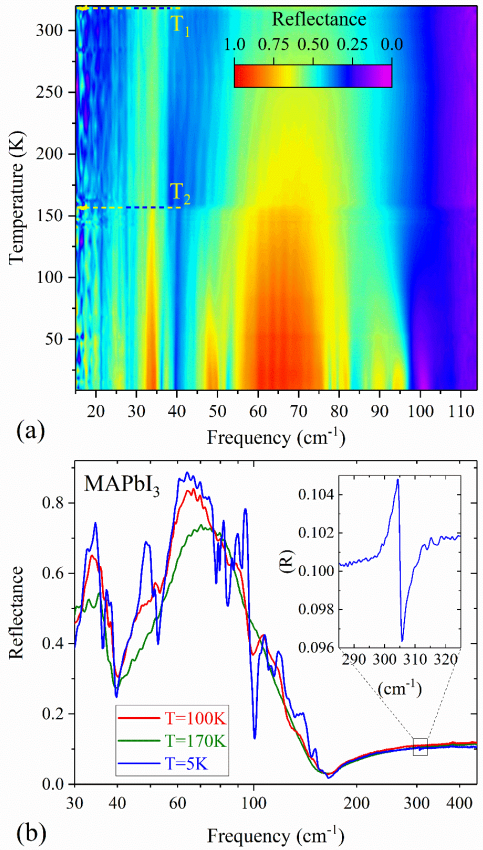

Fig. 10. Reflection spectra of a $MAPbI_3$ single crystal (a) presented as the intensity map in the wave number – temperature axes and (b) at several selected temperatures. Horizontal arrows in (a) indicate structural phase transitions.

$$R(\omega) = \left|\frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1}\right|^2$$

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_{i=1}^{N} \frac{\omega_{0i}^2 f_i}{\omega_{0i}^2 - \omega^2 + i\omega\gamma_i}$$

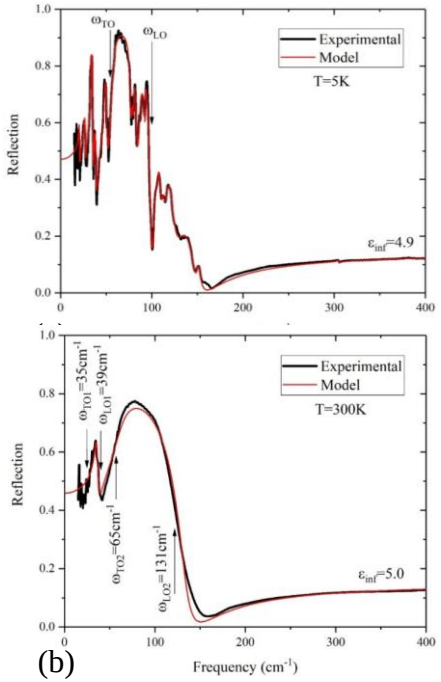

Fig. 11. The reflection spectrum (black line) at 5 K (a) and 300 K (b) and the result of fitting by Eqs. (S1), (S2) (red dashed line).

Table 1. The frequencies ω_{TO} and ω_{LO} of the optical modes, observed in the far-IR spectra of $MAPbI_3$ at 5 K. $\varepsilon_\infty = 4.9$, $\varepsilon_0 = 27.5$.

No	Ref. (1), 10 K ω_{TO} (cm^{-1})	This work, 5 K ω_{TO} (cm^{-1})	This work, 5 K ω_{LO} (cm^{-1})	Tentative assignment
1	17	20.5	20.7	PbJ_6 octahedra twist
2	22	26.6	27.3	PbJ_6 octahedra twist
3	30	33.5	35.9	Pb–I–Pb rock
4	35	37.5	38.8	Pb–I–Pb rock
5	47	48.6	51.2	Pb–I–Pb bend
6	59	57.5	99.2	Pb–I–Pb stretch
7		78.0*	77.3	Pb–I–Pb bend
8		80.0*	79.6	Pb–I–Pb bend, $CH_3NH_3^+$ libr
9		85.9*	83.9	Pb–I–Pb bend, $CH_3NH_3^+$ libr
10		91.5*	91.3	$CH_3NH_3^+$ translation
11		92.8*	92.5	$CH_3NH_3^+$ translation
12		103.0	105.2	$CH_3NH_3^+$ libr/transl
13		106.3	110.0	$CH_3NH_3^+$ libr/transl
14		111.2	113.9	$CH_3NH_3^+$ rotation along C-N
15		116.0	126.1	
16		133.2	144.3	$CH_3NH_3^+$ libr/transl
17		150.1	152.6	$CH_3NH_3^+$ libr/transl
18		305.06	305.12	$CH_3NH_3^+$ torsion

