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Study on nanoconfinement effect in inorganic mesoporous matrices

- PhD Thesis Abstract -

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Keywords: nanoconfinement, shape-stabilized phase change materials, mesoporous silica, eutectic mixture, bismuth, stearic acid, differential scanning calorimetry (DSC).

Table of contents

I.	Literature review.....	4
I.1.	Mesoporous silica	4
I.1.1.	Introduction	4
I.1.2.	Types of mesoporous silica	4
I.1.3.	Synthesis techniques.....	6
I.1.3.1.	Synthesis of pristine mesoporous silica	6
I.1.3.2.	Post-synthesis functionalization	8
I.1.3.3.	Doping of mesoporous silica	8
I.1.4.	Physico-chemical properties and characterization techniques	8
I.1.4.1.	Porosity	9
I.1.4.2.	Mesoporous silica pore array.....	10
I.1.4.3.	Morphology assessment	10
I.1.4.4.	Chemical composition (EDX, FTIR)	11
I.2.	Phase change materials	11
I.2.1.	Latent heat storage through phase change	13
I.2.2.	Types of phase change materials.....	13
I.2.3.	Shape-stabilized phase change materials	14
I.2.4.	High-temperature phase change materials	15
I.2.5.	Mesoporous silica-based phase change materials	16
I.2.6.	Synthesis methods for phase change materials composite materials.....	16
I.2.7.	Properties and characterization techniques	17
I.3.	Nanoconfinement effects on phase change	19
I.3.1.	Non-melting layer	20
I.3.2.	Melting point depression, Gibbs-Thomson equation	20
I.3.3.	Mathematical models for computing non-melting layer volume.....	22
I.3.4.	Composite materials based on organic phase change materials and porous silica.....	24
I.3.4.1.	Paraffins	24
I.3.4.2.	Fatty acids and derivatives.....	30
I.3.4.3.	Poliethylene Glycol.....	36
I.3.4.4.	Small organic compounds.....	41

I.3.5.	Composite materials based on inorganic phase change materials and porous silica.....	42
I.3.5.1.	Hydrated salts	42
I.3.5.2.	Molten salts	44
I.3.5.3.	Metals and alloys	45
II.	Original contributions.....	47
II.1.	Justification for the choice of topic	47
II.2.	PhD thesis objectives.....	47
II.3.	Materials and methods.....	48
II.3.1.	Materials.....	48
II.3.2.	Thermal conductivity	48
II.3.3.	Specific heat.....	49
II.3.4.	Characterization techniques for mesoporous silica and composites	49
II.4.	Phase change materials based on mesoporous silica and molten salts (NaNO ₃ : KNO ₃)	50
II.4.1.	Synthesis of mesoporous aluminosilicates	51
II.4.2.	Characterization of aluminosilicates.....	52
II.4.3.	Synthesis of phase change materials based on mesoporous silica and molten salts (NaNO ₃ : KNO ₃)	55
II.4.4.	Physico-chemical characterization of phase change materials based on mesoporous silica and molten salts (NaNO ₃ : KNO ₃)	55
II.4.5.	Thermal characterization of phase change materials based on mesoporous silica and molten salts (NaNO ₃ : KNO ₃)	58
II.4.6.	Partial conclusions on phase change materials based on mesoporous silica and molten salts (NaNO ₃ : KNO ₃).....	69
II.5.	Phase change materials based on MCF mesoporous silica and eutectic salt mixture NaCl-NaBr-Na ₂ MoO ₄	71
II.5.1.	Synthesis of MCF mesoporous silica.....	71
II.5.2.	Physico-chemical characterization of MCF mesoporous silica	71
II.5.3.	Synthesis of phase change materials based on MCF mesoporous silica and eutectic salt mixture (NaCl-NaBr-Na ₂ MoO ₄)	72
II.5.4.	Physico-chemical characterization phase change materials based on MCF mesoporous silica and eutectic salt mixture (NaCl-NaBr-Na ₂ MoO ₄)	72
II.5.5.	Thermal characterization phase change materials based on MCF mesoporous silica and (NaCl-NaBr-Na ₂ MoO ₄).....	74
II.5.6.	Partial conclusions on phase change materials based on MCF mesoporous silica and NaCl-NaBr-Na ₂ MoO ₄	80
II.6.	Phase change materials based on mesoporous silica and Bismuth 1.....	82

