# Strong anharmonicity at the origin of anomalous thermal conductivity in $Cs_2NaYbCl_6$

Antonio Cappai *, Claudio Melis*, Francesco Quochi*,
Michele Saba *, Daniela Marongiu*, and Luciano Colombo*
Dipartimento di Fisica, Università di Cagliari, Italy

e-mail: luciano.colombo@dsf.unica.it

## Introduction

Double halide perovskites have gained attention in recent years due to their potential applications in thermoelectric and energy-related devices [1], [2], [3]. In particular, it was recently found that specific perovskites exhibit anomalous dependence on temperature of thermal conductivity that deviates from the standard phonon-dominated behavior $\kappa(T) \sim T^{-1}$, as well as negative thermal expansion coefficients [4]. This deviation has been attributed to several factors such as structural disorder, lattice defects, and grain boundary scattering [5], [6].

Among double halide perovskites, rare earth-based perovskites (as $Cs_2YbNaCl_6$) have shown particularly interesting properties. The possibility to tune the electronic bandgap [7] combined with the intrinsically low thermal conductivities ($1-10$ W m$^{-1}$ K$^{-1}$) make these systems very promising for thermoelectric applications.

## Methods

We perform a full ab-initio study of the (*i*) structural, (*ii*) electronic and (*iii*) lattice dynamical properties of $Cs_2YbNaCl_6$ by using the QuantumEspresso software suite [8], [9]. Ultrasoft pseudopotential (USPP), PBE functional and a plane wave basis set with an energy cut-off of $45$Ry are adopted to describe the conventional cubic cell (40 atoms) used in this study.

The lattice dynamical properties, i.e. the phonon dispersion curves and the phonon lifetimes, are calculated using the finite-displacement (*frozen-phonon*) methodology as implemented in the Alamode software package [10]. Fourth-order anharmonicity is eventually included using the Self-Consistent Phonon approach (SCPH) [11]. The thermal conductivity $\kappa(T)$ is calculated by solving the Boltzmann Transport Equation in the Relaxation Time Approximation (BTE-RTA).

## Results

To validate the computational setup used to modelize the double perovskite structure, a series of benchmark calculations was conducted. The lattice parameter served as the figure of merit, and we achieved a remarkable agreement with the experiment within a margin of 0.6%. We then calculated the harmonic and anharmonic interatomic force constants to determine the phonon dispersion curves and lifetimes, respectively. Our observations revealed that when only cubic anharmonicity is considered to describe phonon scattering processes, the thermal conductivity at 300 K resulted in $0.25$W m$^{-1}$ K$^{-1}$, significantly underestimating the corresponding experimental value of $\kappa^{\rm exp} = 0.55$W m$^{-1}$ K$^{-1}$. In contrast, when we included fourth-order anharmonicity using the SCPH method, we were able to (*i*) resolve the underestimation and (*ii*) explain the anomalous trend of $\kappa(T)$ observed in the experiment. Specifically, we attribute the failure of $T^{-\alpha}$ law in describing $\kappa(T)$ to an unusual increase in the phonon group velocity and lifetimes for $500\text{K} \leq T \leq 800\text{K}$.

## Acknowledgment

We acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No.341 published on March 13, 2022) by the Italian Ministry of University and Research (MUR) funded by the European Union – NextGenerationEU. Award Number: Project code PE_00000021, Concession Decree No. 1561 adopted on October 11, 2022 by the Italian Ministry of Ministry of University and Research (MUR), CUP F53C22000770007, Project title "NEST - Network 4 Energy Sustainable Transition"

