Why the knowledge of the anharmonicity is important for the structural processes that govern the orthorhombic/tetragonal phase transformation in chlorine-substituted $MAPbI_3$

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The anharmonicity of the lead-halide bond influences the optoelectronic properties of hybrid perovskites. Since many optoelectronic properties undergo large changes during the orthorhombic/tetragonal phase transformation, this temperature range is the focus of our investigation. The aim of this study was to determine the anharmonicity of the lead-halide bond in chlorine-substituted $MAPbI_3$ by combining temperature-dependent synchrotron XRD and Pb L3-edge EXAFS measurements from 20 K to 265 K. The partial negative thermal expansion (NTE) behaviour of the $[PbX_6]$ octahedra observed with XRD is related to the negative tension effects of the lead-halide bond in $MAPbI_3$ and $MAPbI_{2.94}Cl_{0.06}$ observed with EXAFS, whereas in $MAPbCl_3$ the positive bond expansion towards higher temperatures is predominant. The experimentally observed EXAFS parameters showed clear effects at 100 % chlorine substitution. The lead-halide bond in the orthorhombic phase of $MAPbCl_3$ was much less anharmonic than in pure $MAPbI_3$. However, after the phase transition to the room temperature phase, $MAPbCl_3$ showed much greater anharmonicity, indicating a significantly changed state of the lead-chlorine bond. At 2 % chlorine substitution, smaller changes became apparent compared to $MAPbI_3$. But significant differences between $MAPbI_3$ and $MAPbI_{2.94}Cl_{0.06}$ could be observed in the degree of anisotropy γ and the asymmetry parameter $C_3/C_2^{3/2}$. By determining the structural parameters that are required for the conversion of the effective force constants k_0 and k_3, into the Morse potential parameters α and D, we found our results to be in conformance with other experimental findings.

Keywords: EXAFS; anharmonicity; halide perovskite; photovoltaics

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