II.6.1.	Synthesis of MCF și SBA-15 mesoporous silica.....	82
II.6.2.	Physico-chemical characterization of MCF and SBA-15 silica	83
II.6.3.	Synthesis of bismuth particles and bismuth-silica composites	84
II.6.3.1.	Impregnation method	84
II.6.3.2.	Encapsulation method	84
II.6.4.	Physico-chemical characterization of bismuth-mesoporous silica composites	85
II.6.5.	Thermal characterization of bismuth-mesoporous silica composites.....	91
1.1.1	Partial conclusions on bismuth-mesoporous silica composites	97
II.7.	Phase change materials based on mesoporous silica and Bismuth through nanocasting	98
II.7.1.	Synthesis and characterization of MCF silica	99
II.7.2.	Synthesis of phase change materials based on mesoporous silica and bismuth obtained by nanocasting and H ₂ reduction	99
II.7.3.	Physico-chemical characterization of phase change materials based on mesoporous silica and bismuth obtained by nanocasting and H ₂ reduction	100
II.7.4.	Thermal characterization of phase change materials based on mesoporous silica and bismuth obtained by nanocasting and H ₂ reduction	102
II.7.5.	Partial conclusion on phase change materials based on mesoporous silica and bismuth obtained by nanocasting.....	108
II.8.	Phase change materials composites based on mesoporous silica and Bismuth and stearic acid	109
II.8.1.	Synthesis of FDU-12 mesoporous silica.....	109
II.8.2.	Physico-chemical characterization of FDU-12 silica	109
II.8.3.	Synthesis of composites based on mesoporous silica and bismuth or stearic acid	111
II.8.4.	Physico-chemical characterization of composites based on mesoporous silica and bismuth or stearic acid.....	111
II.8.5.	Thermal characterization of composites based on mesoporous silica and bismuth or stearic acid	113
II.8.6.	Partial conclusions on composites based on mesoporous silica and bismuth or stearic acid	119
III.	Conclusions	120
IV.	Perspectives	122
V.	List of publications	124
VI.	List of conference participation	124
VII.	References	125

Introduction

The PhD thesis consists of two parts representing literature review and original contributions, ending with the general conclusions and perspectives. The literature review is divided into 3 chapters containing information about mesoporous silica, phase change materials and the effects of nanoconfinement on phase transformations. The first chapter presents information about the types of mesoporous silica, the synthesis methods, as well as the physico-chemical characterization methods used to describe its properties. The second chapter presents information on the types of phase change materials, the methods of obtaining phase change composite materials, as well as on their properties and their physico-chemical characterization. The third chapter describes the effects of nanoconfinement on phase transformations, explaining phenomena such as the formation of the non-melting layer or the depression of the melting point. Also, in this chapter are presented studies on the obtaining of composites based on inorganic or organic phase change materials and mesoporous silica, and the obtained main results.

The second part of the thesis, Original Contributions, contains the topic choice justification, as well as the objectives of the PhD thesis, then continues with the description of the materials and methods used for the characterization of mesoporous supports and phase change composite material. Chapter II.4 presents the study of phase change composite materials based on mesoporous silica and molten salts ($\text{NaNO}_3\text{:KNO}_3$), these materials retaining their thermal energy storage properties in a proportion of 90% up to 50 cycles. Chapter II.5 presents MCF-type silica based phase change materials with various amounts of eutectic mixture of NaCl, NaBr and Na_2MoO_4 . The composite containing 80% eutectic mixture proved the best thermal properties and shape-stabilized. Chapter II.6 presents the obtaining of metallic bismuth-based phase change materials by two methods: impregnation and encapsulation, resulting in materials with stabilized shape, in both cases, having good thermal reliability, but with higher enthalpy obtained in the case of the impregnation method. Chapter II.7 presents the casting method (nanocasting) for obtaining shape-stabilized composites based on metallic bismuth and the optimization of the synthesis parameters to obtain the best thermal properties. The last chapter of the Original Contributions part deals with the obtaining of composites based on mesoporous silica and bismuth or stearic acid in order to compare the use of an organic material with an inorganic material. The resulting composite materials presented a thermal stability up to 160 °C when stearic acid was employed and up to 271 °C for bismuth-based composites.

I. Literature study

The literature survey of this PhD thesis focuses on the description of the components of phase-change materials and the nanoconfinement effect that occurs, consisting of three chapters on mesoporous silica, phase-change materials, and the nanoconfinement effect.

I.1. Mesoporous silica

Mesoporous silica can have an ordered pore structure, which depends on the synthesis method. The first such materials synthesized, by the ExxonMobil company, were used for catalytic purposes [1]. Their ordered pore structure of nanometer dimensions, as well as their very good stability make them suitable for catalytic supports. Mesopores serve as hosts for metal particles limiting their sintering at high temperatures [2].

The techniques for the synthesis of mesoporous silica have evolved in the last 30 years in order to be applied in various fields. One of the major topic in which mesoporous silica has been studied is biomedical field. The possibility of easily adjusting the characteristics of mesoporous silica nanoparticles allows obtaining complex nanosystems containing bioactive substances that interact with various components of biological systems [3].

The use of mesoporous silica for stabilized-shape phase-change materials is also a new topic of research. The textural properties of mesoporous silica, as well as its chemical and thermal stability, allow the stabilization of the shape of phase change materials. The mechanism by which this stabilization occurs are associated with capillary forces, nanoconfinement effect, or the presence of interactions between organic molecules and the silica surface [4].

