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# Thermal Properties of Cu–Al–Ge Alloy PCM for Improving Thermal Energy Storage of Current CSP

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**Abstract.** Metallic phase change material was proposed and examined at melting/eutectic temperatures less than 600 °C for latent heat storage in concentrated solar power. The PCM alloy can potentially charge/discharge thermal energy as a sensible/latent heat at the temperature range of 414-527 °C. The working temperatures of PCM alloy are in operation temperatures of current molten-salt based CSP plant. In this study, thermal response testing of PCM alloy and sensible/latent storage unit that PCM alloy was loaded in a ceramic honeycomb were prepared in a laboratory scale. The thermal charging/discharging performance of PCM alloy and sensible/latent storage unit were experimentally examined and compared. The storage unit provided thermal release/absorption behaviour at close to temperatures of the thermodynamic equilibrium state.

**Keywords:** Concentrated Solar Power, Thermal Storage System, Phase Change Material, Alloy

## 1. Introduction

Solar energy is one of the most environmentally friendly energy sources, and the milestones for solar energy exploitation are energy capture, energy conversion, and energy storage. CSP technology has the advantage of higher utilization efficiency of solar energy, extension of the energy operating period from day to night, or from sunny to cloudy weather due to the capability to store energy in the thermal storage system and use it when required. In accordance with relevant physicochemical mechanisms, the working principles of thermal energy storage (TES) are typically classified into three types: sensible heat storage, latent heat storage, and thermochemical heat storage [1].

Molten salts have been widely used as typical liquid heat transfer fluid and sensible TES in current CSP plants due to their non-flammable, non-toxic nature, liquid characteristics at ambient pressure, efficiency and cost-effectiveness. One of these molten salts, solar salt has proven successful even for heat transfer fluid (HTF) and TES in the GWh-scale at an operating temperature range of 290–560 °C. In current CSP researches, it is reported that the upper working temperature targets to enhances until the vicinity of 600 °C by a development of atmosphere control technology in a closed looping system of CSP plant [2, 3, 4]. Recently, Solar Salt in a technical-scale is experimentally tested and evaluated in an open configuration at temperatures up to 600 °C [5], while thermal stability of Solar Salt in a closed configuration at temperatures up to 650 °C is studied to understand the thermodynamic equilibrium [6].

High temperature alloy system has been chosen for its thermal stabilities and remarkably high thermal conductivity fit as a promising PCM candidate in a combination with Solar Salt (HTF) for future application in developing molten-salt based CSP plants with steam or $sCO_2$ Brayton power cycles. Nonetheless, their chemical corrosive behavior when in contact with metallic PCM restricts their application in many scenarios [7]. Thus, it is assumed that metallic PCM is capsulated to protect the chemical corrosive behavior in Solar Salt at high temperatures. Furthermore, the capsulated PCM may be applied in a thermocline storage system composed of crashed rocks (sensible storage media) to enhance thermal storage capacity/density.

In this study, eutectic Cu–Al–Ge alloy was experimentally examined as new PCM for improving thermal storage capacity of current CSP which utilize nitrate molten salt as a heat transfer fluid (HTF). The metallic PCM is assumed for use in thermocline thermal storage tank in which solid filler (sensible storage material) and the PCM. The followability of thermal charge/discharge of the PCM alloy was examined and compared to the phase diagram based on thermodynamic equilibrium. Finally, the cyclic thermal charge/discharge properties of the PCM and sensible/latent storage unit were experimentally studied under inert gas and air stream at different heating and cooling rates to evaluate it as a potential PCM thermal storage material. The thermal properties of the PCM with temperature was measured during the heat charge and discharge modes.

## 2. Thermal response testing of PCM alloy and sensible/latent storage unit to evaluate thermal charging/discharging performance

The purpose of this study is to examine and evaluate thermal charging/dis-charging performances (repeatability under various atmosphere, and followability of thermal charging/dis-charging temperature against the phase diagram) for use in a sensible/latent heat storage system in a molten-salt based CSP plant. A massive alloy was purchased from Furuuchi Chemical Co., Japan. The alloy (diameter < 10 mm and thickness < 5 mm) was polished by emery papers (#200 - #1000) and chemically washed and cleaned to remove oil and dust from the surface. The phase of the sample was measured by X-ray diffraction (XRD) (D2Phaser, Burker using $CuK_\alpha$ radiation (λ = 0.15418 nm), 30 kV - 10 mA at 25 °C). The crystalline solid phases were identified by comparison with standard reference patterns of the Crystallography Open Database (COD).