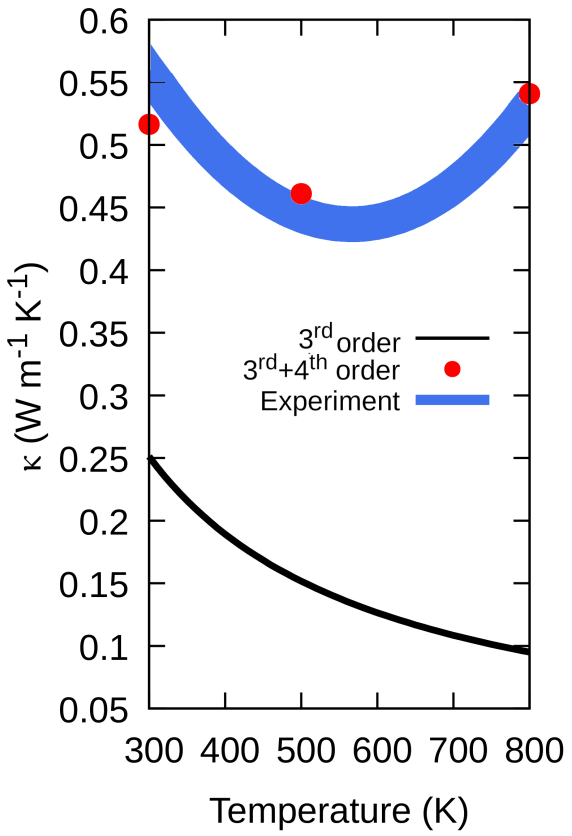


Fig. 1. $Cs_2NaYbCl_6$ thermal conductivity $\kappa$ as a function of the temperature. The black line shows the theoretical prediction of $\kappa(T)$ based solely on cubic anharmonicity. The conspicuous underestimation of the anomalous experimental trend (blue band) is eventually resolved by the inclusion of fourth-order anharmonicity (red points)

## References


[1] Fatemeh Heidari Gourji and Dhayalan Velauthapillai. A review on cs-based pb-free double halide perovskites: From theoretical and experimental studies to doping and applications. *Molecules*, 26(7):2010, 2021.

[2] Sebastian F Hoefler, Gregor Trimmel, and Thomas Rath. Progress on lead-free metal halide perovskites for photovoltaic applications: a review. *Monatshefte für Chemie-Chemical Monthly*, 148:795–826, 2017.

[3] Shadrack J Adjogri and Edson L Meyer. A review on lead-free hybrid halide perovskites as light absorbers for photovoltaic applications based on their structural, optical, and morphological properties. *Molecules*, 25(21):5039, 2020.

[4] Ikuya Yamada, Kazuki Tsuchida, Kenya Ohgushi, Naoaki Hayashi, Jungeun Kim, Naruki Tsuji, Ryoji Takahashi, Masafumi Matsushita, Norimasa Nishiyama, Toru Inoue, et al. Giant negative thermal expansion in the iron perovskite srcu3fe4o12. *Angewandte Chemie International Edition*, 50(29):6579–6582, 2011.

[5] Tianjun Liu, Sheng-Ying Yue, Sinclair Ratnasingham, Thibault Degousée, Pritesh Varsini, Joe Briscoe, Martyn A. McLachlan, Ming Hu, and Oliver Fenwick. Unusual thermal boundary resistance in halide perovskites: A way to tune ultralow thermal conductivity for thermoelectrics. *ACS Applied Materials & Interfaces*, 11(50):47507–47515, 2019. PMID: 31752489.

[6] Animesh Bhui, Tanmoy Ghosh, Koushik Pal, Kewal Singh Rana, Kaushik Kundu, Ajay Soni, and Kanishka Biswas. Intrinsically low thermal conductivity in the n-type vacancy-ordered double perovskite cs2sni6: Octahedral rotation and anharmonic rattling. *Chemistry of Materials*, 34(7):3301–3310, 2022.

[7] Adil Alshoaibi, Mohammed Benali Kanoun, Bakhtiar Ul Haq, Salem AlFaify, and Souraya Goumri-Said. Ytterbium doping effects into the ba and ti sites of perovskite barium titanate: Electronic structures and optical properties. *Results in Physics*, 18:103257, 2020.

[8] P Giannozzi, S Baroni, and N Bonini. J. phys.: Condens. matter. 21, 2009.

[9] Qian Zhang, Shuhui Tao, Ruowei Yi, Chunhui He, Cezhou Zhao, Weitao Su, Alexander Smogunov, Yannick J Dappe, Richard J Nichols, Li Yang, et al. P. giannozzi et al., advanced capabilities for materials modelling with quantum espresso. *J. Phys.: Condens. Matter*, 29:465901, 2017.

[10] T Tadano, Y Gohda, and S Tsuneyuki. Anharmonic force constants extracted from first-principles molecular dynamics: applications to heat transfer simulations. *Journal of Physics: Condensed Matter*, 26(22):225402, may 2014.

[11] Terumasa Tadano and Shinji Tsuneyuki. Self-consistent phonon calculations of lattice dynamical properties in cubic $srtio_3$ with first-principles anharmonic force constants. *Phys. Rev. B*, 92:054301, Aug 2015.