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Experimental study on the properties of millimeter-sized NaCl-KCl/MgO ceramic particles for high-temperature solar-thermal phase change applications

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Abstract: The development of molten salt composite phase change materials (CPCMs), which can store both sensible and latent heat, is a promising strategy to enhance the thermal energy storage capacity in solar thermal systems. Currently, bulk CPCMs are primarily prepared using the mixed sintering method, but their application is limited by issues such as easy collapse, leakage, and the fact that they can only be stacked for use. To address these issues, this study proposes a novel method that combines extrusion-spheronization with mixed sintering to produce composite phase change particles with high fluidity, excellent leakage resistance, and high energy storage density. An MgO skeleton is incorporated into the NaCl-KCl phase change material to provide structural support, prevent leakage and deformation, and enhance the thermal conductivity. The enthalpy value of the CPCM reaches 146 kJ/kg, and its thermal conductivity is as high as 4.57 W/(m·K). With 15% $MnFe_2O_4$, the solar spectral absorbance reaches 86.62%.

1. Introduction

The transition towards sustainable energy systems, driven by global carbon peaking and carbon neutrality goals, is crucial. Despite progress, most industries still rely on high-carbon energy sources, resulting in excessive energy consumption and low efficiency.[1] The adoption of clean energy, renewable sources, and efficient energy forms is essential to achieving sustainability. However, the intermittent nature of renewable energy presents significant challenges. Thermal energy storage provides an effective solution to these issues.[2] Thermal storage is typically achieved via sensible heat, latent heat, or chemical heat storage mechanisms. Among these, phase change thermal storage offers high energy density, making it particularly promising for solar energy applications.

Nevertheless, pure phase change materials (PCMs) face limitations, including low thermal conductivity and susceptibility to leakage. In high-temperature solar applications, molten salt-based inorganic PCMs have garnered significant attention for their high energy storage capacity. However, issues such as leakage and corrosion of molten salts remain a concern.[3] Encapsulation technologies, to fabricate shape-stable PCMs (SSPCMs), mitigate these risks by enhancing heat transfer and reducing leakage.[4] Three primary methods are commonly used to encapsulate PCMs: impregnation, sintering, and encapsulation.

Sintering packaging involves mixing high-temperature molten salts and additives in specific proportions, followed by molding and high-temperature firing to produce composite materials that integrate PCMs. These composites offer high energy storage density and leak resistance, particularly when combined with materials of high thermal conductivity. Ceramic matrix composites, such as those using silicon carbide (SiC), magnesium oxide (MgO), aluminum oxide (Al_2O_3), and silica (SiO_2), have significant industrial potential by improving both thermal conductivity and leak resistance, while enhancing the heat storage capacity of PCMs.[5-8] For instance, Liu et al.[9] developed stable $NaNO_3$/MgO thermal storage composites using cold sintering, which maintained stability after 500 cycles, demonstrating excellent chemical compatibility and thermal stability. Similarly, Hou et al.[10] prepared MgO based composite phase change materials (CPCMs). The thermal conductivity of pure PCMs (NaCl-KCl-$MgCl_2$) is 0.33 W/(m·K), and the thermal conductivity can reach 2.86 W/(m·K) when only magnesium oxide is used as packaging material (including 45 wt.% PCMs).

The mixed sintering method has gained attention for its potential in large-scale production, especially for CPCMs.[4] It has the advantages of simple process and easy operation, and can easily control the content of high-temperature PCM. Sang et al.[11] proposed a block shaped composite material using ternary carbonate (K_2CO_3-Li_2CO_3-Na_2CO_3) as a high-temperature thermal energy storage material and magnesium oxide ceramic as a support material for concentrated solar power generation, to prevent molten salt leakage and related corrosion. However, there are also some defects in the use of these large-sized or block shaped composite phase change materials, such as ease of collapse and leakage, short

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service life, and can only be stacked for use, which is not conducive to transfer and replacement. In contrast, granular sensible heat materials, such as sand and rock, offer advantages in storage, transfer, and mobility, providing more versatility. Inspired by these advantages, the preparation of millimeter-sized phase change granular materials presents significant potential.

In this study, composite phase change particles were prepared using extrusion-spheronization and mixed sintering techniques, achieving a performance that combines high liquidity, high leakage resistance, and high energy storage density. Sodium chloride-potassium chloride (NaCl-KCl) was selected as the PCM for high-temperature solar energy applications. To address PCM leakage, MgO was used as the ceramic matrix, and manganese iron black ($MnFe_2O_4$) was incorporated to enhance spectral absorption and improve the photothermal response rate. This preparation process is well-suited for large-scale industrial production and holds promise for various industrial applications. Moreover, the particles demonstrate excellent fluidity, thereby expanding the range of potential applications.

