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Research Progress on Phase Change Cold Storage Materials: Postprint

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Abstract

Phase change cold storage materials exhibit high energy storage density and hold broad application prospects in efficient energy utilization and energy conservation. This paper classifies phase change cold storage materials with solid-liquid phase transition points below 20 ℃, comprehensively summarizes various types of phase change materials that are currently well-researched and commercially available along with their thermophysical parameters, and compares the thermophysical and chemical properties of different categories of phase change materials. Finally, this paper provides an outlook on the research and application prospects of phase change cold storage materials.

Full Text

Review of Phase Change Materials for Cold Thermal Energy Storage

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Abstract: Phase change materials for cold storage exhibit high energy density and offer broad application prospects for efficient energy utilization and energy conservation. This paper categorizes phase change materials with solid-liquid phase transition points below 20 ℃ and comprehensively summarizes the thermophysical properties of various types of phase change materials that have been extensively studied or commercialized. The thermophysical and chemical properties of different categories are compared, and future research and application prospects for cold storage phase change materials are discussed.

Keywords: cold thermal energy storage; phase change materials; thermophysical properties; latent heat

1. Classification of Phase Change Materials for Cold Storage

Phase change materials can be classified into four types: solid-solid, solid-gas, liquid-gas, and solid-liquid, as shown in [Figure 1: see original paper]. However, the first three categories are difficult to implement at scale due to significant pressure changes and low phase change enthalpy. In contrast, solid-liquid phase change materials generally offer better practicality and can be broadly divided into three major categories: organic materials, inorganic materials, and eutectic materials.

Cold thermal energy storage (CTES) is a technology that stores cooling capacity below ambient temperature for later use. It serves as a supplement and adjustment to refrigeration technology, providing an economically feasible method to coordinate the temporal and intensity mismatches between cooling supply and demand. To date, CTES has been widely applied in civil and industrial air conditioning systems, refrigerators and cold storage facilities, refrigerated vehicles, and building energy efficiency, creating a win-win situation for both power systems and users. CTES is primarily divided into three methods: sensible heat storage, latent heat storage, and thermochemical storage. Among these, latent heat storage using phase change materials (PCMs) has attracted extensive attention due to its energy storage density being 5–14 times higher than the other two methods.

Phase change materials can undergo phase transitions at constant or near-constant temperatures while absorbing or releasing substantial thermal energy, effectively exhibiting very high specific heat within their phase transition temperature range. The heat stored through latent heat storage can be expressed as:

$$\int mc_s dT + m\Delta H_{ls} + \int mc_l dT$$

where T_1, T_{pc}, and T_2 represent the initial temperature, phase change temperature, and final temperature in Kelvin, respectively; m is mass in kg; c_s and c_l are the specific heats of solid and liquid phases in $\mathrm{J} \cdot \mathrm{g}^{-1} \cdot \mathrm{K}^{-1}$; and ΔH_{ls} is the latent heat of phase change in $\mathrm{J} \cdot \mathrm{g}^{-1}$.

Leveraging the advantages of stable phase transition temperatures and high energy storage density, numerous scholars have dedicated efforts to developing new PCMs and measuring their thermophysical properties such as phase transition temperature and latent heat. For instance, Xu et al. prepared a metal-based composite high-temperature thermal storage material using binary eutectic carbonate (Li_2CO_3-K_2CO_3) as the PCM and copper foam as the matrix, which demonstrated high thermal conductivity and storage density. Differential scanning calorimetry measurements revealed a phase change temperature of 486.7 ℃ and latent heat of 326.8 $\mathrm{J \cdot g^{-1}}$. Zuo et al. investigated the thermal performance of caprylic acid, lauric acid, and their binary system using differential scanning calorimetry and low-temperature microscopy, showing that eutectic formation occurred at higher caprylic acid mass fractions, with a eutectic melting temperature of 7.44 ℃ and latent heat of 136.43 $\mathrm{J \cdot g^{-1}}$. Chen et al. prepared and characterized a dodecane/expanded graphite composite PCM for cold storage, reporting a phase change temperature of -10.62 to -9.82 ℃ and latent heat of 124.8–125.1 $\mathrm{J \cdot g^{-1}}$. Xiao et al. prepared a graphite foam/paraffin composite PCM using vacuum injection, finding that compared with pure paraffin, the composite showed no significant change in phase change temperature, a 4% reduction in latent heat, and a 311-fold increase in thermal conductivity.