The density ρ of prepared PCM alloy was measured by the following equation,

$$\rho = \frac{|A|}{|B|} \times \rho_0 \qquad (1)$$

where A and B are mass of PCM alloy in air and water, respectively. $\rho_0$ is corresponding to density of water ($\rho_0 = 0.99894 \frac{g}{cm^3}\, at\ 16\ ℃$). The measurement was repeated five times to estimate standard deviation.

The PCM alloy was put into ceramic honeycomb of dense cordierite (CH-200, Bocent Adv. Ceramics) to prepare a sensible/latent storage unit. The thermophysical properties of ceramic honeycomb are specific heat capacity of 900 - 1100 J/(kg・K), and thermal conductivity of 1.5 – 2.5 W/(m・K) at 20 -1000 °C. The density of ceramic honeycomb was 770 g/$cm^3$ at 25 °C. The shape of ceramic honeycomb was 100 mm height, 35 mm outer diameter and cell size of 5 mm. The PCM alloy was loaded in 50 vol % cell volume of ceramic honeycomb. The K-type thermocouple was inserted into a center position of cell arrangement to measure temperature change of PCM-packed storage unit. The upper and lower plane that the PCM was loaded in the cell was sealed by inorganic ceramic bond in order to avoid oxidizing in air atmosphere. All preparation procedure of storage unit was performed at Ar atmosphere in the glove box device.

The experimental arrangement for the thermal response testing is shown in the previous literatures [8-11]. For the thermal charging mode, the electric heater was controlled at a constant heating rate of 5-10°C/min, to a temperature of 700°C, exceeding the eutectic and melting temperatures, based on the chemical composition of the sample. The temperature variation of the test container with an endothermic phase change was measured under a controlled heating rate. Subsequently, the test container was subjected to the discharge mode. For discharge, the electric heater was controlled at different cooling rates with 5°-10°C/min, to a temperature of 200 °C. Temperature variation of the test container with an exothermic phase change was measured under a controlled cooling rate. The charging and discharging modes for the sample were repeated in an inert (Ar) and Air atmosphere to evaluate the temperature conformity and repeatability of the phase diagram and the effects on the reproducibility of both modes under different atmospheres and heating/cooling rates. The thermal responses were evaluated during heating and cooling (dT/dt vs. time).

## 3. Results and discussion

Figure 1 shows the phase diagram of PCM alloy. The chemical composition of PCM alloy was 35.8Al-9.2Cu-55.0Ge (wt%). The chemical composition of PCM alloy was plotted in the phase diagram. According to FactSage program [12], Ge solid-solution (Ge) was precipitated in the liquid phase at temperature range of 462-527 °C, the two solid phases of (Ge) and $Al_2Cu$ (binary eutectic composition) were generated from the remaining liquid phase at 462 °C, the three solid phases of (Ge), $Al_2Cu$ and (Al) was transformed from the remaining liquid phase at 414 °C. Thus, the PCM alloy can potentially charge/discharge thermal energy as a sensible/latent heat at the temperature range of 414-527 °C in thermodynamic equilibrium state. The working temperatures of PCM alloy are in operation temperatures of current molten-salt based CSP plant.

The solid/liquid phase transition process of PCM alloy involves melting/solidification of Ge solid-solution, resulting in a mitigation of thermal expansion in the phase transitions [10, 11]. Thus, when PCM alloy is packed in the ceramic container, the loading amount of PCM alloy in the container can increase in comparison to molten salt which is a promising candidate material of latent heat storage. In addition, thermal conductivity of the metallic PCM is generally more than twice. The results indicate that quick thermal response in the thermal storage system is implemented by using the PCM alloy.