2. Experiments

2.1 Raw materials

Sodium chloride (NaCl, AR, 99.5%, Aladdin) and potassium chloride (KCl, 99.8%, Macklin) were mixed in a 1:1.02 molar ratio to prepare the eutectic salt as the phase change material. Magnesium oxide (MgO, AR, 98.0%, Aladdin) was used as the matrix material. Polyvinyl alcohol (PVA, 87.0–89.0% mol/mol, Aladdin) was used as a binder and completely removed during calcination. Manganese ferrite ($MnFe_2O_4$, high temperature 750 T, purchased from Zhejiang Hua Yuan Co. Ltd) was used to enhance spectral absorption.

2.2 Preparation of eutectic salt and CPCMs

The NaCl and KCl salts were mixed in a 1:1.02 molar ratio and ball-milled at 300 rpm for 2 hours. The mixture was then dried at 120°C for 2 h to obtain the NaCl-KCl eutectic salt. A 3 wt.% PVA solution was prepared by dissolving PVA in water and stirring until a homogeneous solution was formed. The NaCl-KCl, MgO, and $MnFe_2O_4$ powders were mixed and ball-milled for uniformity. The PVA solution was added to the powder mixture, which was then extruded into 1 mm diameter bars and spheronized. The bars were calcined at 720 °C for 4 h to remove the PVA binder, resulting in stable composite phase change particles.

3. Results and discussion

3.1 Thermal analyses of MgO and NaCl-KCl

The thermal conductivity of CPCMs is critical for efficient heat storage. Metals, when oxidized, form metal oxides, which generally exhibit lower thermal conductivity than metals but still significantly outperform most phase change materials.[12] MgO, which typically has a theoretical thermal conductivity of 33.49 W/(m·K), significantly enhances the thermal conductivity of the composite materials. As shown in **Fig. 1**, the thermal conductivity of the composite increases with the proportion of MgO, reaching 4.57 W/(m·K) when the PCM to MgO mass ratio is 1:1.5. This is an improvement over the thermal conductivity of NaCl-KCl eutectic salt alone, which is approximately 2.60 W/(m·K).

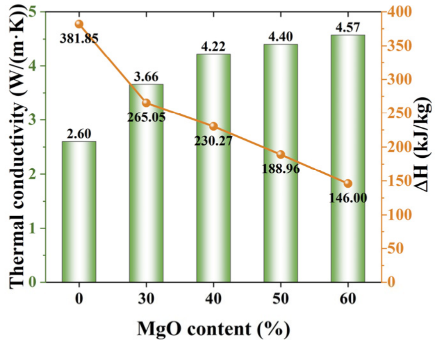

Fig. 1 Thermal conductivity and enthalpy of CPCMs with varying MgO content.

The enthalpy of pure phase change materials can reach 381.85 kJ/kg. However, as the content of MgO increases, the enthalpy of the composite material decreases. Theoretically, the latent heat of the composite is directly proportional to the mass fraction of the pure PCM. This relationship can be expressed by the following formula:

$$\Delta H_{CPCM} = \Phi \Delta H_{PCM} \quad (1)$$

Where ΔH_{CPCM} and ΔH_{PCM} represent the latent heat of the composite material and the pure PCM, respectively, and Φ denotes the mass fraction of PCM in the composite.

It can be observed that there is a slight difference between the experimental results and theoretical values, which may be attributed to the minor leakage of PCM on the particle surface during the mixed sintering process. When the mass ratio of PCM to MgO is 1:1.5, the enthalpy of the composite material is 146 kJ/kg.

3.2 Leakage of NaCl-KCl with MgO

The leakage performance was tested by subjecting the composite particles to 100 heating and cooling cycles in the range of 500-700 °C. As shown in Fig. 2, the enthalpy decreased from 146 kJ/kg to 140.48 kJ/kg after the cycles, indicating a reduction of 3.78%. This demonstrates that the MgO skeleton effectively prevents leakage of the NaCl-KCl PCM during the phase transition.

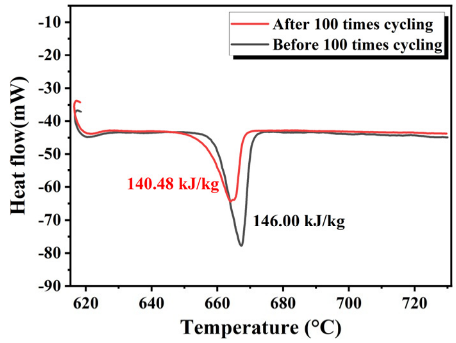

Fig. 2 The enthalpy curve before and after cyclic testing.