However, significant challenges remain in practical PCM selection due to the lack of accurate classification and systematic selection criteria. While previous studies have extensively examined PCMs with phase change temperatures above 20 ℃, materials with transition points below 20 ℃ still hold vast application potential but have not been comprehensively compiled and analyzed. Therefore, this paper first systematically classifies cold storage PCMs and elaborates on the advantages and disadvantages of each category. Second, it summarizes research-stage and commercial PCMs with phase change temperatures below 20 ℃ according to this classification. Finally, it compares the primary thermophysical and chemical properties of different cold storage PCMs to provide references for material selection in future research and engineering applications, thereby promoting broader application of cold storage PCMs across multiple fields.

1.1. Organic Phase Change Materials

Organic PCMs are carbon-based compounds typically categorized as alkanes and non-alkanes. Their latent heat gradually increases with molecular weight and carbon number. These materials offer advantages including chemical stability, high latent heat, stable phase change temperatures (no phase separation), and self-nucleating properties (no supercooling). However, their main drawbacks include gradual degradation of latent heat and low thermal conductivity (0.1–0.7 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$). lists widely studied organic PCMs and their thermophysical parameters.

Alkanes: Alkanes (CH_3-$(CH_2)_n$-CH_3) are saturated hydrocarbons composed primarily of carbon, hydrogen, carbon-carbon single bonds, and carbon-hydrogen single bonds. Generally, both phase change temperature and latent heat increase with carbon number. As shown in , dodecane, tetradecane, and hexadecane exhibit phase change temperatures of -12 ℃, 4.5–5.6 ℃, and 18.1 ℃, respectively. Alkanes are safe, reliable, inexpensive, and non-corrosive, demonstrating chemical inertness and stability below 500 ℃ with minimal volume change and vapor pressure during phase transition, resulting in long service life. Their primary disadvantages are low thermal conductivity, incompatibility with plastic encapsulation, and flammability.

Non-alkanes: Non-alkane PCMs mainly include fatty acids, polyols, and esters. This category encompasses numerous materials with diverse properties. All share flammability, making them unsuitable for high-temperature, flame, or oxidizer environments. Fatty acids ($CH_3(CH_2)_{2n} \cdot COOH$) generally feature high latent heat, long service life, and no supercooling, but cost 2–2.5 times more than alkanes and exhibit corrosiveness. Other non-alkane PCMs typically suffer from low thermal conductivity, low flash points, and toxicity.

To address the low thermal conductivity of organic PCMs, current approaches commonly involve adding nanoscale metals, metal-based materials, graphite powder, or carbon fibers to enhance heat transfer. These additives modify the base fluid structure and generate micro-convection phenomena with the liquid, thereby strengthening energy transfer and improving thermal conductivity.

1.2. Inorganic Phase Change Materials

Inorganic PCMs primarily include hydrated salts, compounds, and metal alloys. They offer advantages of low cost, good thermal conductivity, and non-degrading latent heat, but suffer from supercooling, phase separation, and corrosion of encapsulation materials. lists widely studied inorganic PCMs and their thermophysical parameters.

Hydrated salts: Hydrated salts ($AB \cdot nH_2O$) are crystals formed by the combination of inorganic salts and water. Their solid-liquid transition is essentially a hydration-dehydration process, analogous to freezing and melting in thermodynamics, with phase change enthalpy depending on bond strength between water molecules and salt molecules. The dehydration process exhibits incongruent melting, sometimes losing only part of the crystalline water and sometimes losing it completely. Hydrated salts offer high latent heat, high thermal conductivity, small volume change during phase transition, low thermal stress effects, low toxicity, and low cost. However, supercooling, phase separation, and corrosion of common metals (copper, aluminum, stainless steel) constrain their application in cold storage systems.

To improve the poor nucleation performance of hydrated salts, the common solution is adding nucleating agents to provide crystal nuclei. Xu et al. demonstrated that adding borax to $CaCl_2 \cdot 6H_2O$ in an open system at room temperature could reduce supercooling to 2 ℃, effectively solving the supercooling problem.

Inorganic compounds: Inorganic compounds typically refer to compounds without carbon elements, though they include carbon oxides, bicarbonates, carbonates, and cyanides. Due to generally low latent heat and environmental/health hazards—such as the strong corrosiveness of NaOH listed in —most inorganic compounds have not found widespread application in cold storage systems.

Metal alloys: Although some low-melting-point metals and their alloys have not been widely applied in cold storage due to high density, they offer advantages of high latent heat, high thermal conductivity, high electrical conductivity, low vapor pressure, and minimal volume change during phase transition. Consequently, low-melting-point liquid metals have become indispensable in cooling applications for laser systems, USB flash memory, and smartphones.