I.2. Phase-change materials

Thermal energy storage (TES) is important for sustainable energy production for many industrial processes. Thermal energy can be stored and recovered by heating and cooling the material with thermal energy storage properties or as latent heat from its phase transformation. Sensitive heat refers to the heat energy transferred by heating or cooling the material. The amount of thermal energy consumed to heat one gram of substance by 1°C is called the specific heat (Cp). Latent heat is the heat energy transferred through a phase transformation such as melting or crystallization, evaporation, or condensation. The materials used for this purpose are called phase-change materials (PCM) and can store large amounts of heat at a constant temperature. Heat can also be stored as reaction enthalpy [5].

Each thermal energy storage system has advantages and disadvantages. Latent and sensitive energy storage are passive and do not require complex operating facilities, which reduce heat storage costs. However, overall sensitive energy storage allows for the storage of small amounts of thermal energy. Specific heat, operating temperature range, cost, and energy density are the most important properties of sensitive heat energy storage material.

Energy storage in the form of latent heat is carried out using phase change materials (PCM). There are many materials that can be used as PCMs. They exhibit high phase transformation enthalpy, minimal subcooling, and rapid crystallization. These materials must

have chemical and thermal stability in the temperature range and environment, in which they are used. Cheap and non-corrosive materials are preferred.

For practical applications, pure PCMs and their mixtures have some drawbacks. Most non-metallic PCMs have low thermal conductivity, present a material leakage and corrosion. These processes are due to volume variation during phase transitions leading to a decrease of the total heat energy storage capacity. In order to remove these impediments, the synthesis of composites or nanocomposites has been proposed. The incorporation of metals, carbon or certain nanoparticles increases the thermal conductivity of the resulting composites [6-8]. PCM composite materials can also be synthesized with their macroscopic shape preservation following the melting of the active phase of thermal energy storage, named stabilized PCMs. They are non-corrosive, without variations in volume and material leakage during use, which significantly increases the life of the system.

1.3. Effects of nanoconfinement on phase transformations

The porous structure of mesoporous silica-based composite materials is influenced by either synthesis method or the nature of the active thermal energy storage phase. The active phase of heat energy storage can be found in silica mesopores (nanoconfined phase) and between silica particles (intergranular or macroscopic phase) [9]. The pores volume must allow the volume changes that occur during the phase transformations. Most liquid substances have a lower density than the solid phase, therefore in the case of mesoporous silica-based composite materials, the silica pores are partially hollow below the melting point of the active phase of heat energy storage.

1.3.1. Non-melting layer

An important feature of nanoconstrained solids in nanostructured pores is the existence of a non-melting layer that occurs at the interface of the solid surface and pores [10]. This layer has a behavior similar to an amorphous solid or a liquid layer that does not participate in the process of storing latent energy from phase transformations, melting or crystallization. For example, in the case of nanoconfined water in a mesoporous silica of the MCM-41 type, it has been estimated that the non-melting layer remains liquid up to a temperature of 21-26 K [11]. It has been found that the thickness of the non-melting layer increases with increasing temperature and pore curvature [12,13]. The thickness of the non-melting layer is an important parameter in assessment of the decrease in thermal energy storage capacity. The layer thickness varies between 0.3 and 2.6 nm, depending on the nanoconfined substance. In the case of small molecules, such as water or carbon tetrachloride [14], the thickness of the non-melting layer can be made up to 4 monomolecular layers, while in the case of large molecules, such as paraffins or fatty acids, the thickness of the layer corresponds to the length of a single molecule. Similar values were obtained for inorganic molecules, e.g. molten salts [15].

II. Original contributions

II.1. Justification of the subject choice

The PhD thesis, "*Study on nanoconfinement effect in inorganic mesoporous matrices*" aims to study phase change materials based on mesoporous silica. Phase-change materials have the disadvantage of volume variation as result of the phase transition, which can lead to leakage in the industrial plants where they are used, as well as to a decrease in thermal energy storage capacity over time. The use of mesoporous silica as a matrix for the incorporation of these substances leads to the obtaining of phase change materials with a stabilized shape.

Mesoporous materials, especially mesoporous silica, have the advantage of a large specific surface area, as well as a total pore volume, which allow the incorporation of substances through capillary forces. Thus, the phase-changing materials interact with the surface of the silica, and the phase transition occurs without changing their volume. This phenomenon, by which molecules are trapped inside nanometer-sized pores, is called nanoconfinement, and is responsible for properties of these substances. Due to the effects of nanoconfinement, phase-change substances can go through the phase transition without changing the volume, but at the same time, changes also occur in the melting enthalpy. The study of the control of the nanoconfinement effect in silica pores can lead to the design of complex composite materials with certain properties, which can be obtained by adjusting the mesoporous matrix and its characteristics. Thus, materials with specific uses can be designed, related to the application in which they are needed.

