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Influence of Shrinkage on Phase Change Material-based Thermal Rectifiers

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ABSTRACT

Thermal rectifiers have recently emerged as a field of interest because of their potential application in a wide-ranging field. Thermal rectifiers can be employed to shield heat-sensitive electronics components, building thermal management and thermal energy conversion. A thermal rectifier allows heat transfer in a preferred direction while curtailing heat transfer in the reverse direction. Recently, the thermal conductivity differential of Phase Change Materials (PCMs) in their different states has been employed to develop thermal rectifiers. However, these studies are limited to analyzing the effect of change in the thermal conductivity alone, neglecting the influence of change in other thermophysical properties. The difference in PCM density in different states leads to the development of void volume upon phase transition, which can significantly alter thermal rectification. Therefore, this study analyzes the interdependent influence of thermal conductivity and density on thermal rectification under a wide range of temperature biases. The presence of void volume under reverse bias augments thermal rectification, whereas it has an adverse effect when developed under the forward bias. A criterion is developed to identify when the influence of density negates that of thermal conductivity, which requires the design of the thermal rectifier to be altered. Furthermore, optimization criteria and expressions for optimal thermal rectification are developed, incorporating the influence of both thermal conductivity and density.

1. Introduction

Thermal rectifiers, analogous to electrical diodes, allow heat transfer only in the preferential direction. Thermal rectifiers can be efficiently employed to shield heat-sensitive electronics components by allowing thermal transport to heat sink while limiting crosstalk between different components safeguarding components with lower maximum operational temperature. Similarly, thermal rectifiers can be employed to allow thermal transport from buildings to surrounding on hot days while curtailing during winters, thus increasing the efficiency of the building thermal management system.

Thermal rectification quantifies the efficacy of a thermal rectifier, which is defined as the ratio of heat transfer under the forward temperature bias to that under reverse temperature bias of the same magnitude. Thermal rectification was first experimentally observed by Starr *et al.* [1] at the interface of copper and copper oxide. O'Callaghan *et al.* [2] developed a thermal rectifier using a series of thin copper disks, each with a smooth and a rough surface stacked such that all smooth surfaces face in the same direction and rough surfaces in the opposite direction. Kobayashi *et al.* [3] utilized two different materials with dissimilar thermal conductivity dependence on temperature. Kobayashi *et al.* [4] further augmented the thermal rectification by employing dissimilar structures. Schmotz *et al.* [5] developed a thermal diode by drilling different shapes using an ion beam. Chang *et al.* [6] differentially loaded heavy molecules in carbon and boron nitride nanotubes to obtain thermal rectification.

The significant difference in the thermal conductivity of Phase Change Materials (PCMs) in different states makes them a potential candidate for the development of thermal rectifiers. Therefore, recent focus has been on the analysis of the potential of PCM-based thermal diodes. The PCM-based thermal rectifiers are categorized in two types, first consists of a PCM and another material whose thermophysical properties do not alter significantly in the operating temperature range, second consists of two PCMs. A single PCM alone cannot be employed as a thermal rectifier; because of symmetry, the thermal resistance to heat flow in both directions will be the same. In both the types of PCM-based thermal rectifiers, PCMs are arranged such that they remain in their higher thermal conductivity state under forwards temperature bias, whereas in their lower thermal conductivity state under reverse thermal

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Nomenclature

H	Height of the thermal rectifier (m)
h	Height occupied by PCM (m)
k	Thermal Conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
L	Length (m)
Q	Heat Transfer Rate (W)
R	Thermal Resistance ($K \cdot W^{-1}$)
T	Temperature (K)
W	Width (m)
Greek	
ρ	Density ($kg \cdot m^{-3}$)
γ	Thermal Rectification
Subscripts	
A	Invariant Material
air	Air
c	Cold
h	Hot
l	Liquid (PCM)
leff	Effective of Liquid (PCM) and air
m	Melting/ Transition
PCM	Phase Change Material
s	Solid (PCM)
seff	Effective of Solid (PCM) and air

bias. The thermal conductivity of PCMs in their solid-state is typically two to five times that in their liquid states [7]. Therefore, PCMs are arranged such that they remain in the solid-state under the forward bias and in the liquid-state under reverse thermal bias.

Meng *et al.* [8] analyzed the performance of two PCM systems comprising of Calcium Chloride and Paraffin wax, and achived a thermal rectification of 3. Cotrill *et al.* [9] developed correlations to analyze two PCM system and optimization criteria, assuming pure conduction thermal transport. Chen *et al.* [10] experimentally studied two PCM thermal rectifier composed of eicosane and PEG 400, and achived a thermal rectification of 1.23. Kalasi *et al.* [11] developed analytical model to study two PCM thermal rectifier considering convection. Contrill and Starno [12] developed analytical model and optimization criteria for single PCM base thermal rectifier. Venkateshwar *et al.* [13] studied the influence of convection on single PCM based thermal rectifier and optimized the design.

However, these studies generally neglect the influence of change in other thermophysical properties with the change in the state. The change in viscosity and density has the potential to alter thermal rectification significantly. The presence of natural convection can augment heat transfer multifold in the liquid-state, reducing the thermal rectification. Similarly, change in the density leads to the creation of void space, which will be either filled by air or gases based on the environment or will remain void if the thermal rectifier is in a vacuum, such as in space. The thermal conductivity of air is of an order less than that of PCMs. Therefore, the development of voids in reverse bias will augment the thermal rectification, whereas will have an adverse effect when developed under forward thermal bias. Although convection has been considered in few stdies, the influence of shrinkage on thermal rectification has been neglected in the literature.

Therefore, in this study, the influence of change in density on the thermal rectification of a single-PCM-based thermal rectifier is analyzed. PCMs can have higher density either in their solid or liquid states, depending upon their molecular arrangement in different states. PCMs such as water have higher density in their liquid state, i.e., $\rho_s/\rho_l < 1$; whereas, PCMs such as *n*-octadecane and coconut oil have higher density in their solid-state, i.e., $\rho_s/\rho_l > 1$. Therefore, models have been developed for both cases and analyzed for a wide range of thermal conductivity and density variations. Furthermore, analytical correlations for optimization, taking into consideration the change in the thermal conductivity and density, have been developed. The present study's findings will assist in the development of efficient thermal rectifiers for thermal circuits, thermal management, and thermal energy conversion applications.

