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LETTER

Solid-state thermal regulation

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Dear Editor,

With the normalization of extreme thermal environments such as high heat flux, thermal shock, and microgravity, the proportion of electronic device failures caused by temperature factors has exceeded 55%. Solid-state thermal regulation, which directly modifies material thermal properties with strong heat flux control capabilities, offers transformative solutions for thermal management challenges. However, thermal carrier phonons, which are a kind of quasiparticles, present an internationally recognized scientific challenge because of their inability to directly couple with external stimuli. Due to the vector characteristics of heat flux: intensity, rate, and direction, solid-state thermal regulation faces three major challenges: unclear pathways for strengthening regulation, poor performance in reversible regulation, and low energy density in reverse regulation. In this letter, we discuss the solid-state thermal regulation at the phonon level to address these three primary challenges, aiming to achieve controllable thermal transport.

INTRODUCTION

Nowadays, extreme thermal environments such as high heat flux, thermal shock, and microgravity are becoming increasingly normal. The proportion of electronic device failures caused by temperature factors has exceeded 55%, and the fields of integrated circuits, electronic countermeasures, and aerospace are facing severe thermal management challenges. There is an urgent need to develop fast and accurate heat flow regulation to stabilize temperature. Solid-state thermal regulation, which directly modifies material thermal properties, has strong heat flux control capabilities, offering transformative solutions for thermal management challenges. For example, Liu et al. introduced antiferroelectrics into the field of thermal regulation and developed a new type of high-performance solid-state thermal functional device that can manipulate the thermal transport in real time.[1] However, thermal carrier phonons are quasiparticles and cannot directly couple with external stimuli, presenting an internationally recognized scientific challenge. Due to the vector characteristics of heat flux: intensity, rate, and direction, solid-state thermal regulation faces three major challenges: unclear pathways for strengthening regulation, poor performance in reversible regulation, and low energy density in reverse regulation. In this letter, we discuss the solid-state thermal regulation at the phonon level to address these three primary challenges (Figure 1), aiming to achieve controllable thermal transport.

STRENGTHENING REGULATION OF SOLID-STATE THERMAL TRANSPORT

Loading pressure, improving crystallinity, and adding high thermal conductivity fillers are three widely employed methods to strengthen thermal transport. However, these methods are not rooted in the phonon level and cannot be easily employed. In 1973, Slack gave a phenomenological formula for phonon thermal conductivity, and accordingly, four criteria for enhancing thermal transport were proposed: strong bond strength, light mass, simple structure, and weak anharmonicity;[2] in 2013, Lindsay et al. pointed out that acoustic-optical phonon band gap and phonon branch bunching effects can suppress scattering and enhance thermal transport;[3] in 2022, Liu et al. proposed a new criterion for enhancing thermal transport by high crystal symmetry, and introduced the space group symmetry operation number *SO* to evaluate the degree of crystal symmetry.[4] Based on the new criterion, the semiconductor bcc-C6 that owns *SO* of 96 in the Database of carbon allotropes was found to have an ultra-high thermal conductivity of 1053 W/m-K at room temperature, and the reason why diamond has the highest thermal conductivity can be elucidated, because space group of diamond has the highest *SO* of 192 among all 230 space groups.

Because of these criteria from the view of phonon, lattice contraction, high crystal symmetry, high electron density distribution symmetry, quasi-one-dimensional structure, and phonon focusing were proposed to strength thermal transport. The underlying mechanism for these methods is improving phonon velocity, phonon specific heat, and/or phonon lifetime, which are the three factors dominating the phonon thermal transport. For example, through increasing phonon velocity and suppressing phonon scattering (inverse of phonon lifetime), lattice contraction was employed to successfully enhance thermal conductivity in TiS_3[5] and WO_3.[6] In addition to a single mechanism, multiple mechanisms can be combined together to enhance the ability of thermal transport strengthening. A breakthrough is in alloyed/doped systems. Through combining lattice contraction, high crystal symmetry, and high electron density distribution symmetry, compared with pristine Si, the thermal conductivity in Si-C alloys increases rather than decreases for the first time despite the lattice, mass, and potential distortions.[7]

Strengthening thermal transport, as one important type of solid-state thermal regulation, is crucial to alleviate or even eliminate the thermal dissipation issue in microelectronic devices. The basic rule is to enhance phonon velocity, phonon specific heat, and/or phonon lifetime. Single mechanism or multiple mechanisms can be employed to enhance these three factors, realizing the enhancement of phonon transport.

