Abstract

The escalating global energy demand across various sectors underscores the need for clean and sustainable energy sources. Among these alternatives, thermoelectric (TE) energy conversion has emerged prominently, capitalizing on the widespread availability of waste heat, finding applications in small-scale devices like wristwatches to larger-scale space technologies. TE materials hold significant potential for both power generation and the recovery of waste heat, facilitating the conversion of thermal energy into electricity. A dimensionless constant, called the figure of merit (zT) describes the energy conversion efficiency of a thermoelectric material, which is intricately linked to both the electronic and lattice thermal transport properties. The search for superior thermoelectric materials or methodologies to elevate thermoelectric efficiency is ongoing due to the comparatively lower efficiency offered by the existing thermoelectric materials. To tune, or rather, enhance the zT of a thermoelectric material, the primary aim involves synergistically enhancing the power factor ($S^2\sigma$) while concurrently reducing the thermal conductivity ($\kappa = \kappa_e + \kappa_L$). The current thesis focuses on exploring innovative techniques to enhance the thermoelectric characteristics of two-dimensional materials within the framework of Density Functional Theory (DFT). The DFT-based first-principles calculations not only provide fundamental insights into the electronic and phononic mechanisms influencing the thermoelectric effect but also facilitate a swift and cost-effective initial assessment of potential materials. This approach can effectively support and direct future experimental endeavours. Accurate determination of lattice thermal conductivity (κ_L) is pivotal in effectively screening potential thermoelectric materials, given its significant influence on the energy conversion efficiency of semiconducting materials. Strategies for manipulating κ_L within a broad range become imperative due to the demand for low κ_L materials to enhance thermoelectric performance and high κ_L materials for efficient heat dissipation. Here, in this thesis, we have attempted to improve the thermoelectric and thermal transport characteristics of different two dimensional (2D) materials by employing various mechanical strains, such as in-plane uniaxial strain and hydrostatic pressure. By examining the four-phonon scattering, this thesis emphasizes the importance of higher-order anharmonicity in accurately predicting the lattice thermal transport properties of two-dimensional materials.

In the first part of the thesis, we explored pathways to maximize the energy conversion efficiency of a thermoelectric material by tuning its electronic and vibrational properties, employing monolayer (ML) MoS_2 as a prototype material. The findings, as reported in this thesis, effectively illustrate that different mechanical strains, such as in-plane uniaxial strain and hydrostatic pressure, can adeptly engineer the thermoelectric capabilities of ML-MoS_2. Notable enhancement in the thermoelectric performance has been achieved by applying direction-specific in-plane tensile strains or hydrostatic pressure on ML-MoS_2. The application of in-plane tensile strains along the two orthogonal directions, namely arm-chair (AC) and zig-zag (ZZ) direction, induces a detrimental effect on the electronic power factor, however, concurrently reduces the lattice thermal conductivity (κ_L) significantly. We have found a notable increase in the charge carrier mobility (μ) and consequently, the relaxation time (τ) with in-plane strains. The large decrease in κ_L and increase in τ, induced by the uniaxial strains, in general and strains along the ZZ direction, in particular, act in unison to result in an anisotropic enhancement of the thermoelectric efficiency (zT) of ML-MoS_2. The in-plane uniaxial strain, although improves the thermoelectric performance of ML-MoS_2, have detrimental effect on the power factor and is extremely challenging to realize in experiments. We then attempted to optimize the thermoelectric zT of ML-MoS_2 by hydrostatic pressure, a method more feasible for experimental implementation. The hydrostatic pressure induced valley convergence of the conduction band valleys at K-point and Λ-point leads to a substantial increase in the Seebeck coefficient (S) and the power factor ($S^2\sigma$) of ML-MoS_2. Additionally, the electronic mobility (μ) and relaxation time (τ) are found to increase remarkably owing to the very low deformation potential associated with the conduction band valley at Λ-point. Moreover, the hydrostatic pressure causes significant reduction in the κ_L of ML-MoS_2, resulting from the increase in crystal anharmonicity and quadraticity in the ZA phonon dispersion. These combined effects viz., enhanced power factor and relaxation time, coupled with the decreased κ_L work synergistically to yield a notable improvement in the thermoelectric performance of ML-MoS_2. Thus, the approach using hydrostatic pressure not only resolves the issues encountered with the in-plane strains, but also outperforms the direction-specific uniaxial strains in terms of the resulting thermoelectric efficiency.

The second part of the thesis investigates the significance of higher-order anharmonicity in the lattice thermal transport of 2D-materials like ML-MoS_2 and ML-ZnO, by analyzing four-phonon scattering in addition to the intrinsic three-phonon scattering. Implementation of in-plane mechanical strain served a dual purpose: tuning the thermal transport characteristics and providing deeper insights into the underlying mechanisms at play. Both in ML-MoS_2 and ML-ZnO, owing to certain vibrational and structural characteristics, such as the quadratic dispersion of the ZA mode, large frequency gap in the phonon dispersion and reflection symmetry imposed additional selection rule, the phonon lifetime is found to be very high when only three-phonon scattering is considered. The subsequent incorporation of the four-phonon scattering in the thermal transport calculations significantly reduces the phonon lifetime and thereby, their contribution in thermal transport. To accurately depict the phonon transport mechanism and, consequently, the lattice thermal conductivity (κ_L) of ML-MoS_2, the incorporation of four-phonon scattering in thermal transport calculations is crucial. Notably diminishing the contribution of ZA phonons in κ_L, the inclusion of four-phonon scattering aligns the computed κ_L more closely with experimental observations, rectifying the prior overestimation from three-phonon based calculations. The strong coupling between the four-phonon scattering mechanism and the dispersion characteristics of the ZA phonons is elucidated by applying in-plane mechanical strains. Contrary to conventional expectations observed in ML-MoS_2 and any other bulk materials, the κ_L of ML-ZnO displays a substantial increase under the influence of in-plane tensile strains. This anomaly offers an avenue to significantly enhance the material's thermal transport properties. The tensile strain induced quadratic to linear transition of the ZA mode dispersion and thereby, the resulting increase in group velocity and decrease in phonon population is largely responsible behind this unusual behaviour. The four-phonon scattering strength although found to be significantly high in ML-ZnO, does not alter the increasing trend of κ_L with tensile strain. Similar to ML-MoS_2, the four-phonon scattering strength and thereby, the significance of higher-order anharmonicity reduces with increasing tensile strain, owing to the increasing linearity in the ZA phonon dispersion. These findings offer pivotal insights into the phonon transport mechanism and thereby, significantly advance the thermal transport studies concerning any 2D materials, in general.