The PhD thesis also aimed to study various phase-change substances, both inorganic and organic, such as: mixtures of salts (NaNO_3 : KNO_3), eutectic mixtures of salts (NaCl - NaBr - Na_2MoO_4), bismuth and fatty acids (stearic acid) in order to assess the variation of nanoconfinement effect depending on the nature of the phase-change substance.

The need to study these materials is motivated by the increasing demand for materials that can store thermal energy efficiently. Climate change has led to an increase in the need to produce green energy, which directly impacts the importance to study phase-change materials. Such materials can be used in solar energy concentration plants for the storage of thermal energy in order to produce electricity.

II.2. Objectives of the doctoral thesis

The aim of the PhD thesis was to obtain shape stabilized-phase change materials based on mesoporous silica for efficient thermal energy storage. In order to fulfill this purpose, the following objectives were considered:

- (i) evaluation of the obtaining method of silica-based phase-change composite materials;
- (ii) properties assessment of different heat energy storage agents: eutectic salt mixture, organic substances and metals;
- (iii) the incorporation of heat energy storage agents into different mesoporous silica matrices with various mesoporous structure;
- (iv) physico-chemical characterization of the phase change materials based on mesoporous silica;
- (v) thermal characterization of phase change composite materials based on mesoporous silica;
- (vi) evaluation of the aluminium doping effect of mesoporous silica on the composite phase change material properties.

II.3. Materials and methods

Both mesoporous supports and composite materials were characterized using various physico-chemical characterization methods such as: small-angle and wide-angle X-ray diffraction, nitrogen adsorption-desorption isotherms, scanning or transmission electron microscopy, as well as FTIR spectroscopy for structurally and morphologically characterization of resulting materials.

Thermal properties are of great importance for phase-change materials, as they provide information about their reliability and usability in practical applications. Thus, the thermal properties of these materials, as well as their ability to retain their stabilized shape, were studied by thermogravimetric analysis and differential scanning calorimetry coupled with optical microscopy.

II.4. Composite materials with phase change based on mesoporous silica and molten salts (NaNO_3 : KNO_3)

This chapter deals with the incorporation of aluminum into the mesoporous silica lattice for obtaining phase-change composite materials containing NaNO_3 : KNO_3 eutectic mixture (1:1 molar). Mesoporous matrices with ordered hexagonal pore framework, such as SBA-15, but also with disordered pore structure with ink-bottle type pores, such as MCF, were synthesized. Shape-stabilized phase change composite materials with a content of 90% wt. eutectic mixture were obtained and their reliability, thermal stability and thermal energy storage capacity were studied. The variation of the freezing and melting point and the melting enthalpy were correlated with

pore size, eutectic mixture surface tension and non-melting layer formation of the eutectic mixture. Composites based on mesoporous matrix prepared without swelling agent exhibited very high melting enthalpy ($76\text{--}77\text{ J g}^{-1}$ compared to 96 J g^{-1} of the eutectic mixture), thermal stability up to $500\text{ }^{\circ}\text{C}$ and good thermal reliability following heat stress (95% of the initial storage capacity). The incorporation of aluminum into the mesoporous matrix structure led to the increase of the nanoconfined fraction of the eutectic mixture.

Figure 1 shows the DSC curves of the eutectic mixture and composite materials **(A)** and the DSC curves in the temperature range of $140\text{--}220\text{ }^{\circ}\text{C}$ for samples which were prepared using between 10% and 75% trimethylbenzene (TMB) in the synthesis **(B)**. All PCMs showed the effect of the phase transition associated with the melting of the macroscopic eutectic mixture, the intergranular particles. Compared to the eutectic mixture, the intergranular phase did not exhibit subcooling and significant deviations in terms of melting point and freezing point. In the case of the sample $(\text{Na, K})\text{NO}_3@(\text{Al}(0.10)\text{T}(0.00))$, two effects associated with the macroscopic intergranular phase are observed.

The thermal reliability of the materials was determined by DSC, by performing 50 heating-cooling cycles between 50° and $350\text{ }^{\circ}\text{C}$ (**Figure 2**). Every 5th cycle was recorded and the total enthalpy was calculated as the average values obtained in each cycle. The values were normalized in relation to the first measurement, which was considered 100% (Figure 28). The eutectic mixture and the composites based on the matrix $\text{Al}(0.33)\text{T}(0.00)$ and $\text{Al}(0.33)\text{T}(0.10)$ did not show enthalpy losses following the heating-cooling cycles (Figure 2). On the other hand, the composite containing $\text{Al}(0.10)\text{T}(0.00)$ as a matrix exhibited a gradual loss of enthalpy after 20 heating-cooling cycles. This loss of enthalpy could be explained by the fact that a small amount of aluminum salt was used in the synthesis of the $\text{Al}(0.10)$ matrix, which caused differences in textural properties.