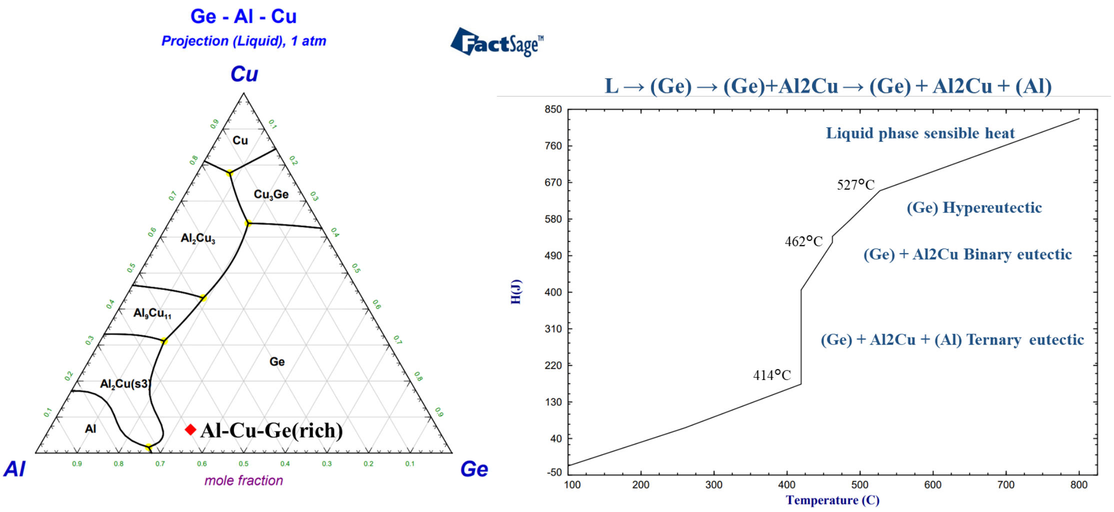


***Figure 1.*** *Phase diagram of Ge-Al-Cu Alloy at 1 atm. A chemical composition of metallic PCM is plotted in the phase diagram.*

Figure 2 shows X-ray diffraction (XRD) pattern of PCM alloy prepared in this study. Three solid phases of Ge solid-solution, $Al_2Cu$, and Al appeared in the PCM alloy. The solid phases were corresponded to thermodynamic stable phases reported in FactSage software. The density of prepared PCM alloy was measured by Archimedes method. The results are listed in Table 1. The average density of PCM alloy was 3.926 g/cm$^3$ at 16 °C, and standard deviation (STD) was 0.362. For comparison, density of alumina was measured. The values of density and STD were 3.853 g/cm$^3$, and 0.016, respectively. The value of density was corresponded to the literature. Thus, the measurement provided reliable value of density at the temperature. Currently, the temperature dependence of density for PCM alloy in a range of $T$ < 700 °C are evaluated in our laboratory.

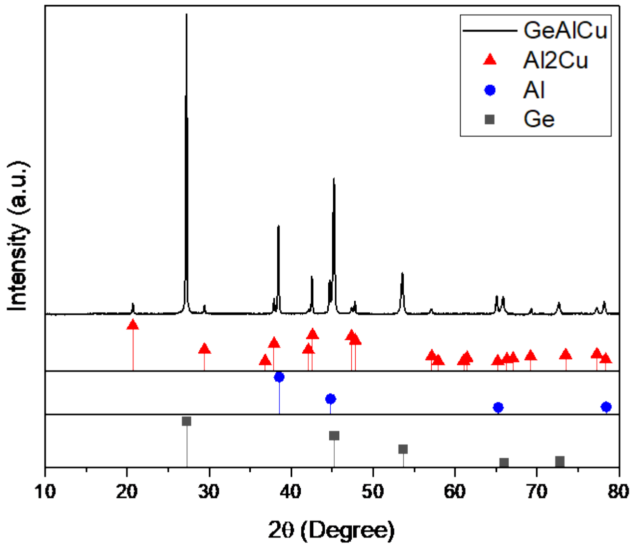


***Figure 2***. *XRD pattern of the prepared metallic PCM. The identified solid phases are shown in the figure.*

***Table 1.*** *Measurement of density of PCM alloy.*

| | Measurement | A [g] | B [g] | Temperature [° C] | Density [g/cm$^3$] |
|---|---|---|---|---|---|
| Al-Cu-Ge | # 1 | 0.3838 | -0.0972 | 16 | 3.944 |
| | # 2 | 0.3839 | -0.0973 | 16 | 3.941 |
| | # 3 | 0.3840 | -0.0975 | 16 | 3.934 |
| | # 4 | 0.3841 | -0.0985 | 16 | 3.895 |
| | # 5 | 0.3836 | -0.0979 | 16 | 3.914 |
| | Average | 0.3839 | -0.0977 | | 3.9257 |
| | Standard Deviation | 0.0002 | 0.0005 | | 0.3618 |