(1) J. Phys. Chem. C 2015, 119, 25703

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Absorption spectra of a $MAPbI_3$ single crystal

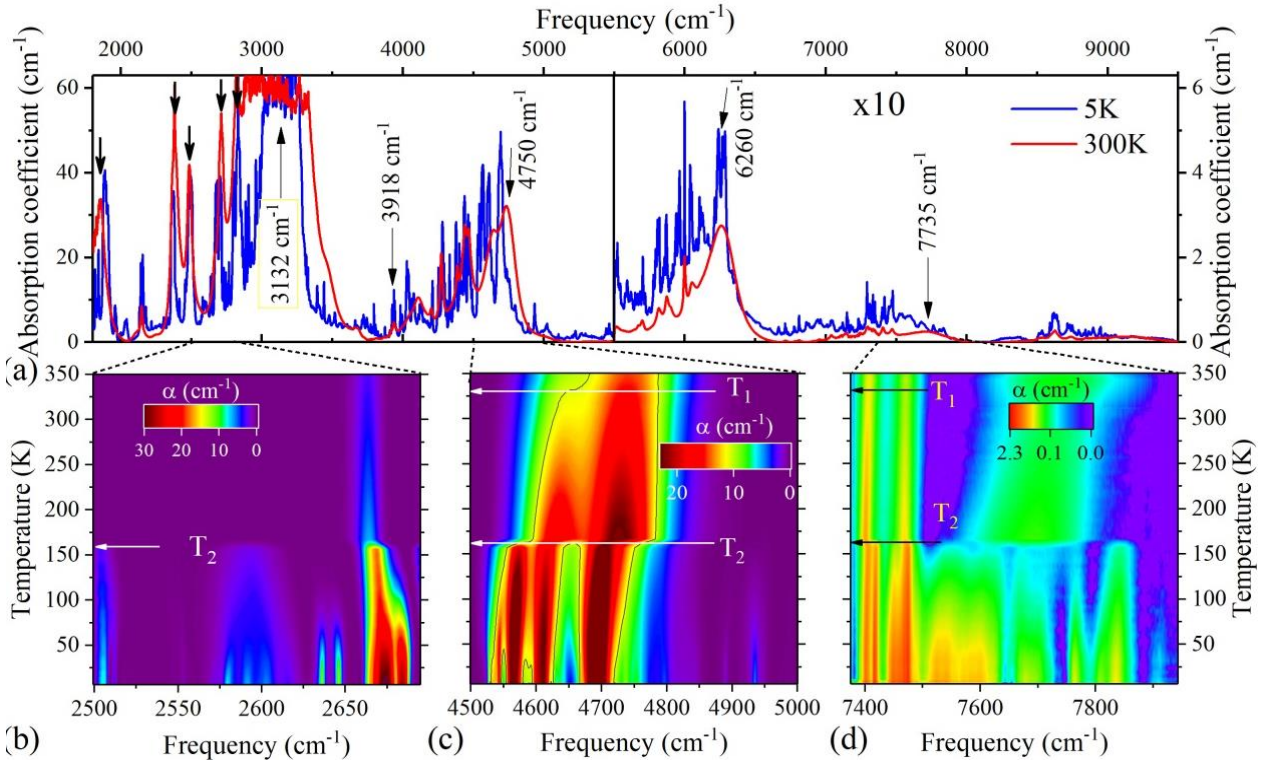

Fig. 12. Absorption spectra (a) at the temperatures of 300 and 5 K; (b,c,d) presented as color intensity maps in the frequency – temperature axes for selected frequency regions. In (b), the contribution from the strong band at about 3000 cm^{-1} is subtracted. Temperatures T_1 and T_2 of the structural phase transitions are marked by horizontal arrows.