Optical microscopy images (**Figure 3**) confirm the densification of the composite by $\sim 5\text{--}10\%$ after the composite heating to a temperature higher than the melting point of the eutectic. No further changes are observed after the composite was maintained at $450\text{ }^{\circ}\text{C}$ for one hour.

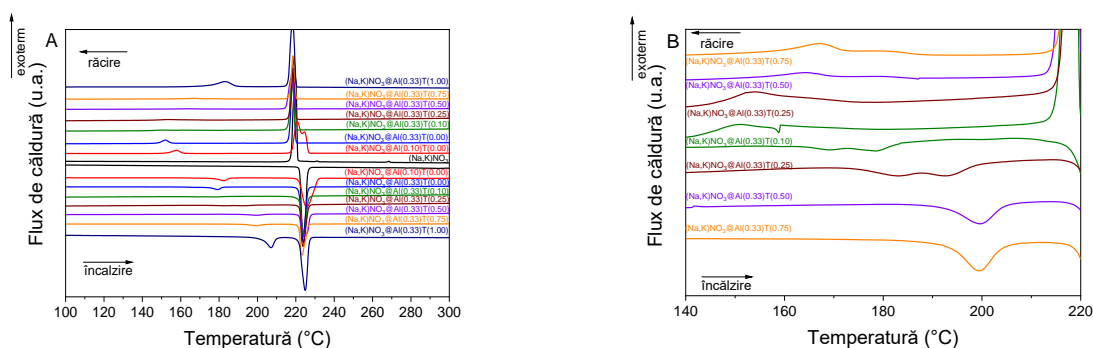


Figure 1: DSC curves of eutectic mixture and composite materials **(A)** and DSC curves in the temperature range, $140\text{--}220\text{ }^{\circ}\text{C}$, for samples with 10-75 % TMB in synthesis **(B)**.

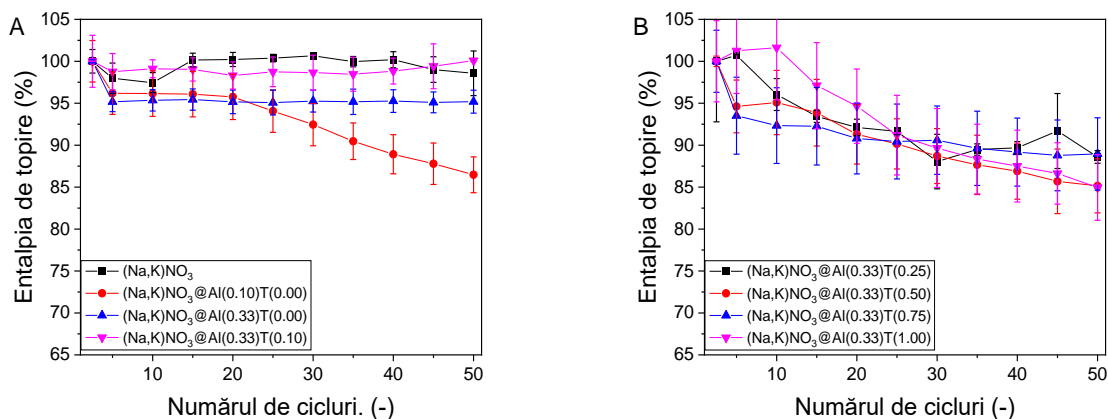


Figure 2: Thermal reliability of materials and eutectic mixture over 50 heating-cooling cycles (A,B)

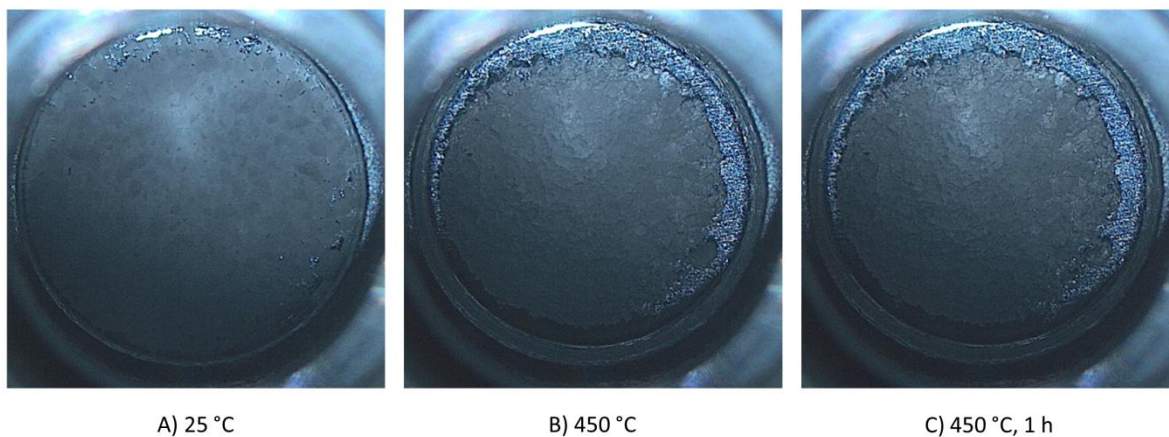


Figure 3: Optical microscopy images of (Na,K)NO₃@Al(0.33)T(1.00) sample at 25 °C (A), 450 °C (C) and at 450 °C after one hour.