The repeatability of the charge/discharge performance was evaluated via 10 cycle tests using a few dozen gram samples (Figure 3). From a thermodynamic viewpoint, the PCM alloy should behave reproducibly based on the phase diagram (Figure 1) during the thermal response test if it does not chemically react with the container and stream gas. From a kinetics viewpoint, for the phase transition between solid and liquid phases, it is desirable that charge/discharge responds quickly at the eutectic/melting temperatures assigned in the phase diagram. As seen in Fig. 3, exothermic peaks appeared at the eutectic temperatures of

(Ge)/$Al_2Cu$/(Al) at 414 °C and (Ge)/$Al_2Cu$ at 462 °C and melting point of (Ge) at 527 °C. Endothermic peaks were observed at temperatures of 414 and 462 °C, while broad variation appeared due to melting of (Ge) at 527 °C. The results of thermal response testing indicate that endothermic/exothermic peaks reproducibly appeared at the eutectic/melting temperatures. Thus, in further testing, a chemical compatibility of container (capsulation) material at high temperature over melting temperature of PCM alloy and chemical compatibility with HTF (molten salt, solar salt) are studying to evaluate a compatibility for use in the current CSP plant in the present study.

The authors prepared sensible/latent storage unit that the PCM alloy was loaded into ceramic honeycomb as a capsulation of alloy PCM. The ceramic honeycomb (square pole shape, 150×150×300mm) was commercially available as a raw material of sensible thermal storage on the market in Japan. It was mechanically cut into columnar shape (100 mm height, 35 mm outer diameter) to set into a self-generating test equipment of my laboratory. The schematic drawing of ceramic honeycomb used in this study is shown in Figure 4(a). The alloy PCM was loaded row by row of the columnar, and thermocouple was inserted into the center of the columnar to detect the temperature variation of storage unit under various gas stream (Figure 4 (b, c)).

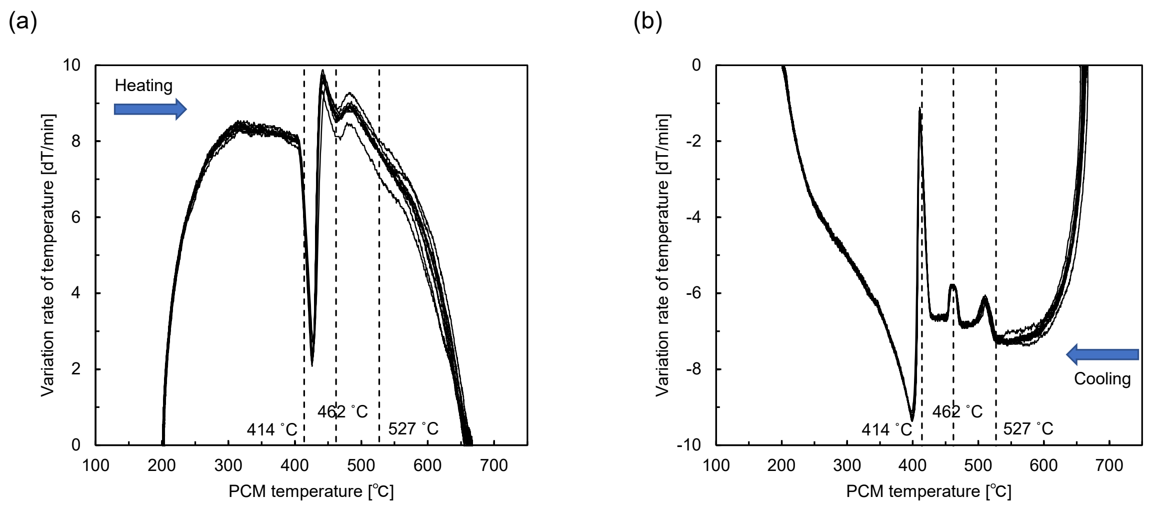


***Figure 3***. *Thermal charging/discharging performance of PCM alloy at high temperatures of 200-650 °C in an inert atmosphere.*