2. Influence of shrinkage

Figure 1 shows PCM-based thermal rectifier schematic diagrams in forward and reverse biases in different states, assuming no change in the density. Cottrill and Strano [12] discussed modeling and optimization of a single PCM-based thermal diode, assuming no change in the density. Therefore, the same has not been reiterated here, and the focus has been on modeling and optimizing single-PCM-based thermal rectifiers considering changes in both thermal conductivity and density.

The volume of PCM with higher density in the liquid-state expands upon solidification. Therefore, thermal rectifiers comprising this PCM category will be designed to accommodate PCM in solid-state. Hence, a void space will develop upon melting. As PCM will melt and shrink under gravity, a void space on top of the liquid layer will generate. The void space will be filled by air when the thermal rectifier is in ambient or another gas/vacuum when inside a hermetically sealed chamber. Fig. 2 shows schematic diagrams of PCM-based thermal rectifiers in different states under different biases, with PCM having higher density in liquid state.

Figure 3 show schematic diagrams of thermal rectifier containing PCM with higher density in solid state under different conditions. PCM with higher density in their solid-state will expand upon melting. Therefore, thermal rectifiers with PCM having a higher density in the solid-state are designed such that the complete volume is filled when PCM is in the liquid-state, i.e., the void volume is developed upon solidification.

2.1. Modeling

The modeling of the single-PCM based thermal rectifier has been based on the following assumptions:

1. The thermal rectifier is horizontally oriented, i.e., the right and left boundaries are exposed to constant temperatures.
2. The flow of PCM in its liquid state is absent.
3. PCM in the liquid state is incompressible.
4. PCM is initially in its lower density state.
5. Thermophysical properties are temperature independent.

The rationale for the assumption is that the present study focuses on understanding the direct influence of change in thermal conductivity and density on thermal rectification. The vertical orientation will lead to the generation of shrinkage-induced motion of PCM, which will influence the heat transfer. A future study needs to be conducted to analyze the vertical orientation. Advection has been neglected in the present study as the dimension of thermal rectifiers are typically of same order as that of boundary layer thickness, which curtails advection. This is the primary reason for neglecting advection in various previous studies on PCM-based thermal rectifiers. Thermophysical properties are assumed to be temperature independent as their variation with temperature is limited compared to upon phase transition.

Figure 2a shows the schematic of the thermal rectifier with higher density in liquid state under the forward bias, and PCM in an entirely solid-state. The resistance of invariant material (R_A) is directly computed as

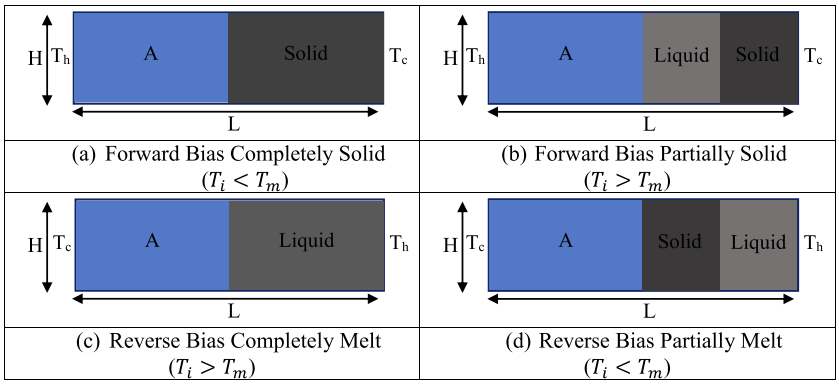


Fig. 1. Schematic diagrams of conventional thermal rectifiers under different conditions.

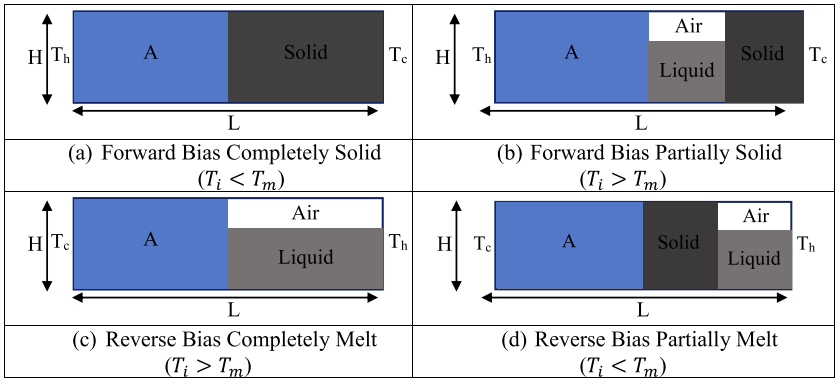


Fig. 2. Schematic diagrams of thermal rectifiers comprising PCM with higher density in liquid state under different conditions.

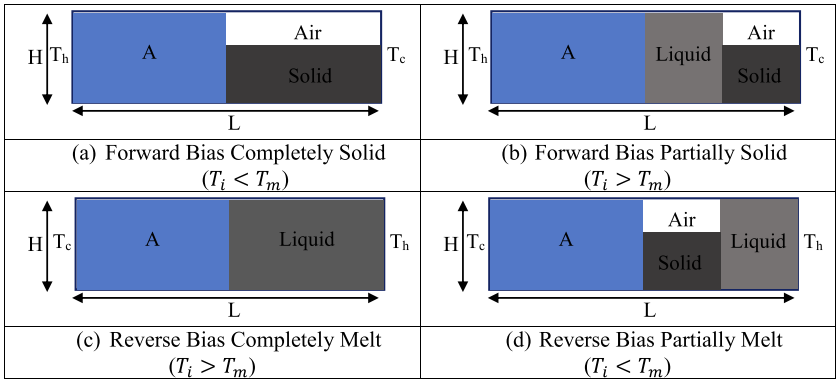


Fig. 3. Schematic diagrams of thermal rectifiers comprising PCM with higher density in solid state under different conditions.

