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SODIUM ORTHOSILICATE AND FUMED SILICA AS STABILIZER OF Li_2SO_4–Na_2SO_4 SOLID-SOLID PCMS

Summary

The Li_2SO_4–Na_2SO_4 (LNS) system is a promising candidate for thermal energy storage in the 450–550 °C range due to the solid–solid transition of $LiNaSO_4$. However, its practical application is constrained by structural deformation during cycling. In this study, the effect of several additives, including MgO, graphite, and bentonite, was evaluated, showing limited effectiveness in improving system stability. In contrast, the incorporation of sodium orthosilicate (Na_4SiO_4) and fumed silica (SiO_2) proved significantly more effective. Both binders promote the formation of a silica matrix that confines the LNS and enhances structural stability. Nevertheless, some aspects must be considered. In the case of sodium orthosilicate, Na^+ migration into the LNS matrix occurs, requiring adjustment of the initial composition to achieve a final 50:50 molar ratio. For fumed silica, compatibility with the operating atmosphere must be verified. Structural and microstructural analyses (SEM, XRD, RAMAN) clarified the stabilization mechanisms associated with binder incorporation. Moreover, thermal and cycling tests confirmed preservation of the initial enthalpy and improved shape stability, with no deformation after 100 cycles between 300 and 580 °C.

Keywords: Solid–solid PCMs; Thermal energy storage; Li_2SO_4–Na_2SO_4 system; Sodium orthosilicate; Fumed silica; Shape stabilization

Field of application for the findings: Thermal energy storage – Innovative materials for TES

Addressed audience: Researcers, academy

1. Introduction

The growing energy demand and the integration of intermittent renewable sources call for efficient thermal energy storage systems, particularly at high temperatures, as required in industrial processes and concentrating solar power plants. In this context, latent heat storage using solid–solid phase change materials (PCMs) is of great interest, since it offers high energy densities and reversible transitions without the corrosion or segregation issues typically associated with solid–liquid materials.

Within this framework, the Li_2SO_4–Na_2SO_4 (LNS) system emerges as a particularly attractive candidate, as it exhibits two notable compositions associated with solid–solid transitions: 21/79 and 50/50 molar. In particular, the 50:50 composition undergoes a solid–solid transition with an energy density of ≈158 J g^{-1}, good reversibility, and potential compatibility with air, as demonstrated by Doppiu et al. (2019). However, its practical implementation has been limited by the instability observed after successive thermal cycles, manifested primarily as structural deformation and loss of mechanical integrity, although without significant reduction in transition enthalpy, as reported by Taeño et al. (2024).

To address these limitations, different inorganic additives (MgO, expanded graphite, bentonite, among others) have been evaluated, but none stabilized the cycling behavior of LNS. Motivated by the structural role of silicates in ceramics, as reposted by Bayoumi et al. (2022), sodium orthosilicate (Na_4SiO_4) was investigated as a stabilizer. In parallel, fumed silica (SiO_2) was considered due to its high specific surface area. In both cases, the additives promote the formation of a silica matrix capable of confining the PCM and mitigating structural deformation during repeated thermal cycling.

2. Methodology and characterization

The Li_2SO_4–Na_2SO_4 (LNS) composition was prepared from commercial salts (≥99%, Alfa Aesar) by ball milling followed by thermal treatment at 550 °C. Sodium orthosilicate (15 wt%) was incorporated with adjusted stoichiometry to compensate for Na^+ migration and to ensure a final 50:50 composition. Since sodium orthosilicate was initially supplied as a powder, it was first dissolved in water to prepare a 30 wt% aqueous solution. This solution was then mixed with the LNS powder in a mortar while applying shear in order to ensure homogeneous dispersion of the precursor. The mixtures were subsequently pressed and pretreated at 120 °C to remove residual water and promote silica gel formation.

For the preparation of the fumed silica composites, fumed silica (5 wt%) was weighed inside a glovebox to ensure accurate mass determination due to its highly hygroscopic nature. The silica was then mixed with the LNS powder and deionized water (15 wt%). The mixture was manually ground in a mortar while applying shear to promote the formation of links between the fumed silica particles, enabling the development of a continuous silica-based matrix.

Structural and microstructural characterization was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM-EDS), and Raman spectroscopy, while differential scanning calorimetry (DSC) was used to determine the transition enthalpy. Thermal cycling tests (100 cycles) between 300 and 580 °C were performed to assess shape stability and durability.

3. Results and conclusions

X-ray diffraction (XRD) patterns of the Li_2SO_4–Na_2SO_4 (50:50) composition stabilized with sodium orthosilicate indicate that the predominant crystalline phase corresponds to $LiNaSO_4$. After thermal treatment and subsequent cycling, a secondary phase attributable to lithium silicate appears, suggesting partial interaction between the LNS system and the orthosilicate stabilizing agent. Despite this interaction, $LiNaSO_4$ remains the dominant phase, indicating that the functional salt composition is preserved. In the case of the fumed silica composite, no additional crystalline phases are detected by XRD due to the amorphous nature of the silica matrix. Consequently, Raman spectroscopy was employed to further investigate the structure of the silica network.