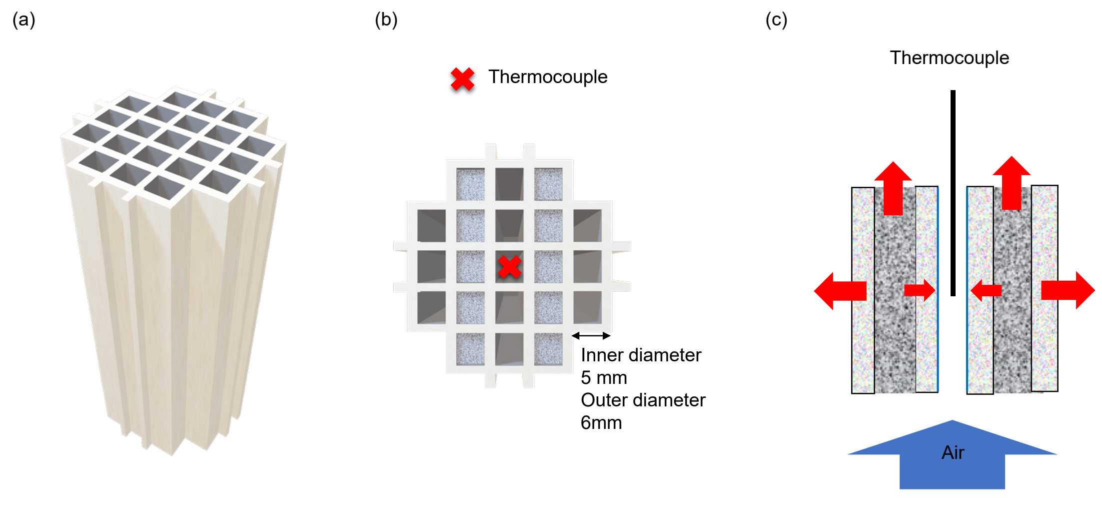


***Figure 4***. *(a) Honeycomb ceramic, (b) honeycomb sensible/latent storage unit, and (c) thermal performance test of charging/discharging mode at high temperatures.*

Figure 5 shows thermal behaviour of honeycomb sensible/latent storage unit during the charge and discharge modes. When the storage unit was cooled with a rate of 5 K/min during the discharging mode, the storage unit released the stored heat at their three temperatures (Figure 5 (b)). This result indicate that the latent heat stored in the PCM alloy was released through the wall of ceramic honeycomb into gas stream without major time delay under close to thermodynamic equilibrium state. For the charging mode, it was observed that the all endothermic peaks was timely delayed. The extent of time delay for the storage unit was much more than that for PCM alloy. The result indicate that a heat transfer from hot gas stream through a wall of ceramic honeycomb into PCM alloy was relatively poor in this setup. Thus, the authors are presently searching for the candidate materials of capsulation with superior thermal diffusivity and thermal durability at high temperatures.

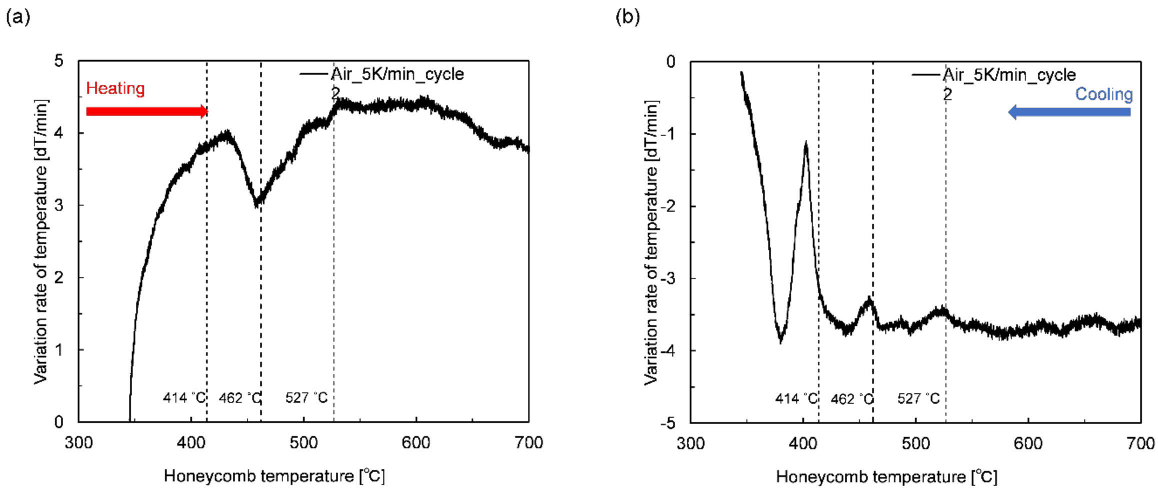


***Figure 5***. *Thermal (a) charging and (b) discharging performances of honeycomb sensible/latent storage unit at high temperatures of 350-700 °C in an air atmosphere.*