$$R_A = \frac{L_A}{k_A HW}, \tag{1}$$

where k_A, L_A, H, and W are the thermal conductivity of invariant material, its length, height, and in-plane depth respectively. The thermal resistance of PCM in the solid-state is calculated as

$$R_s = \frac{L_{PCM}}{k_s HW}, \tag{2}$$

where k_s is the thermal conductivity of PCM in solid-state and L_{PCM} is the length of the PCM. The heat transfer rate and temperature at the interface of PCM and invariant material can be obtained by solving

$$Q = \frac{T_h - T_c}{R_A + R_s} = \frac{T_h - T_i}{R_A}. \tag{3}$$

The heat transfer rate and temperature computed at the interface are

$$Q = \frac{k_s k_A HW(T_h - T_c)}{k_A L_{PCM} + k_s L_A}, \tag{4}$$

$$T_i = \frac{k_s L_A T_c + k_A L_{PCM} T_h}{k_A L_{PCM} + k_s L_A}. \tag{5}$$

The heat transfer rate obtained in Eq. (4) is valid only when PCM is completely in solid-state, i.e., $T_i \leq T_m$. If $T_i > T_m$ then PCM will partially be in the liquid-state, as shown in Fig. 2b. The thermal resistance of invariant material will remain the same. However, the thermal resistance of solid PCM will change as the length has altered. The volume of PCM in the solid and liquid-state under quasi-steady state is unknown. The length of the solid region is assumed to be L_s, and the modified thermal resistance of solid PCM is

$$R_s = \frac{L_s}{k_s HW}. \tag{6}$$

The thermal resistance of PCM in the liquid-state will depend both on the length of PCM in the liquid-state and the height of melt PCM. The thermal resistance of liquid PCM and air are

$$R_l = \frac{L_{PCM} - L_s}{k_l h_l W}, \tag{7}$$

$$R_{air} = \frac{L_{PCM} - L_s}{k_{air}(H - h_l)W}, \tag{8}$$

where h_l is the height of liquid PCM, k_l and k_{air} are the thermal conductivities of liquid PCM and air, respectively The effective resistance of air and liquid PCM is calculated as

$$\frac{1}{R_{leff}} = \frac{1}{R_l} + \frac{1}{R_{air}}. \tag{9}$$

The temperature at the interface of the solid and liquid PCM will be the phase transition temperature, i.e., T_m . The following correlation is obtained based on the thermal energy balance

$$Q = \frac{T_h - T_i}{R_A} = \frac{T_i - T_m}{R_{leff}} = \frac{T_m - T_c}{R_s}. \tag{10}$$

The thermal resistance of solid PCM and effective thermal resistance of liquid PCM and air depends upon the length of solid PCM and the height of liquid PCM. It is computed by applying the law of mass conservation as

$$\rho_s L_s HW + \rho_l (L_{PCM} - L_s) h_l W = \rho_s L_{PCM} HW, \tag{11}$$

where ρ_s and ρ_l are the densities of PCM in solid and liquid-states, respectively. The heat transfer rate calculated using Eqs. (6) – (11) is

$$Q = \frac{k_A HW[(T_h - T_m)\{k_{air}(\rho_l - \rho_s) + k_l\rho_s\} + k_s(T_m - T_c)\rho_l]}{k_{air}L_A(\rho_l - \rho_s) + k_A L_{PCM}\rho_l + k_l L_A \rho_s}. \tag{12}$$

Figure 2c shows the schematic diagram of the thermal diode under reverse thermal bias and PCM completely in the liquid-state. The thermal resistance of invariant material remains the same as given by Eq. (1). The thermal resistance of liquid PCM and air as given by Eqs. (7) and (8) will be modified as the length occupied by liquid PCM and air is L_{PCM} rather than $(L_{PCM} - L_s)$. The effective thermal resistance of liquid PCM and air can be calculated using correlation given by Eq. (9) using modified thermal resistances of liquid PCM and air. The application of thermal energy balance yields

$$Q = \frac{T_i - T_c}{R_A} = \frac{T_h - T_i}{R_{leff}}. \tag{13}$$

The effective thermal resistance of liquid PCM and air depends upon the height of liquid PCM, which is obtained from mass conservation

$$\rho_l L_{PCM} h_l W = \rho_s L_{PCM} HW. \tag{14}$$

The heat transfer rate (Q) and temperature at the interface (T_i) are calculated as

$$Q = \frac{k_A HW(T_h - T_c)[k_{air}(\rho_l - \rho_s) + k_l\rho_s]}{k_{air}L_A(\rho_l - \rho_s) + k_l L_A \rho_s + k_A L_{PCM}\rho_l}, \tag{15}$$

$$T_i = \frac{[k_{air}(\rho_l - \rho_s) + k_l\rho_s]T_h L_A + k_A L_{PCM}\rho_l T_c}{[k_{air}(\rho_l - \rho_s) + k_l\rho_s]L_A + k_A L_{PCM}\rho_l}. \tag{16}$$

The heat transfer rate (Q) is calculated using Eq. (15) under reverse bias only when PCM is completely in the liquid-state, i.e., the temperature at interface (T_i) as given by Eq. (16) is greater than melting temperature (T_m). When the temperature at the interface is less than the melting temperature, then PCM will be partially in the solid-state, as shown in schematic diagram 2d. The thermal resistances of invariant material, PCM in solid-state, PCM in the liquid-state, and air is calculated using the correlations given by Eqs. (1) and (6)-(8), respectively. However, due to change in the boundary condition, thermal energy balance yields

$$Q = \frac{T_h - T_m}{R_{leff}} = \frac{T_m - T_i}{R_s} = \frac{T_i - T_c}{R_A}. \tag{17}$$

The mass conservation will remain the same as given by Eq. (11). The heat transfer rate (Q) for thermal rectifier under reverse bias and PCM in a partially melted state is

$$Q = \frac{k_A HW[(T_h - T_m)\{\rho_s(k_l - k_{air}) + \rho_l k_{air}\} + \rho_l k_s(T_m - T_c)]}{\rho_l(L_{PCM}k_A + L_A k_s)}. \tag{18}$$

The thermal rectification (γ) is defined as the absolute ratio of heat transfer rate under forward temperature bias to that under reverse temperature bias, as given by

$$\gamma = \frac{|Q_f|}{|Q_r|}, \tag{19}$$

where Q_f and Q_r are the heat transfer rates under forward and reverse temperature biases, respectively.

