

## THE BROAD RANGE SPECTROSCOPY OF HYBRID PEROVSKITES $\text{CH}_3\text{NH}_3\text{PBX}_3$ ( $\text{X}=\text{I}, \text{Br}$ )\*

V.E. ANIKEEVA<sup>1,2</sup>, O.I. SEMENOVA<sup>3</sup>, M.N. POPOVA<sup>1</sup>, K.N. BOLDYREV<sup>1,2</sup>

<sup>1</sup> Institute of Spectroscopy of the Russian Academy of Sciences, Troitsk, Russian Federation

<sup>2</sup> HSE University, Moscow, Russian Federation

<sup>3</sup> Institute of Semiconductor Physics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation

Hybrid perovskites became one of the most popular functional materials in the field of photovoltaics. The complex structure of these compounds with the general formula  $\text{ABX}_3$  (where A is molecular organic cation  $\text{CH}_3\text{NH}_3$  or  $\text{CH}(\text{NH}_2)_2$ , B is cation of Pb or Sn, and X is halide anion I, Br, Cl) provides a number of unique optoelectronic properties such as long diffusion lengths [1], high carrier mobility [2] and optimal band gap for solar cells [3]. Many of transport properties are closely related to electron-phonon interactions and phonon spectra. Phonon modes in hybrid perovskites are distributed in three regions: vibrations of the lead halide inorganic cage and translational/librational modes of the  $\text{CH}_3\text{NH}_3$  cation are distributed between  $\sim 15$  and  $100 \text{ cm}^{-1}$  ( $0.45 - 3 \text{ THz}$ ),  $\text{CH}_3\text{NH}_3$  rocking modes, C–N stretching, and  $\text{CH}_3$  and  $\text{NH}_3$  bending vibrations occupy the spectral interval  $900 - 1600 \text{ cm}^{-1}$ , while C–H and N–H stretching mode frequencies are between  $3000$  and  $3200 \text{ cm}^{-1}$  [4]. Moreover, depending on the temperature, there are three structural phases for  $\text{CH}_3\text{NH}_3\text{PbI}_3$ : cubic ( $T > 330 \text{ K}$ ), tetragonal ( $330 \text{ K} < T < 160 \text{ K}$ ) and orthorhombic ( $T < 160 \text{ K}$ ); and four structural phases for  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ : cubic ( $T > 236 \text{ K}$ ), tetragonal I ( $236 \text{ K} < T < 155 \text{ K}$ ), tetragonal II ( $155 \text{ K} < T < 149 \text{ K}$ ) and orthorhombic ( $T < 149 \text{ K}$ ).

In this work, high quality  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  single crystals were studied by optical high-resolution spectroscopy in the wide frequency ( $15 - 19000 \text{ cm}^{-1}$ ) and temperature ( $5 - 300 \text{ K}$ ) ranges. The study in a wide frequency range made it possible to observe features at the temperatures of all phase transitions in both crystals as in the multiphonon absorption spectra and as near the fundamental absorption edge. So, for example, in Fig. 1 shows the temperature dependence of the shift of the peak position around  $6010 \text{ cm}^{-1}$  on cooling (blue) and heating (red) for  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ . A sharp shift in position indicates a structural phase transition of the first order. Also the spectral changes appear at the  $T = 70 \text{ K}$ , which correlate with the transition to the tunneling splitting. Several low-frequency modes predicted by calculations were experimentally observed for the first time in both  $\text{CH}_3\text{NH}_3\text{PbI}_3$  [5] and  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ .

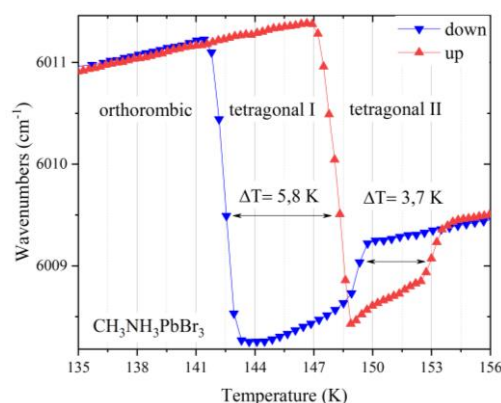


Fig.1. The hysteric dependence of peak positions near  $6010 \text{ cm}^{-1}$  from temperature during phase transitions in  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  (blue – for cooling, red – for heating).

### REFERENCES

- [1] Q. Dong, Y. Fang, et al., “Electron-hole diffusion lengths  $> 175 \mu\text{m}$  in solution-grown  $\text{CH}_3\text{NH}_3\text{PbI}_3$  single crystals,” *Science*, vol. 347, no. 6225, pp. 967–970, February 2015.
- [2] G. A. Elbaz, “Transport Phenomena in Lead Halide Perovskites and Layered Materials,” Columbia University, 2017.
- [3] D. I. Kim, J. W. Lee, R. H. Jeong, and J.-H. Boo, “A high-efficiency and stable perovskite solar cell fabricated in ambient air using a polyaniline passivation layer,” *Sci Rep*, vol. 12, no. 1, Art. no. 1, January 2022.
- [4] F. Brivio *et al.*, “Lattice dynamics and vibrational spectra of the orthorhombic, tetragonal, and cubic phases of methylammonium lead iodide,” *Phys. Rev. B*, vol. 92, no. 14, p. 144308, Oct. 2015.
- [5] K. N. Boldyrev, V. E. Anikeeva *et al.*, “Infrared Spectra of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  Hybrid Perovskite: Signatures of Phase Transitions and of Organic Cation Dynamics,” *J. Phys. Chem. C*, vol. 124, no. 42, pp. 23307–23316, Oct. 2020.

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