3.3 Solar absorption properties

Black powder materials such as iron oxide (Fe_3O_4), manganese dioxide (MnO_2), manganese ferrite ($MnFe_2O_4$), and a 1:1 mixture of iron oxide and manganese dioxide are known for their excellent spectral absorption properties at high temperatures, which enhance the photothermal conversion capabilities of materials. [13]

High-temperature experiments were conducted to observe the color changes of these materials, as shown in **Fig. 3**. The results revealed that Fe_3O_4 changed significantly from black to reddish-brown after treatment at 720°C for 2 h. In contrast, the color of MnO_2, $MnFe_2O_4$, and the Fe_3O_4-MnO_2 mixture remained largely unchanged. The color change of Fe_3O_4 can be attributed to oxidation at high temperatures, resulting in the formation of reddish-brown iron oxide (Fe_2O_3). he chemical equation for this reaction is as follows:

$$4Fe_3O_4 + O_2 \overset{\text{高温}}{=} 6Fe_2O_3 \quad (2)$$

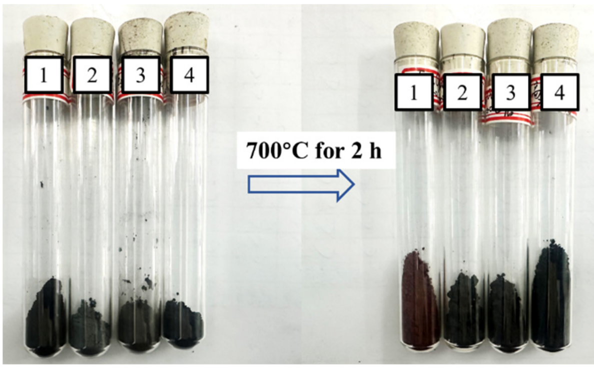

Fig. 3 Color comparison before and after high-temperature treatment. (1) Fe_3O_4, (2) MnO_2, (3) the Fe_3O_4-MnO_2 mixture, and (4) $MnFe_2O_4$.

After high-temperature treatment, the powders were thoroughly mixed with MgO and NaCl-KCl in varying proportions via ball milling. Since MgO and NaCl-KCl are white powders, their proportions did not affect the spectral absorption measurements. Various light-absorbing materials, including Fe_3O_4, MnO_2, and $MnFe_2O_4$, were added in mass fractions of 5%, 10%, 15%, 20%, and 100% of the total mass of the non-light-absorbing materials. The spectral absorption properties of the resulting mixtures were tested, with the results presented in **Fig. 4**. The spectral absorption rate increased with higher content of light-absorbing materials. Notably, at 15% content, the spectral absorption capacity was significantly improved compared to 10%. However, no significant improvement was observed at 20% compared to 15%. At 15% content, the performance of different light-absorbing materials varied. $MnFe_2O_4$ (87.17%) and MnO_2 (81.83%) showed notably better spectral absorption than Fe_3O_4 (35.30%) and the Fe_3O_4-MnO_2 mixture (68.34%), with $MnFe_2O_4$ showing the highest performance.

Increasing the content of light-absorbing materials resulted in a reduction in the PCM content of the composite, which in turn affected the enthalpy of the material, leading to a theoretical decrease in enthalpy. Therefore, the experimental results suggest that the optimal content of light-absorbing materials is 15%.

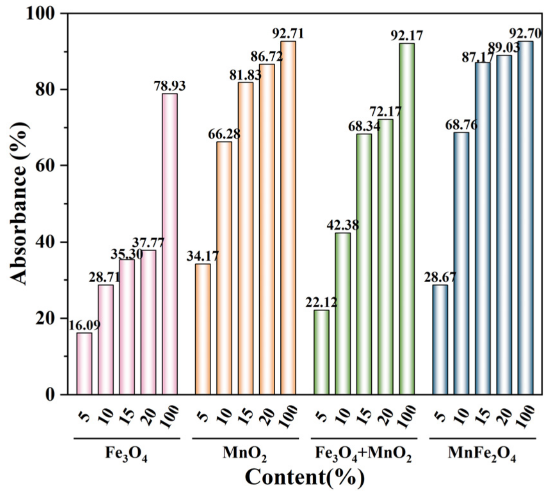

Fig. 4 Spectral absorbance of various light-absorbing materials at different concentrations.

After adding 15% MnFe2O4 mixing with MgO and NaCl-KCl to form composite phase change particles, their spectral absorption properties were retested. As shown in **Fig. 5 (a)**, the solar spectral absorptance of the composites with $MnFe_2O_4$ across the full range of 300-2000 nm is higher than that of the materials without $MnFe_2O_4$. **Fig. 5 (b)** shows that the average spectral absorption rate of particles without hyperspectral absorption material is only 41.81%, whereas the average absorption rate of $MnFe_2O_4$-mixed particles is 86.62%, representing an increase of 107.18%. This demonstrates that $MnFe_2O_4$ significantly enhances the spectral absorption properties of the composites.