Figure 3 shows the thermal rectifier composed of PCM having higher density in solid state, under different conditions. Fig. 3a shows the thermal rectifier under the forward bias with PCM completely in the solid-state. The orientation of solid PCM and air in Fig. 3a is analogous to liquid PCM and air in Fig. 2c. Therefore, the thermal resistance circuit will be similar, and the same approach can be utilized to calculate the heat transfer rate (Q) and interface temperature (T_i) as discussed above for Fig. 2c, with two subtle differences, i.e., temperature bias is inverse and mass conservation equation based on $\rho_s > \rho_l$, and it yields:

$$Q = \frac{k_A HW(T_h - T_c)[k_{air}(\rho_s - \rho_l) + k_s\rho_l]}{k_{air}L_A(\rho_s - \rho_l) + k_s L_A \rho_l + k_A L_{PCM}\rho_s}, \tag{20}$$

$$T_i = \frac{[k_{air}(\rho_s - \rho_l) + k_s\rho_l]T_c L_A + k_A L_{PCM}\rho_s T_h}{[k_{air}(\rho_s - \rho_l) + k_s\rho_l]L_A + k_A L_{PCM}\rho_s}. \tag{21}$$

The heat transfer rate (Q) calculated using Eq. (20) is valid when PCM is completely in the solid-state, i.e., $T_i \le T_m$. If $T_i > T_m$ then PCM is partially in the liquid-state, as shown in Fig. 3b, which is analogous to Fig. 2d. Therefore, using a similar approach as for Fig. 2d we can calculate the heat transfer rate for thermal rectifier as shown in Fig. 3b:

$$Q = \frac{k_A HW[(T_m - T_c)\{\rho_l(k_s - k_{air}) + \rho_s k_{air}\} + \rho_s k_l(T_h - T_m)]}{\rho_s(L_{PCM}k_A + L_A k_l)}. \tag{22}$$

Figure 3c shows the schematic diagram of the thermal rectifier under reverse bias with PCM completely in the liquid-state. The thermal circuit of the thermal rectifier in Fig. 3c is analogous to that in Fig. 2a, and the heat transfer rate and interface temperature for the thermal rectifier in Fig. 3c are

$$Q = \frac{k_l k_A HW(T_h - T_c)}{k_A L_{PCM} + k_l L_A}, \tag{23}$$

$$T_i = \frac{k_l L_A T_h + k_A L_{PCM} T_c}{k_A L_{PCM} + k_l L_A}. \tag{24}$$

The heat transfer rate under reverse bias calculated using Eq. (23) is true when PCM is completely in the liquid-state, i.e., $T_i \ge T_m$. If the PCM is partially in the solid-state, an approach similar to that used for computing heat transfer rate for Fig. 2b can be employed for Fig. 3d. The heat transfer rate for thermal rectifier under reverse bias and PCM partially in the solid-state is

$$Q = \frac{k_A HW[(T_m - T_c)\{k_{air}(\rho_s - \rho_l) + k_s\rho_l\} + k_l(T_h - T_m)\rho_s]}{k_{air}L_A(\rho_s - \rho_l) + k_A L_{PCM}\rho_s + k_s L_A \rho_l}. \tag{25}$$

2.2. Results and discussion

Figure 4 shows the effect of temperature bias, change in thermal conductivity, and density change on thermal rectification of single-PCM-based thermal rectifier, with PCM having a higher density in the liquid-state. The length of the PCM and non-PCM regions have been assumed to be equal for the analysis. The thermal conductivity of invariant material (k_A) is assumed to be the geometric mean of the thermal conductivities of PCM in solid and liquid states. Fig. 4 demonstrates that an increase in the thermal conductivity ratio (k_s/k_l) and decrease in the density ratio (ρ_s/ρ_l) augments thermal rectification. The increase in the thermal conductivity ratio increases the change in the thermal resistance upon changing the state of the PCM. Therefore, the thermal rectification increases with an increase in the thermal conductivity ratio between solid and liquid states. The decrease in the ratio of PCM density in solid to liquid state increases the void volume upon melting, which gets filled with air. The increase in air volume increases the thermal resistance as the thermal conductivity of air is less than that of PCM. Therefore, thermal rectification increases with a decrease in the density difference as air under reverse bias reduce the heat transfer rate.

Furthermore Fig. 4 shows that increasing thermal conductivity ratio and decreasing density ratio by the same factor alters the thermal rectification by a similar magnitude, i.e., the effect of thermal conductivity and density on thermal rectification is similar in magnitude. Therefore, it is essential to consider the change in thermal conductivity as well as density upon phase transition while developing and analyzing thermal rectifiers. The increase in thermal conductivity ratio leads to a decrease in the thermal resistance ratio of solid and liquid PCM by the same factor, whereas a decrease in the density ratio by the same factor leads to a decrease in the volume of solid volume to liquid by the same factor. The decrease in the height of the liquid PCM increases the thermal resistance. The thermal conductivity of air is negligible compared to that of PCM, i.e., its thermal resistance is multifold higher compared to PCM; hence, the effective thermal resistance of liquid PCM and air while being arranged in parallel is close to that of liquid PCM. Therefore, the thermal resistance ratio of liquid to solid PCM increases upon decreasing the density ratio by a similar factor. This leads to a similar influence of the increase in thermal conductivity and density ratios on augmentation thermal rectification.

The influence of an increase in the thermal conductivity ratio and a decrease in density ratio on thermal rectification diminishes at higher thermal conductivity and lower density ratios. As the thermal conductivity ratio increases and the density ratio decreases, the difference in the thermal resistance of liquid and solid PCM increases. The higher thermal resistance implies that the temperature gradient will be higher for the same heat transfer rate. Therefore, when the thermal conductivity ratio is high, PCM remains entirely in solid-state under the forward bias, whereas in partial melt state under reverse bias. As the thermal conductivity ratio increases, the thermal resistance of solid PCM decreases, thereby having a smaller temperature gradient, i.e., the solid–liquid interface shifts towards the hot side, reducing the length of PCM in the liquid state. The decrease in the length of the PCM in liquid state reduces its thermal resistance, reducing the effect on overall effective thermal resistance and, in turn, on heat transfer rate. Therefore, an increase in the thermal conductivity ratio and density ratio has limited influence on thermal rectification when either of them approaches extreme, as observed from Fig. 4. It can be mathematically illustrated that the thermal rectification reaches an asymptotic value at a higher thermal conductivity ratio and lower density ratio. When PCM is in solid-state under the forward bias and partially melt state under reverse bias, the thermal rectification can be calculated using Eqs. (4), (18), and (19), as

$$\gamma = \frac{\frac{k_s}{k_l}\left(\frac{T_h-T_m}{T_m-T_c}+1\right)\frac{\rho_l}{\rho_s}}{\left(1-\frac{k_{air}}{k_l}\right)\left(\frac{T_h-T_m}{T_m-T_c}\right)+\frac{\rho_l}{\rho_s}\left[\frac{k_{air}}{k_l}\left(\frac{T_h-T_m}{T_m-T_c}\right)+\frac{k_s}{k_l}\right]}. \tag{26}$$

Solving Eq. (26) for the limit when $k_s/k_l \to \infty$ yields,

$$\gamma \to \left(\frac{T_h-T_m}{T_m-T_c}+1\right). \tag{27}$$

Similarly solving Eq. (26) for $\rho_s/\rho_l \to 0$ yields

$$\gamma \to \frac{\frac{k_s}{k_l}\left(\frac{T_h-T_m}{T_m-T_c}+1\right)}{\frac{k_{air}}{k_l}\left(\frac{T_h-T_m}{T_m-T_c}\right)+\frac{k_s}{k_l}} \approx \left(\frac{T_h-T_m}{T_m-T_c}+1\right). \tag{28}$$

The thermal rectification is bound by the temperature bias differential, which is evident from Fig. 4. Moreover, Eqs. (27) and (28) demonstrate that the thermal rectification is bound by the same limit for both thermal conductivity and density ratios, thus reiterating that the influence of change in thermal conductivity and density upon phase transition on thermal rectification is similar.