Different features in parameters of optical modes

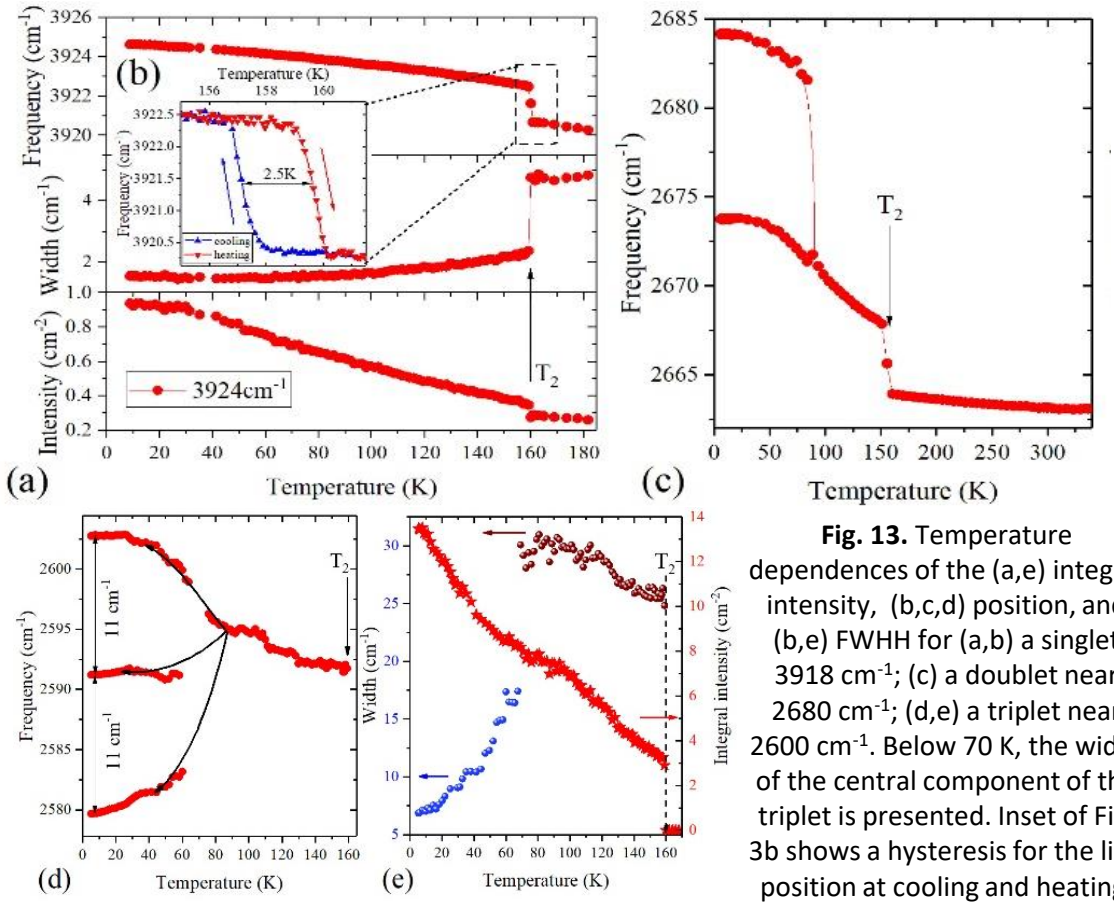

Fig. 13. Temperature dependences of the (a,e) integral intensity, (b,c,d) position, and (b,e) FWHH for (a,b) a singlet 3918 cm^{-1}; (c) a doublet near 2680 cm^{-1}; (d,e) a triplet near 2600 cm^{-1}. Below 70 K, the width of the central component of the triplet is presented. Inset of Fig. 3b shows a hysteresis for the line position at cooling and heating.

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1. The high-resolution terahertz (far IR) reflection and mid- and near-infrared absorption studies of $MAPbI_3$ hybrid perovskite single crystals are performed in a broad range of temperatures (5 – 350 K).
2. Several new low-frequency modes not reported before are observed.
3. The multiphonon spectrum is found to be highly sensitive to structural phase transitions in $MAPbI_3$ and to changes in the rotational dynamics of the $CH_3NH_3^+$ molecular cation.
4. At the lowest temperatures, tunneling occurs between several potential minima, which leads to tunneling splitting of the spectral line associated with the corresponding vibrational mode.
5. The presence of a noticeable bias and a hysteretic character of the behavior of the absorption edge of the zone at temperatures below the phase transition, which probably indicates the ongoing restructuring of the lattice in this region.

Thank you for attention!

Vasilisa Anikeeva

anikeeva.ve@phystech.edu