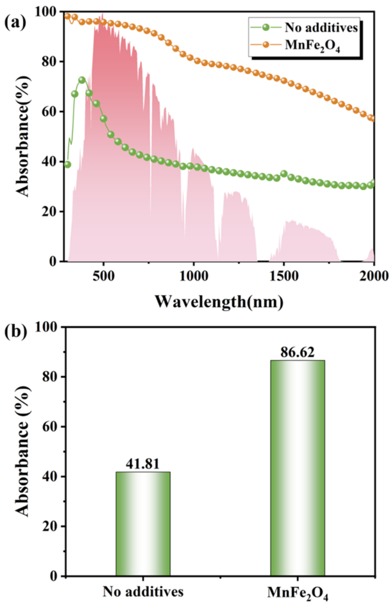

Fig. 5 (a) The spectral absorptance of the composites with and without $MnFe_2O_4$; (b) the average solar spectral absorptance of the composites with and without $MnFe_2O_4$.

3.4 Chemical compatibility of CPCM

Fig. 6 presents the X-ray diffraction (XRD) patterns of $MnFe_2O_4$, NaCl-KCl, MgO, and NaCl-KCl/MgO/$MnFe_2O_4$ composite phase change material (CPCM). The analysis of the diffraction spectra shows that the peaks of the CPCM sintered at 720°C align perfectly with those of each individual component, with no additional peaks appearing. This indicates that no chemical reactions occurred between the components, confirming the excellent chemical compatibility of the materials during high-temperature sintering.

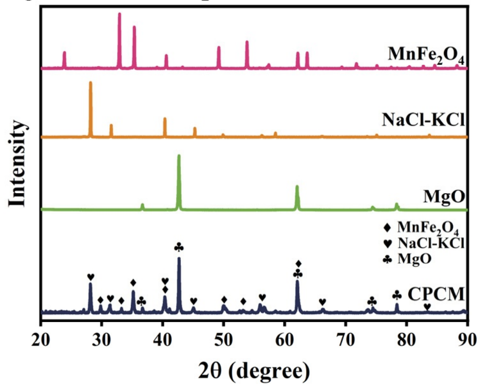

Fig. 6 XRD patterns of $MnFe_2O_4$, NaCl-KCl, MgO, and CPCM

3.5 Thermal responses of CPCM

Photothermal experiments were conducted to observe the temperature changes of the CPCM and pure PCM (NaCl-KCl), recorded using infrared imaging. As shown in **Fig. 7 (a)**, the upper sample represents the CPCM, while the lower sample corresponds to the pure PCM. The samples, each weighing 3.5 g, were placed in fixed positions and subjected to a light intensity of approximately 0.18 W/cm². From the infrared temperature images, it is evident that the photothermal response of the composite material is significantly faster than that of the pure PCM.

As shown in **Fig. 7 (b)**, the temperature versus time curve reveals that the CPCM reached a stable temperature of approximately 92.05 °C in 276.92 s, while the pure PCM only reached 42.70 °C after 288.56 s. The heating rate of CPCM is 0.33 K/s, compared to 0.15 K/s for the pure PCM, indicating a 120% increase in photothermal response speed. This experiment confirms that the CPCM demonstrates efficient photothermal conversion.

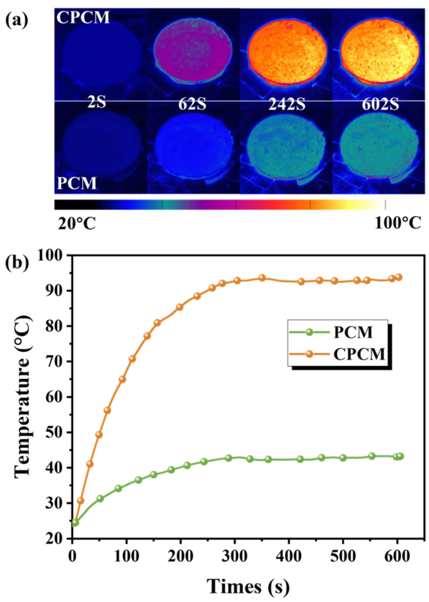

Fig. 7 (a) Surface infrared temperature image of CPCM and pure PCM; (b) variation of the highest surface temperature.

4. Conclusions

This study presents a method that combines high-temperature photothermal conversion with phase change thermal storage to prepare high-temperature composite phase change particles. By using NaCl-KCl eutectic salt as the PCM and MgO as the supporting matrix, a high-temperature chloride salt thermal storage material was developed through extrusion-spheronization and mixed sintering. The preparation process is simple, scalable, and suitable for practical applications. At a PCM loading of 40%, the enthalpy reaches 146 kJ/kg, with a thermal conductivity of 4.57 W/(m·K) and a solar absorption rate of 86.62% with 15% $MnFe_2O_4$.

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