Figure 5 shows the effect of thermal conductivity, density on thermal rectification at different temperature biases, for single-PCM based thermal rectifier with PCM having higher density in solid-state. The increase in the thermal conductivity ratio (k_s/k_l) augments the thermal rectification, whereas an increase in the density ratio (ρ_s/ρ_l) harms thermal rectification. The increase in thermal conductivity ratio reduces the thermal resistance of solid PCM compared to liquid PCM, thus augmenting heat transfer under the forward bias, leading to an increase in the thermal rectification. The void volume developed increases with an increase in ρ_s/ρ_l , which reduces the effective thermal conductivity of solid PCM and air, reducing the heat transfer primarily under forward bias, thus adversely affecting the thermal rectification. Therefore, it is significant to analyze the influence of density, as most PCMs has $\rho_s > \rho_l$, so thermal rectifiers designed neglecting the influence of change in density will underperform.

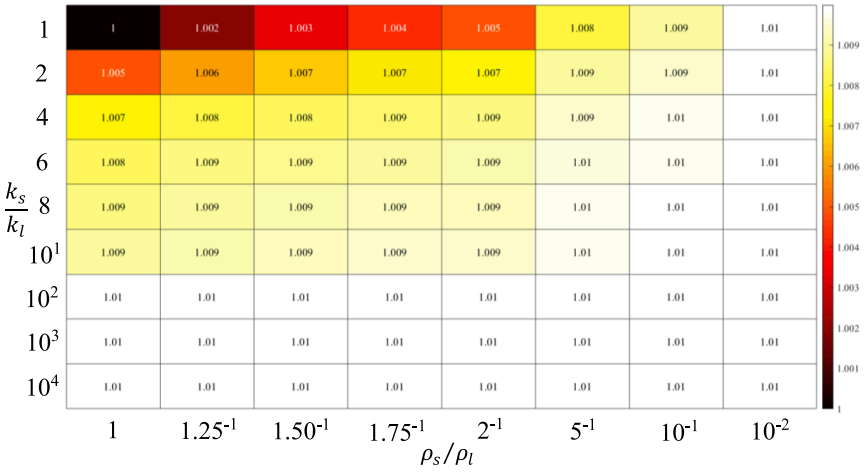
The adverse effect of higher density of solid PCM sometimes negates the influence of higher thermal conductivity of solid PCM, leading to $\gamma < 1$, as observed from Fig. 5. A thermal rectification of less than one implies that the heat transfer rate under reverse temperature bias is higher than under the forward temperature bias, i.e., the thermal rectifier fails to meet its operational requirement. This calls for an alteration in the design of the thermal rectifier. However, prior to alteration in the design, it is essential to comprehend the criterion under which $\gamma > 1$ for the present design, which is developed by comparing the effective thermal resistance of solid PCM and air to that of liquid PCM:

$$\frac{1}{k_l} > \frac{\rho_s}{k_s\rho_l + k_{air}(\rho_s-\rho_l)}. \tag{29}$$

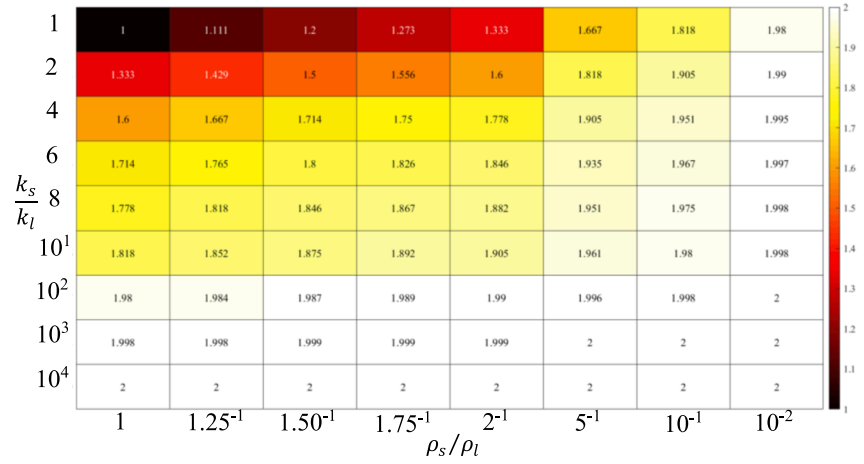
When $k_{air} \to 0$, i.e., thermal rectifier is in vacuum, the above criterion reduces to

$$\frac{1}{k_l} > \frac{\rho_s}{k_s\rho_l}. \tag{30}$$

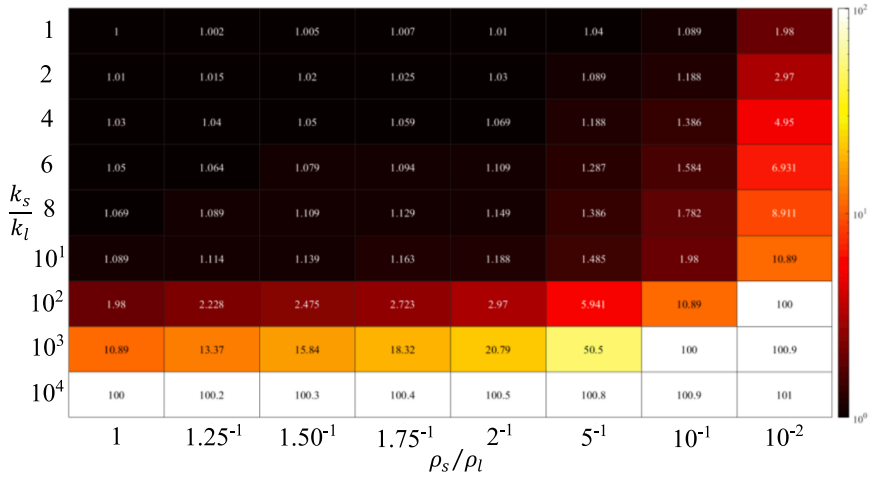
If the above criterion is not satisfied, the thermal rectifier needs to be designed such that it remains in the liquid state under the forward bias and solid-state under reverse bias, contrary to the previous design. This requires PCM to remain close to higher temperature isothermal boundary under the forward bias, i.e., the present design needs to be inverted. Therefore, for the modified thermal rectifier Fig. 3c and d depict different conditions under the forward bias and Fig. 3a and b depict different conditions under reverse bias. Similarly, the thermal rectification of such thermal rectifiers can be calculated using the same approach as discussed above. The heat transfer rates given by Eqs. (23) and (25) will be for the forward bias and Eqs. (20) and (22) will be for