II.5. MCF-type mesoporous silica - based phase change materials and NaCl-NaBr-Na₂MoO₄ eutectic mixture

In this chapter, high-temperature phase-change materials for concentrated solar energy (CSP) technology are presented. For this application, a ternary eutectic mixture consisting of 5%(mol) NaCl, 40%(mol) NaBr and 55% (mol) Na₂MoO₄ was used due to its high melting point of 524 °C and high enthalpy value, 215 Jg⁻¹. The optimal matrix for the ternary eutectic has been identified as mesocellular foam silica (MCF) [16]. Thus, for the first time, the effect of active phase loading on the final material was investigated. High temperature MCF-based PCMs with 70%, 80%, 85% and 92.5% (gr) eutectic mixture were obtained by an optimized impregnation method and the thermal properties like shape stability, heat storage capacity, thermal stability and reliability were investigated.

The crystallinity of the eutectic mixture is of great importance for the thermal energy storage. This was evidenced by wide-angle X-ray diffraction analysis (**Figure 4**). The X-ray diffractograms of the composite materials were similar to those of the eutectic mixture, which confirmed that the active heat energy storage agent was found in crystalline form in the composite materials[16].

The thermal properties of silica - eutectic mixture composites were determined by DSC analysis (**Figure 5**) by performing multiple heating-cooling cycles. Melting enthalpy and melting point were determined from the second cycle, with no corrections for adsorbed water.

The ternary mixture exhibits two endothermic events at 454.5 °C and 522.1 °C, respectively (**Figure 5A**). The event that occurs at lower temperature corresponds to the solid-solid phase transition of Na_2MoO_4 in the eutectic. According to the literature, this component has the solid-solid phase transition, from cubic to the orthorhombic structure, in the temperature range of 444 °– 460 °C [17]. This phase transformation was also confirmed in a previous study [16]. After a heating cycle of the eutectic mixture, a total enthalpy of 216.2 Jg^{-1} was determined from which 137.3 Jg^{-1} corresponds to the eutectic melting and the difference corresponds to the solid-solid phase transition (**Table 1**).

Phase change materials exhibit two more endothermic events during heating. These phenomena are most likely due to the solid-solid and solid-liquid phase transitions of the nanoconfined phase in the pores, since the temperatures at which they occur are lower than those of the macroscopic phase. The exothermic event that occur in the cooling cycle of materials indicate that the phase transitions are reversible.

The sample containing 92.5% eutectic mixture behaved similarly to the eutectic mixture (**Figure 5E**). In this case, an increase in the melting temperature was observed, which indicated a deviation from the stoichiometry. The solid-liquid transition of the sample containing 85% eutectic mixture showed two overlapping effects suggesting the presence of the eutectic mixture in the silica mesopores or in the intergranular space (**Figure 5D**). In the case of samples with a higher amount of mesoporous silica, an additional transition at low temperature might be observed, because of the solid-solid transition of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in nanoconfined phase.

