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THE BROAD RANGE SPECTROSCOPY OF HYBRID PEROVSKITES $CH_3NH_3PBX_3$ (X=I, BR)*

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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 ABX_3 (where A is molecular organic cation CH_3NH_3 or $CH(NH_2)_2$, 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 CH_3NH_3 cation are distributed between ~15 and 100 cm^{-1} (0.45 – 3 THz), CH_3NH_3 rocking modes, C−N stretching, and CH_3 and NH_3 bending vibrations occupy the spectral interval 900 – 1600 cm^{-1}, while C−H and N−H stretching mode frequencies are between 3000 and 3200 cm^{-1} [4]. Moreover, depending on the temperature, there are three structural phases for $CH_3NH_3PbI_3$: cubic (T > 330 K), tetragonal (330 K < T < 160 K) and orthorhombic (T < 160 K); and four structural phases for $CH_3NH_3PbBr_3$: cubic (T > 236 K), tetragonal I (236 K < T < 155 K), tetragonal II (155 K < T < 149 K) and orthorhombic (T < 149 K).

In this work, high quality $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ single crystals were studied by optical high-resolution spectroscopy in the wide frequency (15 – 19000 cm^{-1}) and temperature (5 – 300 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 cm^{-1} on cooling (blue) and heating (red) for $CH_3NH_3PbBr_3$. A sharp shift in position indicates a structural phase transition of the first order. Also the spectral changes appear at the T = 70 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 $CH_3NH_3PbI_3$ [5] and $CH_3NH_3PbBr_3$.

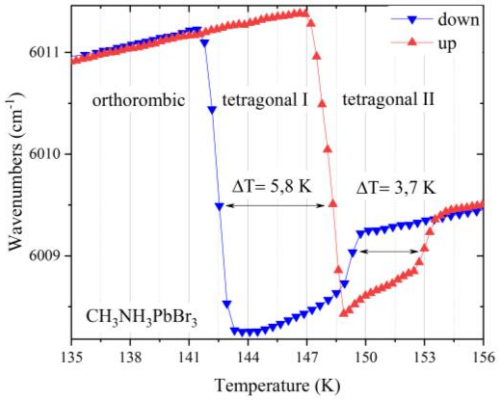

Fig.1. The hysteretic dependence of peak positions near 6010 cm^{-1} from temperature during phase transitions in $CH_3NH_3PbBr_3$ (blue– for cooling, red – for heating).

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