REVERSIBLE REGULATION OF SOLID-STATE THERMAL TRANSPORT

In the past few decades, numerous efforts have been made to regulate the thermal conductivity of solid materials. However, most of these methods are "irreversible", meaning that the thermal conductivity remains largely unchanged once the material has been synthesized. In contrast to irreversible approaches, reversible regulation of thermal conductivity is more useful since it would enable real-time manipulation of heat flux and help maintain a constant device temperature despite varying heat loads. In various materials, many methods have been tried to reversibly regulate thermal conductivity, such as electrochemical manipulated ions insertion/removal, light-triggered change in morphology of molecular chains, and temperature-triggered phase transition. For high-performance reversible regulation, it should satisfy four conditions: (i) a wide regulation range; (ii) a short regulation time; (iii) a long lifetime of regulation; and (iv) a large regulation temperature range. Due to the lack of direct connection between phonon and external stimuli, it has been difficult to find a material that fulfills all the four essential conditions.

Ferroelectric materials

Ferroelectrics (FEs) are materials that exhibit spontaneous electric polarization, which can be reversed by applying an external electric field. In FEs, domain wall scattering and structural phase transition are the two main mechanisms that have been developed to reversibly regulate thermal conductivity. For domain wall scattering, due to the mismatch between domain size and phonon mean free path, the regulation range is typically smaller than 1.2 at room temperature. For structural phase transition, a high-contrast (>2.2), long-lifetime (>10^7), and fast-speed (<150 ns) regulation has been reported in experiment by external field triggered antiferroelectric-ferro-