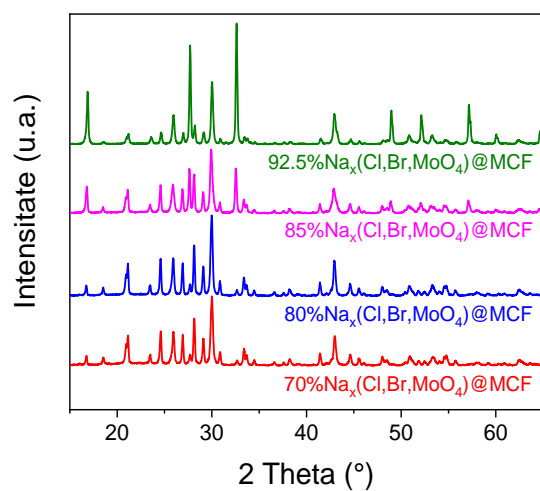
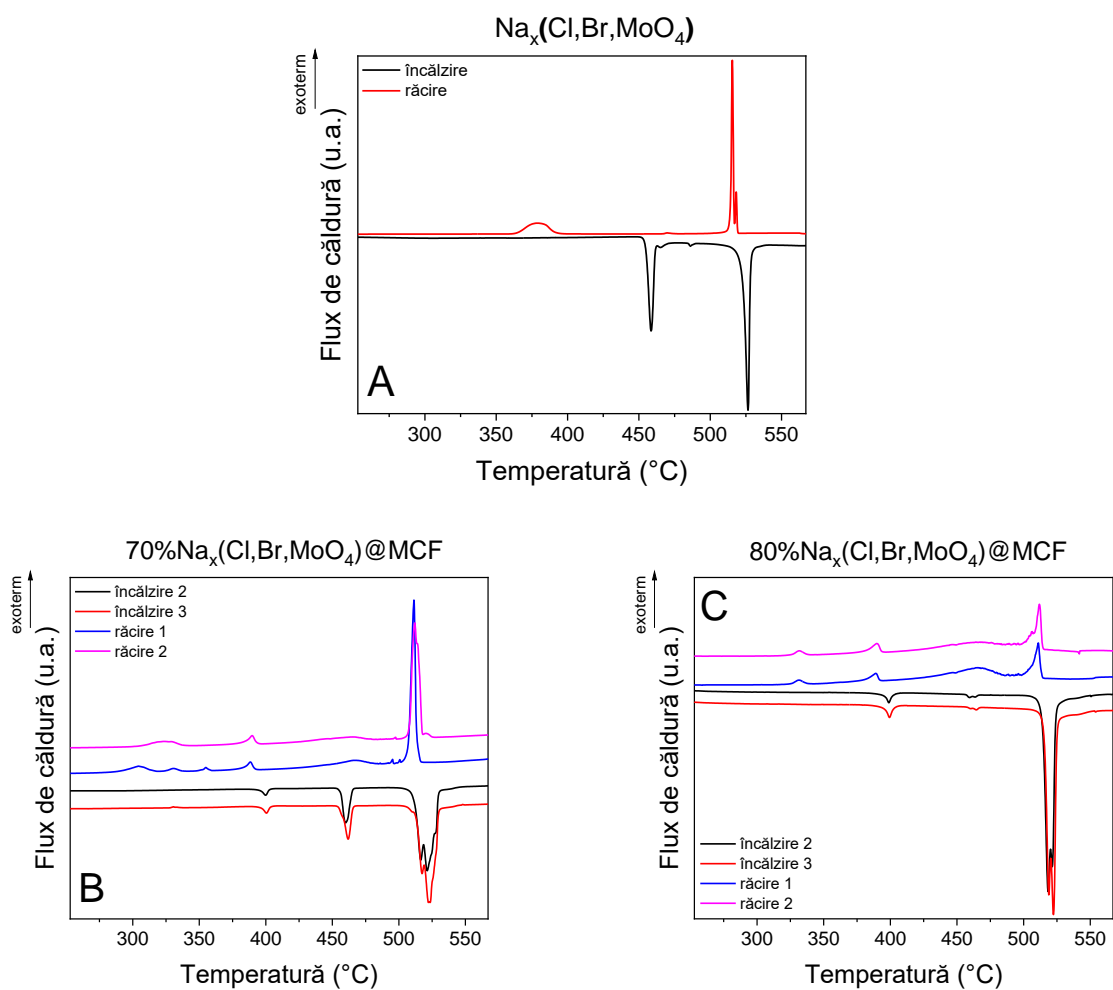


Figure 4: Wide-angle X-ray diffractograms of composite materials



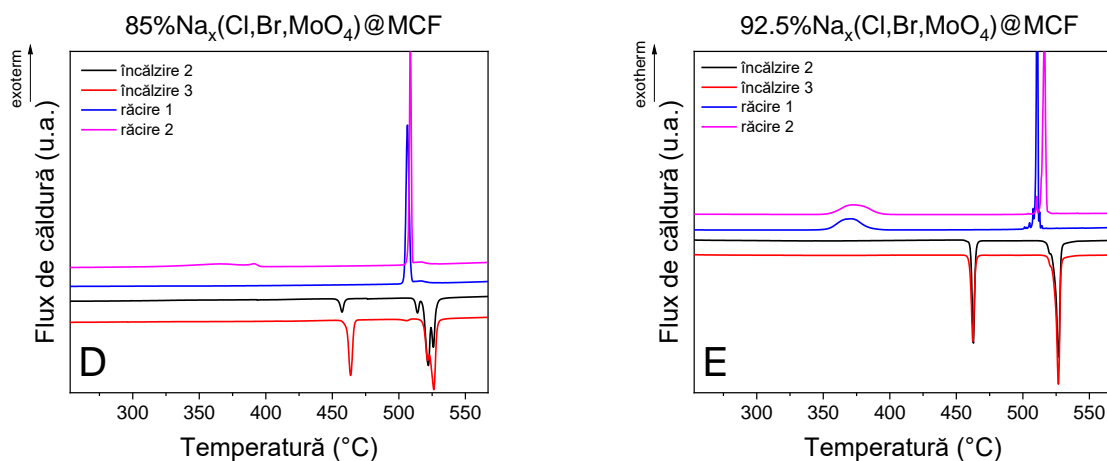


Figure 5: DSC curves of composite materials containing $\text{Na}_x(\text{Cl}, \text{Br}, \text{MoO}_4)$

Table 1: Thermal properties of composite materials: melting temperature (T), melting enthalpy (ΔH), NC-nanoconfinement.