Figure 6 shows the photographs of honeycomb sensible/latent storage unit taken from the test container after the thermal response testing. A part of white-colored material is inorganic ceramic bond to seal PCM alloy in the structure. It appeared that the honeycomb structure was endured without visible external failure and crack during the testing. Furthermore, the PCM alloy was maintained without leakage in the structure. However, a part of the ceramic bond flowed downward to the outer surface of honeycomb, leading to reducing the sealing performance. Thus, in order to develop the thermally-durable honeycomb sensible/latent storage unit, improvements of sealing method, increase of PCM loading amount, investigations of mechanical strength and heat shock testings under severe heating/cooling conditions are required in further study.

(a) (b)

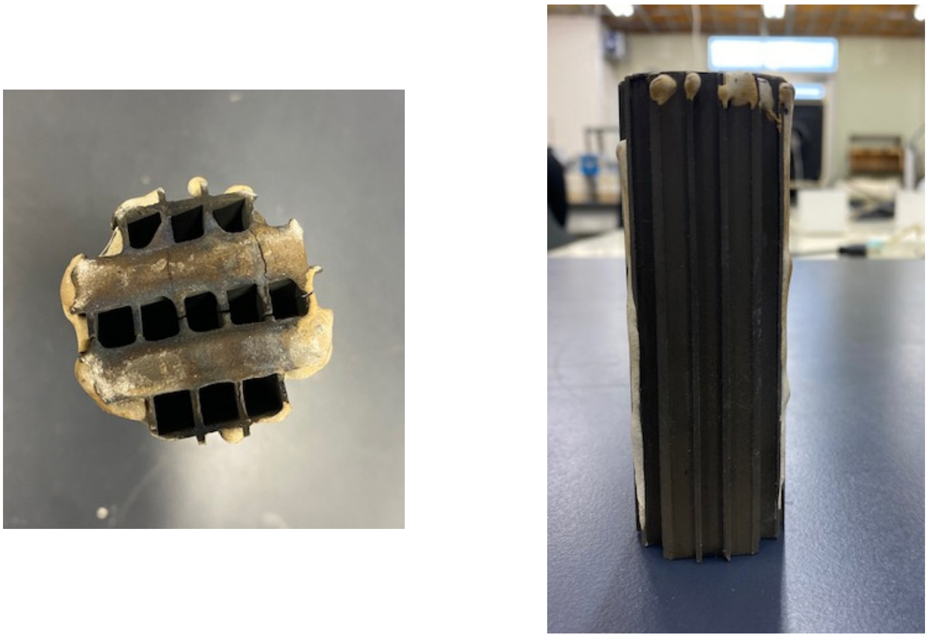

***Figure 6***. *Photographs of honeycomb sensible/latent storage unit after the thermal response testing: (a) top view and (b) side view. A white colored material appeared in the upper and lower plane is inorganic ceramic bond.*

## 4. Conclusion

Aluminium-Copper-Germanium alloy was examined as a phase change material at temperatures of 200-650 °C for use of thermal storage system in concentrated solar power. The thermal charge and discharge performance was evaluated in this study. The results of thermal response testing indicated that endothermic/exothermic peaks reproducibly appeared at the eutectic/melting temperatures (414-527°C). Thus, the alloy PCM behaved consistently, based on thermodynamic equilibrium in a gas stream, and responded under the limited conductive heat transfer without the effect of alloy oxidation under inert atmosphere.

The alloy PCM was loaded in a ceramic honeycomb, and the PCM-packed sensible/latent storage unit was prepared in this study. The thermal charge and discharge performance was evaluated in an air stream in test equipment of laboratory. The latent heat stored in the PCM alloy was released/absorbed through the wall of ceramic honeycomb into gas stream without major time delay under close to thermodynamic equilibrium state.

## Data availability statement

The original contributions presented in the study are included in the article. Further inquiries can be directed to the corresponding author.

## Author contributions

NG contributed to perform conceptualization, methodology, validation, software, formal analysis, writing–original draft, writing–review and editing, visualization, supervision, project administration, funding acquisition; TY contributed to conduct formal analysis, whole investigation, visualization; TK and YI contributed to discussion and support; TH contributed to investigation, and part of funding acquisition.

## Competing interests

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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