(a) $\frac{T_h-T_m}{T_m-T_c} = 10^{-2}$

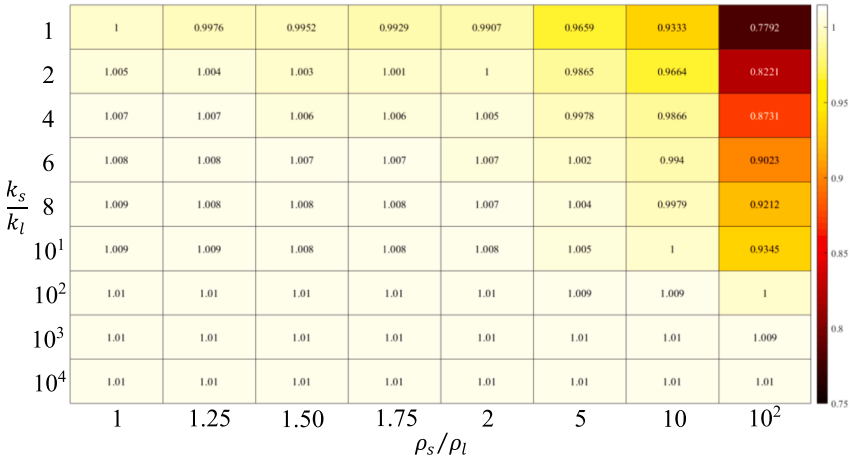


(b) $\frac{T_h-T_m}{T_m-T_c} = 10^{0}$

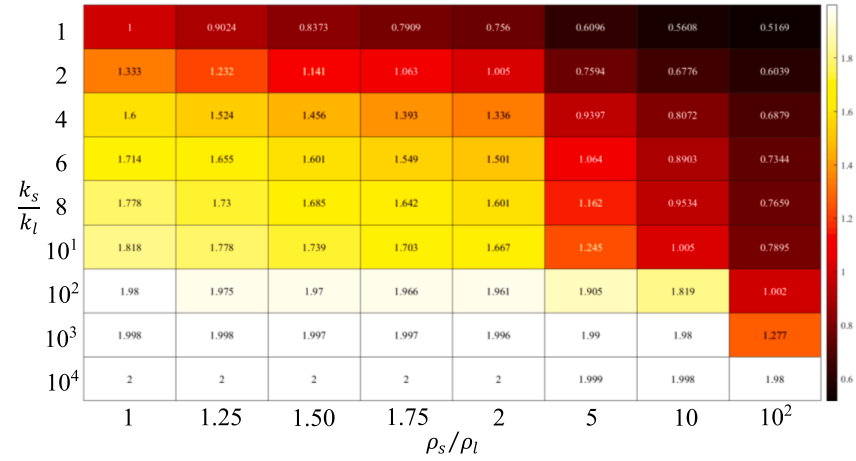


(c) $\frac{T_h-T_m}{T_m-T_c} = 10^{2}$

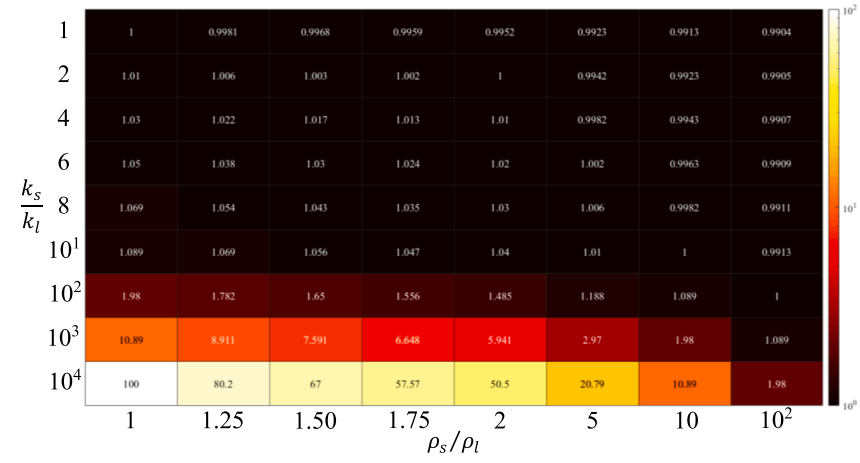
Fig. 4. Influence of change in thermal conductivity and density on thermal rectification of thermal rectifier with $\rho_s/\rho_l < 1$ under different thermal bias.



(a) $\frac{T_h - T_m}{T_m - T_c} = 10^{-2}$



(b) $\frac{T_h - T_m}{T_m - T_c} = 10^{0}$



(c) $\frac{T_h - T_m}{T_m - T_c} = 10^{2}$

Fig. 5. Influence of change in thermal conductivity and density on thermal rectification of thermal rectifier with $\rho_s/\rho_l > 1$ under different thermal bias.

the reverse bias, i.e., the thermal rectification will be inverse. Fig. 6 shows thermal rectification for conventional and modified thermal rectifier based on criterion given by Eq. (29), i.e., thermal rectification is computed for conventional rectifier when Eq. (29) is satisfied and for modified rectifier when Eq. (29) is not satisfied.