1.3. Eutectic Phase Change Materials

Eutectic PCMs are typically crystalline mixtures formed by two or more low-melting-point components during crystallization, subdivided into organic eutectic materials and inorganic eutectic materials (primarily eutectic salt solutions). Their greatest advantage lies in the ability to control phase change temperature by adjusting component ratios. For example, crystallization of tetradecane with octadecane, docosane, or heneicosane achieves phase change temperature ranges of -4 to 5.56 ℃. Additionally, eutectic PCMs offer high thermal conductivity, high density, no phase separation, and no supercooling, though their latent heat and specific heat are relatively lower compared to alkanes and hydrated salts. and list widely studied organic and inorganic eutectic PCMs and their thermophysical parameters.

To obtain eutectic PCMs with suitable phase change temperatures and high latent heat, numerous researchers have experimentally measured thermophysical parameters at different component ratios to identify optimal properties. Li et al. investigated a ternary eutectic PCM of glycerol, sodium acetate, and water at mass ratios of 2:2:6, 1:2:7, 1:1:8, and 2:1:7, finding that the 1:1:8 mixture yielded optimal properties with a phase change temperature of -14 ℃ and latent heat of 172 $\mathrm{J \cdot g^{-1}}$. Yang et al. prepared a binary eutectic PCM of caprylic acid and tetradecanol, varying caprylic acid mass fraction from 0% to 75%, and determined that 74% caprylic acid provided the best stability, resulting in a phase change temperature of 6.9 ℃ and latent heat of 151 $\mathrm{J \cdot g^{-1}}$.

1.4. Commercial Phase Change Materials

Beyond research-stage materials, many PCMs have matured for commercial application. summarizes products from companies such as Cristopia and Rubitherm GmbH. Commercial cold storage PCMs are dominated by eutectic salt solutions (61%) and organic alkanes (29%), with smaller quantities of fatty acids and hydrated salts. Eutectic salt solutions have become the preferred choice for low-temperature cold storage systems below 0 ℃ due to their adjustable phase change temperatures through solute concentration modification. Organic alkanes, offering chemical stability and low manufacturing costs, have found extensive application in high-temperature cold storage systems above 0 ℃.

2. Analysis of Phase Change Materials for Cold Storage

[Figure 2: see original paper] illustrates the relationship between latent heat and phase change temperature for different PCM categories. Organic materials exhibit phase change temperatures primarily between -10 and 20 ℃, with latent heat ranging from 80 to 280 J · g^{-1}, peaking in the -5 to 5 ℃ range. Inorganic materials (except low-melting-point metals) generally have phase change temperatures above 0 ℃, with the widest latent heat span of 10–330 J · g^{-1}. Water shows the highest latent heat, followed by hydrated salts, while other inorganic compounds and metal alloys have relatively lower values. Organic eutectic materials distribute mainly between -10 and 20 ℃, with half concentrated near 5 ℃ and latent heat ranging from 110 to 270 J · g^{-1}, also peaking near 5 ℃. Eutectic salt solutions show the largest temperature span, reaching below -60 ℃, with generally lower phase change temperatures and latent heat ranging from 110 to 320 J · g^{-1}, increasing as temperatures approach 0 ℃. Commercial materials span -35 to 20 ℃, with sub-zero products dominated by eutectic salt solutions that generally outperform research-stage materials at equivalent temperatures, exhibiting latent heat of 130–390 J · g^{-1}. Notably, Teappcm' s product TH-4 achieves exceptionally high latent heat of 286 J · g^{-1}.

Selecting appropriate PCMs is crucial for cold storage systems. Phase change temperature matching system requirements is the primary selection criterion, while thermophysical properties, chemical characteristics, and kinetic properties also constrain applications. compares key thermophysical and chemical properties affecting PCM applications, providing practical selection guidance. Additionally, economic factors including production costs, recycling, and environmental performance represent important considerations.

Table 6. Comparison of properties for phase change materials for cold storage

Property	Organic PCMs	Inorganic PCMs	Eutectic PCMs
Phase change temperature range	Wide	Medium	Adjustable via composition
Latent heat	High	High	Medium
Thermal conductivity	Low	High	High
Specific heat	High	Medium	Medium
Volume change	Low	Low	Low
Supercooling	Absent	High	Absent
Phase separation	Absent	High	Absent
Corrosivity	Low	High	Low
Stability	Medium	High	High
Cost	Medium	Low	Medium

3. Research Perspectives

With increasing societal demand for cooling in air conditioning, cold storage, and other applications, cold storage systems based on PCMs offer promising market potential for energy conservation and rational energy utilization. Research on PCMs as the core component of these systems is therefore particularly important. This paper systematically summarizes research-stage and commercial solid-liquid PCMs with phase change temperatures below 20 ℃, analyzing and comparing their thermophysical and chemical properties. Overall, eutectic salt solutions and organic PCMs represent the most investigated and commercially utilized solid-liquid PCMs for temperatures below and above 0 ℃, respectively.

