Struktūrinio fazinio virsmo $CH_3NH_3PbCl_3$ hibridiniame perovskite tyrimas EPR spektroskopija

EPR spectroscopy of structural phase transition in $CH_3NH_3PbCl_3$ hybrid perovskite

Gediminas Usevičius[1], Michael Allan Hope[2], Justinas Turčak[1], Jūras Banys[1], Mantas Šimėnas[1]
[1]Faculty of Physics, Vilnius University, Sauletekio av. 9, 10222 Vilnius, Lithuania
[2] Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland
gediminas.usevicius@ff.vu.lt

Recently, hybrid organic-inorganic compounds have attracted an immense attention of the scientific community due to their diverse physical and chemical properties. The most interesting and researched subgroup of hybrid perovskites is methylammonium lead halides $CH_3NH_3PbX_3$ (where X = I, Br, Cl), due to their potential applications in efficient and low-cost solar cells, LEDs, and photodetectors [1]. Such properties of these materials is a result of multiple physical attributes such as a suitable band gap and a low carrier recombination [2]. The latter is related to the dynamics of methylammonium cations, whose motion is tightly connected to the structural phase transitions in the material.

Here, we use electron paramagnetic resonance (EPR) spectroscopy to study the dynamics of methylammonium cations and structural phase transitions in methylammonium lead chloride $CH_3NH_3PbCl_3$. In this work, we employ temperature dependent multifrequency continious-wave (CW) and pulsed EPR spectroscopy to characterize paramagnetic Mn^{2+} probe ions in $CH_3NH_3PbCl_3$.

The temperature dependent CW spectra reveal the first order phase transition at ~175 K. By simulating the experimental CW spectra, we are able to determine the temperature dependence of the zero-field splitting (Fig. 1). It shows a rapid increase with decreasing temperature below 175 K, indicating deformation of the inorganic framework at the tetragonal-orthorhombic phase transition.

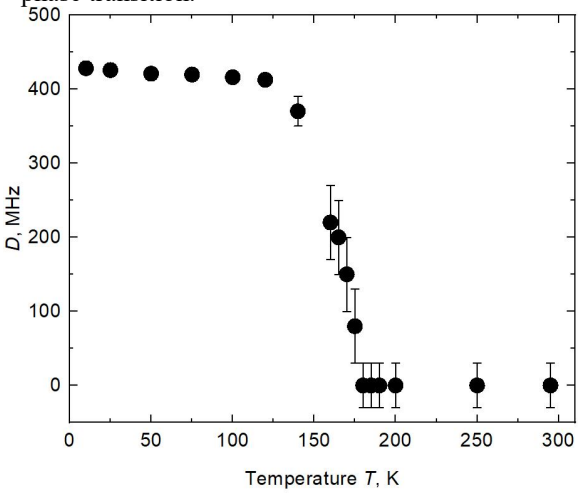

Fig. 1. Temperature dependence of the zero-field splitting.

Using pulsed EPR spectroscopy, we measure relaxation time T_1 and decoherence time T_2 of the Mn^{2+} center in $CH_3NH_3PbCl_3$. The former is explained by the first-order Raman effect due to optical phonons and the direct relaxation, as depicted in Fig. 2. We relate the obtained phonon energy of 61(4) cm^{-1} to the dynamics of the inorganic framework.

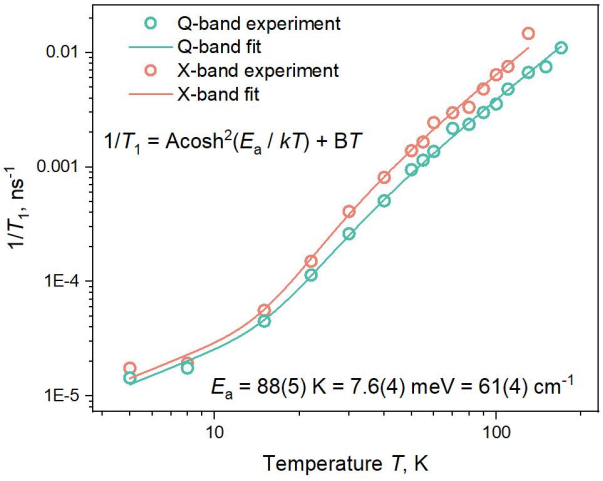

Fig. 2. Temperature dependence of the T_1 relaxation time measured with X- (9.5 GHz) and Q- (35 GHz) band EPR. The experimental data was fitted using the Raman mechanism involving optical phonons.

Keywords: EPR, perovskite, lead halides, phase transition.

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Literature

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