Figure 6 shows that the influence of the thermal conductivity and density ratios on thermal rectification diminishes with an increase in thermal conductivity and density ratios, i.e., thermal rectification approaches an asymptotic value. In the conventional thermal rectifier, when the thermal conductivity ratio is high, PCM remains in the solid-state under the forward bias and partial melt state under reverse bias, so the thermal rectification is

$$\gamma = \frac{(T_h - T_c)[k_{air}(\rho_s - \rho_l) + k_s\rho_l]}{k_{air}(T_m - T_c)(\rho_s - \rho_l) + k_s(T_m - T_c)\rho_l + k_l(T_h - T_m)\rho_s}. \tag{31}$$

Solving the above equation for $k_s/k_l \to \infty$ yields

$$\gamma \to \left(\frac{T_h - T_m}{T_m - T_c} + 1\right). \tag{32}$$

The thermal rectification of conventional thermal diode is bound by Eq. (32), when $L_A = L_{PCM}$ and $k_A = \sqrt{k_s k_l}$. In a conventional thermal rectifier, when the density ratio increases, thermal rectification decreases, and subsequently, thermal rectification reaches less than one when Eq. (29) is not satisfied, which requires design modification. Therefore, as the density ratio increases modified thermal rectifier is employed. The higher density ratio in modified thermal rectifier leads to PCM being in the liquid state under the forward bias and partial melt state under forward bias, so the thermal rectification is

$$\gamma = \frac{k_l(T_h - T_c)}{(k_s - k_{air})(T_m - T_c)\rho_l + \rho_s\{k_{air}(T_m - T_c) + k_l(T_h - T_m)\}}. \tag{33}$$

Solving the above equation for $\rho_s/\rho_l \to \infty$ yields

$$\gamma \to \frac{k_l(T_h - T_c)}{k_{air}(T_m - T_c) + k_l(T_h - T_m)}. \tag{34}$$

The above correlation can be simplified if $k_{air}/k_l = 1$, i.e., when the thermal rectifier is in a vacuum, as

$$\gamma \to \left(\frac{T_m - T_c}{T_h - T_m} + 1\right). \tag{35}$$

The thermal rectification for modified thermal rectifier is bound by inverse of temperature bias differential, i.e., higher thermal rectification can be achieved when $(T_m - T_c)/(T_h - T_m)$, contrary to that observed for conventional thermal rectifier, as evident from Fig. 6.

2.3. Optimization

Thermal rectification depends upon thermophysical properties of PCM in solid and liquid states, the thermal conductivity of invariant material, the lengths of PCM and non-PCM, and temperature bias. The criteria for optimal thermal rectification has been developed and the correlation for highest achievable thermal rectification for a given PCM has been developed.

Ideally, for a single PCM based thermal rectifier with PCM having higher density in liquid state, PCM should be in the solid-state under the forward bias and in the liquid-state under reverse bias. Mathematically, it implies that the interface temperature under both forward and reverse bias, as given respectively by Eqs. (5) and (16), should be equal to transition temperature (T_m). Solving these two equations, we obtain the optimal temperature bias differential as:

$$\frac{T_h - T_m}{T_m - T_c} = \sqrt{\frac{k_s\rho_l}{k_l\rho_s + k_{air}(\rho_l - \rho_s)}}, \tag{36}$$

Substituting the optimal temperature bias differential, given by Eq. (36) in Eq. (5) yields the optimal thermal conductivity of invariant material as:

$$k_A = \frac{L_A\sqrt{\rho_l k_s[(\rho_l - \rho_s)k_{air} + \rho_s k_l]}}{\rho_l L_{PCM}}, \tag{37}$$

The optimal thermal rectification is achieved upon computing heat transfer rates via Eqs. (4) and (15) exposed to optimal temperature bias differential and invariant material having optimal thermal conductivity, which is given by

$$\gamma = \frac{\sqrt{\rho_l k_s[(\rho_l - \rho_s)k_{air} + \rho_s k_l]}}{(\rho_l - \rho_s)k_{air} + \rho_s k_l} = \sqrt{\frac{\rho_l k_s}{(\rho_l - \rho_s)k_{air} + \rho_s k_l}}. \tag{38}$$

Assuming $k_{air}/k_l = 0$, i.e., either thermal rectifier is in near-vacuum, or thermal conductivity of liquid PCM is of multi-order higher magnitude, then Eq. (37) can be further simplified as

$$\gamma \to \sqrt{\frac{\rho_l}{\rho_s}\frac{k_s}{k_l}}. \tag{39}$$

The expressions for the optimal thermal rectification (i.e., Eqs. (38) and (39)) are different from those for the highest thermal rectification expressed by Eqs. (27) and (28). Eqs. (27) and (28) gives the highest thermal rectification when $k_A = \sqrt{k_s k_l}$ and $L_A = L_{PCM}$ under specific temperature bias, whereas Eqs. (38) and (39) provides optimal thermal rectification when k_A , L_A , L_{PCM} , and $(T_h - T_m)/(T_m - T_c)$ are optimized based on the thermophysical properties of PCM. Therefore, thermal rectification as expressed by Eqs. (27) and (28) are bound by the temperature bias, whereas thermal rectification as expressed by Eqs. (38) and (39) can approach infinity when either thermal conductivity ratio approaches infinity or density ratio approaches zero.

The design of a thermal rectifier comprising of PCM with higher density in solid-state depends upon the domination of either effect of density or thermal conductivity, as discussed in the previous subsection. However, the condition for the optimal thermal rectification is same for both the design. When the effect of density dominates, PCM is required to be in the liquid state under forward bias and solid-state under reverse bias, and vice-versa when the effect of thermal conductivity dominates, i.e., in both the cases, the phase transition temperature needs to coincides with the interface between PCM and invariant material. The ideal temperature bias differential is computed by equating Eqs. (21) and (24). The optimal thermal conductivity of invariant material is obtained by substituting the ideal temperature bias differential in Eq. (21) as per

$$\frac{T_h - T_m}{T_m - T_c} = \sqrt{\frac{\rho_l k_s + (\rho_s - \rho_l)k_{air}}{\rho_s k_l}}, \tag{40}$$

$$k_A = \frac{L_A k_l}{L_{PCM}}\sqrt{\frac{\rho_l k_s + (\rho_s - \rho_l)k_{air}}{\rho_s k_l}}. \tag{41}$$