Despite significant progress, several areas warrant further investigation:

1. **Organic PCMs** offer a wide temperature application range without supercooling or phase separation, but their low thermal conductivity requires continued research on enhancement methods.
2. **Inorganic PCMs** provide strong thermal conductivity and storage capacity at low cost, but suitable nucleating agents and anti-supercooling additives must be identified to optimize performance.
3. **Eutectic PCMs** enable temperature control through composition adjustment, yet methods to increase latent heat and specific heat need further study.
4. **Composite PCMs** should be investigated to overcome limitations of single-component materials and achieve superior thermophysical properties and stability.
5. Current research often focuses only on phase change temperature and latent heat, while other parameters such as specific heat, density, and thermal conductivity receive less attention. Establishing comprehensive PCM thermophysical property databases requires accurate measurement of these additional parameters to facilitate material selection.

References

[1] Zhai X Q, Wang X L, Wang T, et al. A Review on Phase Change Material for High Temperature Thermal Energy Storage in Air-Conditioning System: Materials and Applications [J]. Renewable and Sustainable Energy Reviews, 2013, 22: 108-120
[2] Wang Hui, Liu Zhongbao, Chen Xiangfeng. Application Research of Refrigerator With Cool Storage Materials [J]. Refrigeration, 2014, 33(9): 26-29
[3] Fioretti R, Principi P, Copertaro B. A Refrigerated Container Envelope With a PCM (Phase Change Material) Layer: Experimental and Theoretical Investigation in a Representative Town in Central Italy [J]. Energy Conversion and Management, 2016, 122: 147-156
[4] Yang Ying, Zhang Wei, Dong Zhao, et al. Preparation and Thermal Per-

formance of New Composite Phase Change Storage Materials for Refrigerated Vehicle [J]. New Chemical Materials, 2013, 41(11): 41-43

[5] Comodi G, Carducci F, Nagarajan B, et al. Application of Cold Thermal Energy Storage (CTES) for Building Demand Management in Hot Climates [J]. Applied Thermal Engineering, 2016, 103: 1186-1195

[6] Veerakumar C, Sreekumar A. Phase Change Material Based Cold Thermal Energy Storage: Materials, Techniques and Applications-A Review [J]. International Journal of Refrigeration, 2016, 67: 271-289

[7] Wang Yuexiang, Wang Zhiqian. Research Progress of Organic Phase Change Materials and Its Composite Technology [J]. Materials Review, 2014, 28(24): 213-215, 228

[8] Xu Yang, Zhu Guihua, Lv Shuo, et al. Preparation and Thermal Properties of Metal-Based Composite High Temperature Phase Change Thermal Storage Material [J]. Journal of Engineering Thermophysics, 2016, 37(7): 1371-1376

[9] Zuo Jianguo, Li Weizhong, Xu Shiming. Thermal Properties of Caprylic Acid and Lauric Acid as Phase Change Cool Storage Material [J]. Acta Energiae Solaris Sinica, 2012, 33(1): 131-134

[10] Chen Jiajie, Xu Tao, Fang Xiaoming, et al. Performance Study on Expanded Graphite Based Dodecane Composite Phase Change Material for Cold Thermal Energy Storage [J]. Journal of Engineering Thermophysics, 2015, 36(6): 1307-1310

[11] Xiao Xin, Zhang Peng. Thermal Characterization of Graphite Foam/Paraffin Composite Phase Change Material [J]. Journal of Engineering Thermophysics, 2013, 34(3): 530-533

[12] Li G, Hwang Y, Radermacher R, et al. Review of Cold Storage Materials for Subzero Applications [J]. Energy, 2013, 51: 1-17

[13] Pereira da Cunha J, Eames P. Thermal Energy Storage for Low and Medium Temperature Applications Using Phase Change Materials-A Review [J]. Applied Energy, 2016, 177: 227-238

[14] Kamali S. Review of Free Cooling System Using Phase Change Material for Building [J]. Energy and Buildings, 2014, 80: 131-136

[15] Cabeza L F, Castell A, Barreneche C, et al. Materials Used as PCM in Thermal Energy Storage in Buildings: A Review [J]. Renewable and Sustainable Energy Reviews, 2011, 15(3): 1675-1695