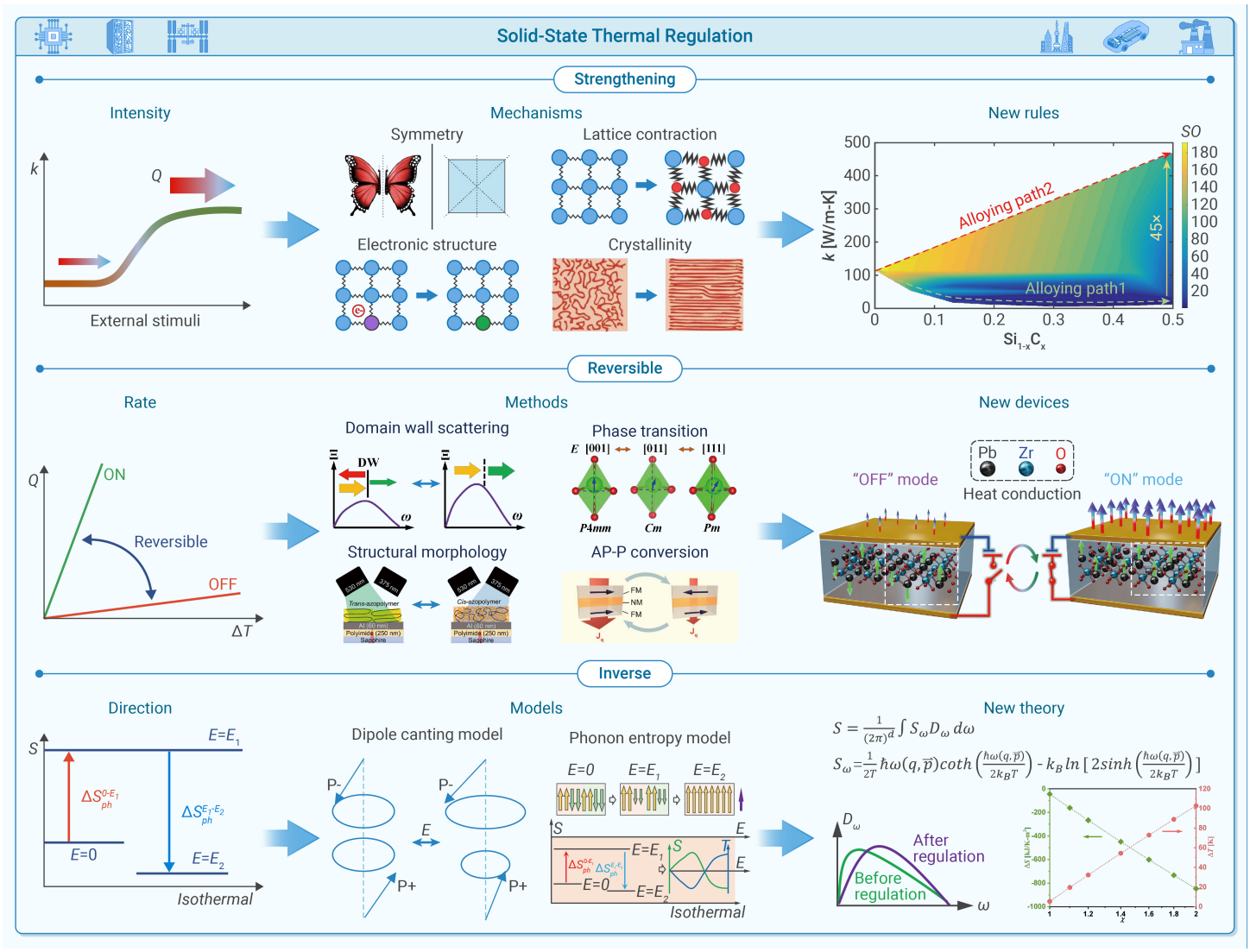

Figure 1. Solid-state thermal regulation

electric phase transition.[1] However, the regulation range of thermal conductivity is still not high. In theory, the displacive phase transition and order-disorder phase transition induced by external field have the potential to achieve a regulation range greater than 5, which is worthy of experimental verification.

Ferromagnetic materials

Ferromagnetics (FMs) are materials that possess a permanent magnetic moment even in the absence of an external magnetic field, displaying large and sustained magnetization. In FMs, spin-phonon coupling (SPC), domain wall scattering, and antiparallel-parallel (AP-P) conversion of magnetization vectors are the three main mechanisms that have been developed to reversibly regulate thermal conductivity. Regarding SPC, due to significant spin fluctuations occurring only near the magnetic transition temperature, which is much lower than room temperature, the temperature range for regulation is not wide, even though the regulation range can reach up to 100 around 10 K. For domain wall scattering, magnon transport can be significantly affected, leading to the change of thermal conductivity. Compared to SPC, domain wall scattering can persist around room temperature, however, the regulation range is much smaller, around 2. For AP-P conversion of magnetization vectors, the thermal conductivity is regulated by the magnetothermal resistance effects. Similar to domain wall scattering, the regulation can also persist around room temperature and the regulation range is about 2.

Polymers

For polymers, the control of structural morphology and H-bond density as well as hydration/dehydration are the three main mechanisms that have been developed to reversibly regulate thermal conductivity. Regarding the control of structural morphology, light triggered chain rearrangement and electric field triggered phase transition are two methods. Regardless of the method, the regulation range is smaller than 3 near room temperature. Temperature triggered phase transition can induce a high regulation range of 10, but it can only work near the phase transition. Since H bonds in polymers can enhance the heat transport, modulating the H-bond density is an efficient method to regulate thermal conductivity. Through changing the orientation of molecular chains, the H-bond density can be modulated. Till now, the reported regulation range is about 2. In many polymeric systems, thermal transport is humidity sensitive. Through hydration and dehydration process, the regulation range can reach up to 4. However, the process needs a long time.