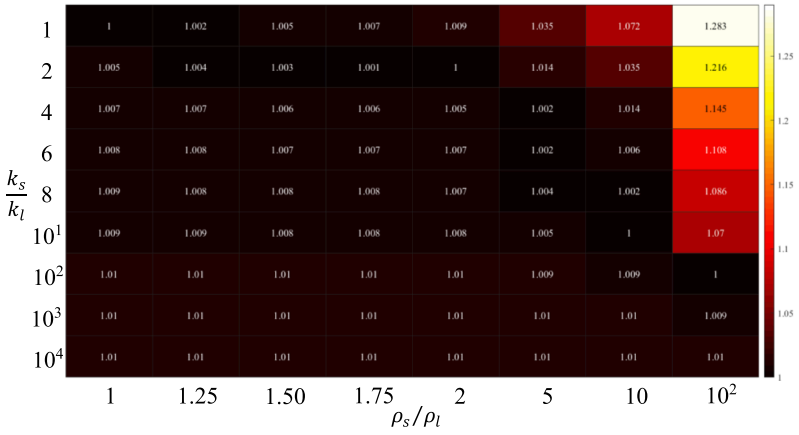
The expression for the optimal thermal rectification when the effect of thermal conductivity dominates is

$$\gamma = \sqrt{\frac{\rho_l k_s + (\rho_s - \rho_l)k_{air}}{\rho_s k_l}}. \tag{42}$$

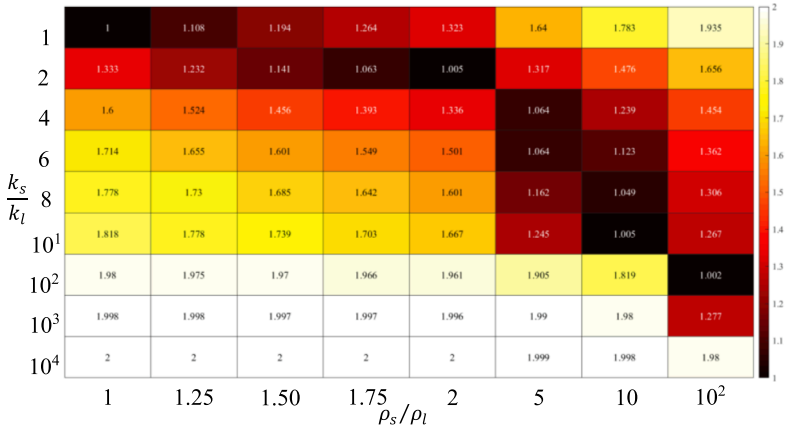
When $k_{air} \to 0$, i.e., thermal rectifier is in a vacuum, the optimal thermal rectification is

$$\gamma \to \sqrt{\frac{\rho_l k_s}{\rho_s k_l}}. \tag{43}$$

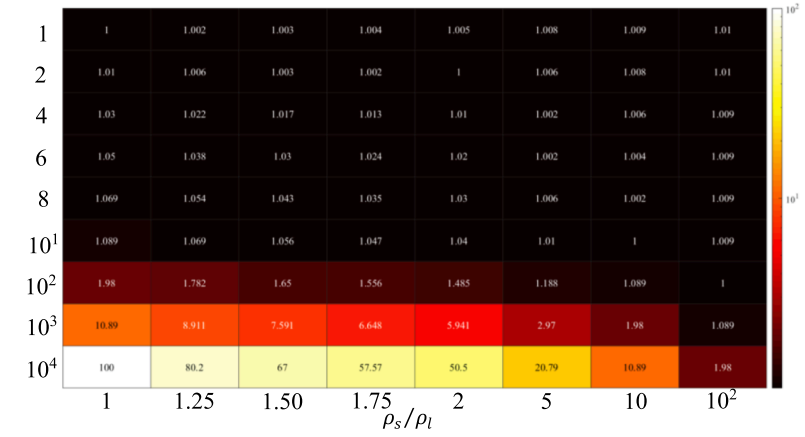
The expression for the optimal thermal rectification when the effect of density dominates is reciprocal of the expression when the effect of thermal conductivity dominates, as the expression for thermal rectification itself is reciprocal, as discussed in the previous sub-section, and is given by



(a) $\frac{T_h - T_m}{T_m - T_c} = 10^{-2}$



(b) $\frac{T_h - T_m}{T_m - T_c} = 10^{0}$



(c) $\frac{T_h - T_m}{T_m - T_c} = 10^{2}$

Fig. 6. Influence of change in thermal conductivity and density on thermal rectification of conventional and modified thermal rectifier with $\rho_s/\rho_l > 1$ under different thermal bias.

$$\gamma = \sqrt{\frac{\rho_s k_l}{\rho_l k_s + (\rho_s - \rho_l) k_{air}}}. \quad (44)$$

When $k_{air} \rightarrow 0$, i.e., thermal rectifier is in a vacuum, the optimal thermal rectification is

$$\gamma \rightarrow \sqrt{\frac{\rho_s k_l}{\rho_l k_s}}. \quad (45)$$

3. Conclusions

Analytical models have been developed to study the effect of change in thermal conductivity and density upon phase transition on thermal rectification. The thermal rectification increases with an increase in the difference in the thermal conductivity of PCM in solid and liquid states. The higher density of PCM in the liquid state augments thermal rectification, whereas, higher density of PCM in the solid-state has an adverse effect on thermal rectification. The development of void space during solidification negates the influence of augmentation in the thermal conductivity, reducing the thermal rectification to below one. A criterion has been developed when the influence of density change negates the influence of thermal conductivity change, which requires an alteration in the design of the thermal rectifier.

The thermal rectification changes by a similar magnitude upon changing the thermal conductivity and density ratios by the same magnitude. The limited difference in thermal conductivity and density yields a thermal rectification of approximately one at large differential temperature bias, i.e., either $(T_h - T_m)/(T_m - T_c)$ or $(T_h - T_m)/(T_m - T_c)$, as PCM remains largely in either liquid or solid-state under both forward and reverse temperature bias. The thermal rectification approaches an asymptotic value governed by temperature bias differential (i.e., $(T_h - T_m)/(T_m - T_c)$), when $L_A = L_{PCM}$ and $k_A = \sqrt{k_s k_l}$, whereas it is independent and can approach infinity when L_A, L_{PCM}, and k_A are optimized. The correlation for optimal thermal rectification has been developed.

Thermal rectifiers may be required to be vertically orientated, in such cases, the models discussed in this manuscript are inapplicable for two reasons. First, the thermal resistance of PCM and air will be in series rather than in parallel as in the present study, which will influence heat transfer rate. Second, shrinkage-induced advection will alter the heat transfer rate. Therefore, a future study on vertically orientated thermal rectifiers is essential.

CRediT authorship contribution statement

K. Venkateshwar: Conceptualization, Methodology, Software, Investigation, Formal analysis, Writing – original draft. **S.H. Tasnim:** Methodology. **S.A. Gadsden:** Formal analysis. **S. Mahmud:** Supervision, Funding acquisition, Formal analysis, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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