Raman analysis of the fumed silica-based system reveals a dominant amorphous SiO_2 glassy background. However, in localized crystallized regions, characteristic bands associated with different degrees of silicate polymerization are observed, indicating the presence of partially structured silicate species within the matrix.

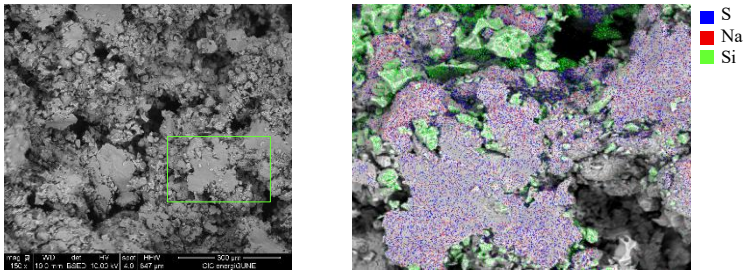

Fig. 1: SEM micrograph (magnified view) and EDS elemental distribution of the LNS (50:50) composite containing 5 wt% fumed silica after thermal cycling

Scanning electron microscopy (SEM) reveals a comparable microstructural motif for both stabilization approaches, consisting of two clearly distinguishable regions: (i) a continuous, relatively smooth phase attributed to the LNS salt, and (ii) a porous phase corresponding to the silica-based matrix. EDS mapping confirms the compositional contrast between these domains, with the porous regions enriched in Si, consistent with a silica network. The silica matrix forms a continuous scaffold that confines the salt phase and buffers thermally induced dimensional changes, thereby limiting macroscopic deformation during cycling. After cycling, partial penetration of the LNS phase into the pores of the silica network is observed, suggesting a physical anchoring mechanism that enhances structural integrity and mitigates segregation.

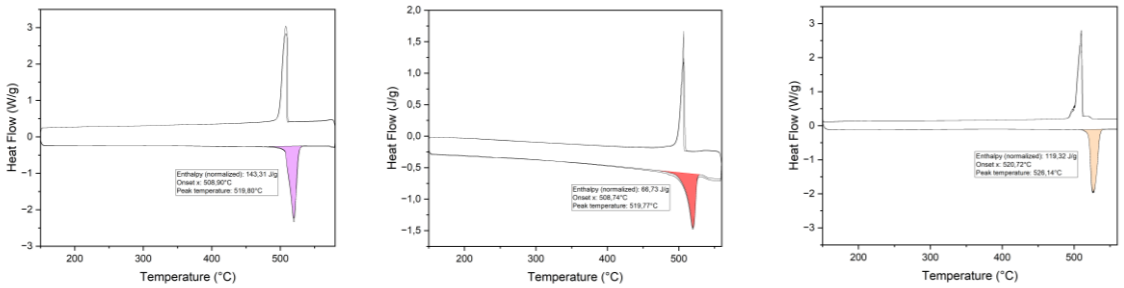

Fig. 2: DSC curves of LNS-based composites after thermal cycling: (left) LNS 25:75 stabilized with 15 wt% Na_4SiO_4, (center) LNS 50:50 containing 5 wt% fumed silica cycled in air, and (right) LNS 50:50 containing 5 wt% fumed silica cycled under inert atmosphere

Consistent with the structural and microstructural observations, differential scanning calorimetry (DSC) measurements confirm that the characteristic solid–solid transition of the 50:50 LNS composition is preserved after stabilization. For the system stabilized with sodium orthosilicate, the transition enthalpy reaches approximately 90% of the theoretical value and remains essentially unchanged during repeated thermal cycling between 300 and 580 °C, indicating the high stability of the silica matrix generated in situ. In contrast, the composite prepared with fumed silica exhibits a gradual decrease in transition enthalpy upon cycling, indicating a progressive loss of storage capacity. However, the stability of this system is strongly influenced by the surrounding atmosphere. When cycling is performed in air, the transition enthalpy progressively decreases to values of approximately 66 J g^{-1}, whereas under an inert atmosphere the material retains significantly higher values, reaching around 125 J g^{-1} after cycling. These results indicate that the silica matrix formed in situ from sodium orthosilicate provides a more effective structural stabilization of the LNS phase than the externally added fumed silica, enabling more stable and reversible operation under repeated thermal cycling conditions. Overall, the results demonstrate that silica matrices generated in situ from sodium orthosilicate provide superior structural and thermal stability compared with externally added fumed silica, making this approach a promising route for high-temperature solid–solid PCM stabilization.

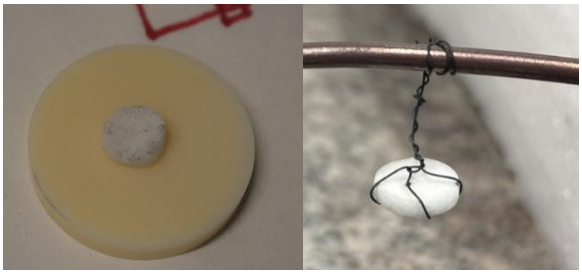

Fig. 3: Photographs of LNS-based composites after thermal cycling in air: (left) LNS 25:75 stabilized with 15 wt% Na_4SiO_4 and (right) LNS 50:50 containing 5 wt% fumed silica

4. References

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