In general, each material has its own limitation and no single material can satisfy all the four essential conditions for high-performance reversible thermal regulation. One possible solution strategy is to develop new materials that combine the advantages from different materials such as ferroelectric polymers.

INVERSE REGULATION OF SOLID-STATE THERMAL TRANSPORT

The third important type of solid-state thermal regulation is inverse regulation, i.e., solid-state refrigeration. Electrocaloric cooling is a very promising solid-state refrigeration technology with the advantages of zero GWP, high

COP, and compact size. Boundary control, composition control, and nanodomain engineering are widely employed to modulate the cooling energy density. However, these methods are phenomenological and empirical, and cannot provide the underlying mechanism at the entropy level. As a result, electrocaloric cooling faces two main challenges: (i) the unclear origin of negative electrocaloric effect; and (ii) the low cooling energy density.

Dipole canting model is firstly proposed to explain the negative electrocaloric effect and the change in dipolar entropy due to dipole destabilization is the core concept.[8] However, a recent calorimetric experiment challenged this model that the dipole destabilization of the antiparallel polarization has weak effects on the negative electrocaloric effect.[9] To uncover the origin, phonon entropy theory was proposed by Liu et al.[10] They developed a first-principles calculation method to reproduce the evolution of the lattice structure along the phase transition path, and accordingly, the phonon entropy change was directly calculated. Through comparing the adiabatic temperature change from phonon entropy change in theory and that from all entropy change in experiment, they uncovered that the negative electrocaloric effect is induced by the latent heat associated with phonon entropy rather than the dipolar entropy.

Furthermore, Liu et al. derived phonon frequency accumulated phonon entropy, which provides modal analysis for regulating electrocaloric cooling for the first time. Based on this new theory, modulating the phonon density of states for low-frequency phonons during the phase transition process can significantly enhance the cooling energy density. An easy way to obtain a high entropy change is to find a material with a low Young's modulus and a large phonon density of states in the low-frequency range.

In general, to improve the cooling energy density is a challenge for solid-state refrigeration especially for electrocaloric cooling. Phonon entropy engineering provides a theoretical tool to address this challenge, which advances the field of solid-state refrigeration.

CONCLUSION

Many important achievements have been made in solid-state thermal regulation, including new criteria of lattice contraction and high crystal symmetry to strengthen thermal transport, antiferroelectric-ferroelectric structural phase transition to improve thermal regulation range, and phonon entropy engineering to enhance cooling energy density. Nevertheless, solid-state thermal regulation is a new area and there is still much challenging work to be done to enhance the regulation capabilities. For strengthening regulation, the concept of path design could be the future research direction, which can actively design the thermal transport behavior. For example, three parameters of lattice contraction rate, crystal symmetry, and electron density distribution can be employed to define the alloy path, and thermal transport behaviors should be totally different along different alloy paths since these three parameters control the phonon velocity, lifetime, and heat capacity. For reversible regulation, developing new materials that combine the advantages from different materials such as ferroelectric polymers is an important direction. In addition, breaking free from conventional single-mechanism paradigms and adopting multi-mechanism synergistic regulation is another important direction. For reverse regulation, phonon entropy theory provides the first theoretical formula to modulate cooling energy density. The future direction is designing the mode dependent phonon entropy behavior to enlarge the cooling energy density. We believe that solid-state thermal regulation would become the next-generation thermal management technology, which can achieve controllable thermal transport.

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AUTHOR CONTRIBUTIONS

Initiation and conceptualization: C.H.L. Investigation: C.H.L., W.C., and Y.T. Funding acquisition: C.H.L and W.L. Supervision: C.H.L. Writing - original draft: W.C., Y.T., and C.H.L. Writing - review and editing: C.H.L.

DECLARATION OF INTERESTS

The authors declare no competing interests.