[16] SU Weiguang, Darkwa J, Kokogiannakis G. Review of Solid-Liquid Phase Change Materials and Their Encapsulation Technologies [J]. Renewable and Sustainable Energy Reviews, 2015, 48: 373-391

[17] Joybari M M, Haghighat F, Moffat J, et al. Heat and Cold Storage Using Phase Change Materials in Domestic Refrigeration Systems: The State-of-the-Art Review [J]. Energy and Buildings, 2015, 106: 111-124

[18] Zalba B, Marín J M, Cabeza L F, et al. Review on Thermal Energy Storage With Phase Change: Materials, Heat Transfer Analysis and Applications [J]. Applied Thermal Engineering, 2003, 23(3): 251-283

[19] Sharma A, Tyagi V V, Chen C R, et al. Review on Thermal Energy Storage With Phase Change Materials and Applications [J]. Renewable and Sustainable Energy Reviews, 2009, 13(2): 318-345

[20] Waqas A, Ud Din Z. Phase Change Material (PCM) Storage for Free Cooling of Buildings-A Review [J]. Renewable and Sustainable Energy Reviews, 2013, 18: 607-625

[21] Chandel S S, Agarwal T. Review of Current State of Research on Energy Storage, Toxicity, Health Hazards and Commercialization of Phase Changing Materials [J]. Renewable and Sustainable Energy Reviews, 2017, 67: 581-596

[22] Raj V A A, Velraj R. Review on Free Cooling of Buildings Using Phase Change Materials [J]. Renewable and Sustainable Energy Reviews, 2010, 14(9): 2819-2829

[23] Sun Jiapeng, Zhou Xiaoqing, Wu Huijun. Experimental Study on the Performance of Nano-Graphite Additives in Organic Phase-Change Cool-Storage Materials [J]. Science-Technology Information Development and Economy, 2012, 22(1): 119-122

[24] Tao Wenbo, Xie Ruhe. Research and Development of Organic Phase Change Materials for Cool Thermal Energy Storage [J]. Journal of Refrigeration, 2016, 37(1): 52-59

[25] Sharma S D, Kitano H, Sagara K. Phase Change Materials for Low Temperature Solar Thermal Applications [R]. Mie, Japan: Mie University, 2004

[26] Xu Yunlong, Liu Dong. Preliminary Supercooling Research on Calcium Chloride Hexahydrate as Phase Change Material [J]. Journal of Materials Engineering, 2006, (S1): 218-221

[27] Chi Wei, Guo Jianzeng, Zhong Xiaohong, et al. Experimental Research and Application Analysis of Solid-to-Liquid Phase-Change Material [J]. High Power Laser and Particle Beams, 2009, 21(8): 1231-1234

[28] Ge Haoshan, Liu Jing. Phase Change Effect of Low Melting Point Metal for an Automatic Cooling of USB Flash Memory [J]. Frontiers in Energy, 2012, 6(3): 320-326

[29] Ge Haoshan, Liu Jing. Keeping Smartphones Cool With Gallium Phase Change Material [J]. Journal of Heat Transfer, 2013, 135(5): 979-985

[30] Li Kuining, Guo Ningning, Wang He. Research on the Organic Phase Change Material for Energy Storage [J]. New Chemical Materials, 2009, 37(4): 87-88

[31] Paksoy H, Yilmaz S, Ozgul G, et al. Thermal Energy Storage for More Efficient Domestic Appliances [C]//Proc Effstock-The 11th International Conference on Thermal Energy Storage. Stockholm, Sweden: 2009: 1-8

[32] Alvarado J L, Marsh C, Sohn C, et al. Thermal Performance of Microencapsulated Phase Change Material Slurry in Turbulent Flow Under Constant Heat Flux [J]. International Journal of Heat and Mass Transfer, 2007, 50(9-10): 1938-1952

[33] Regin A F, Solanki S C, Saini J S. Heat Transfer Characteristics of Thermal Energy Storage System Using PCM Capsules: A Review [J]. Renewable and Sustainable Energy Reviews, 2008, 12(9): 2438-2458

[34] Zheng Danxing, Wu Xianghong. Comprehensive Evaluation of Eutectic Character Used as Low Temperature Thermal Energy Storage [J]. Cryogenics, 2002, (1): 37-45

[35] Khan M I H, Afroz H M M. Diminution of Temperature Fluctuation

Inside the Cabin of a Household Refrigerator Using Phase Change Material [J]. International Journal of Recent Advances in Mechanical Engineering, 2014, 3(1): 43-52

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