Name of the test	NC	Transition	Solid-to-solid		Solid-liquid		Total ΔH	
	Solid (~390 °C)	to Solid (~460 °C)	transition (~460 °C)	(~460 °C)	transition (~520 °C)	(~520 °C)	(Jg ⁻¹)	(%)
	$T(^{\circ}\text{C})$	$\Delta H(\text{Jg}^{-1})$	$T(^{\circ}\text{C})$	$\Delta H(\text{Jg}^{-1})$	$T(^{\circ}\text{C})$	$\Delta H(\text{Jg}^{-1})$	(Jg ⁻¹)	(%)
$\text{Na}_x(\text{Cl}, \text{Br}, \text{MoO}_4)$	-	-	454.5	78.9	522.1	137.3	216.2	-
70% $\text{Na}_x(\text{Cl}, \text{Br}, \text{MoO}_4)$ @MCF	395.7	3.2	456.2	19.4	514.6	104.2	126.7	58.6
80% $\text{Na}_x(\text{Cl}, \text{Br}, \text{MoO}_4)$ @MCF	395.8	2.8	456.8	1.3	515.0	96.0	100.1	46.3
85% $\text{Na}_x(\text{Cl}, \text{Br}, \text{MoO}_4)$ @MCF	-	-	454.6	14.0	518.0	134.4	148.3	68.6
92,5% $\text{Na}_x(\text{Cl}, \text{Br}, \text{MoO}_4)$ @MCF	-	-	460.6	74.1	523.3	137.3	211.4	97.8

II.6. Phase change materials based on mesoporous silica and bismuth 1

Molten salts and eutectic mixtures of salts can be used as active heat energy storage agents at high temperatures, and their advantage is related to their high heat energy storage capacity, relative to mass. However, in the event of material leaks, they can be corrosive. In this context, this chapter presents the study of high-temperature phase-change materials containing bismuth nanoparticles as an active phase of thermal energy storage. Bismuth was chosen due to its melting point of 271 °C, good heat storage densities (54.07 Jg⁻¹; 543.4 Jcm⁻³) and the non-toxic and non-corrosive nature of this element. Thus, the encapsulation of bismuth nanoparticles in three types of mesoporous matrices was performed. Mesoporous silica-metal composites were first reported by our group for thermal energy storage applications. Metal nanoparticles embedded in mesoporous silica have generally been obtained and studied for catalysis, however, the metal fraction rarely exceeds 10 - 20% wt., because the large difference in density and surface tension makes phase separation difficult to avoid. In this study, mesoporous metal-silica composites containing 50 - 70 % wt. metal were obtained, which were obtained by reducing of a

Bi precursor loaded into mesoporous silica. The thermal energy storage potential, the thermal reliability over several heating-cooling cycles and the influence of metal particle nanoconfinement on melting point and enthalpy were investigated by DSC. The shape stability was evaluated by optical microscopy in situ, while the composition and distribution of the metal were determined by thermogravimetry and SEM-EDX. The mesoporous silica matrix was found to limit the presence of metal oxide phases, with the formation of composite materials with thermal energy storage densities similar to metal particles obtained under similar conditions. The advantages of bismuth – mesoporous silica composites over other high-temperature PCMs, such as molten salt-based materials, are related to the higher thermal conductivity of the former due to the metallic component, the thermal stability due to the silica matrix and the high density, which leads to a higher thermal energy storage capacity relative to volume. It should be noted that for stationary applications such as heat energy storage for concentrated solar energy, the larger heat energy storage capacity relative to volume, which allows for either better energy storage or a smaller storage tank size, thus reducing the cost of production and thermal losses.

The morphology of composite materials and the distribution of bismuth in them was studied by SEM-EDX (**Figure 5**). In SEM images that were taken with the backscattered electron detector (**Figure 5**, top), the bismuth phase is associated with the brighter areas due to its high mass number. The mesoporous silica particles MCF are spherical with polydisperse diameters, up to 4 μm , and silica of the SBA-15 type has the characteristic morphology, the particles being in the form of rods (**Figure 5**, top). In composite materials, bismuth particles form agglomerates in both MCF-Bi composites and SBA-15-Bi composites. The composites obtained by the encapsulation method have smaller bismuth particles on the surface, which also form agglomerates. Elemental mapping by EDX analysis showed a uniform distribution of elements, which is better in the case of sample $\text{SiO}_2\text{@Bi(NP)}$ and $\text{SiO}_2\text{@Bi(NP)-A}$ (**Figure 5**, bottom). In the case of these samples, larger agglomerates can be observed compared to those obtained by the impregnation method. The aging step, in the case of synthesis by the encapsulation method, led to a more uniform distribution of bismuth and a reduction in the amount of bismuth present on the surface of silica. The presence of metallic bismuth on the surface of the silica does not allow the use of nitrogen porosimetry because pores are blocked and unrepresentative data would be obtained.

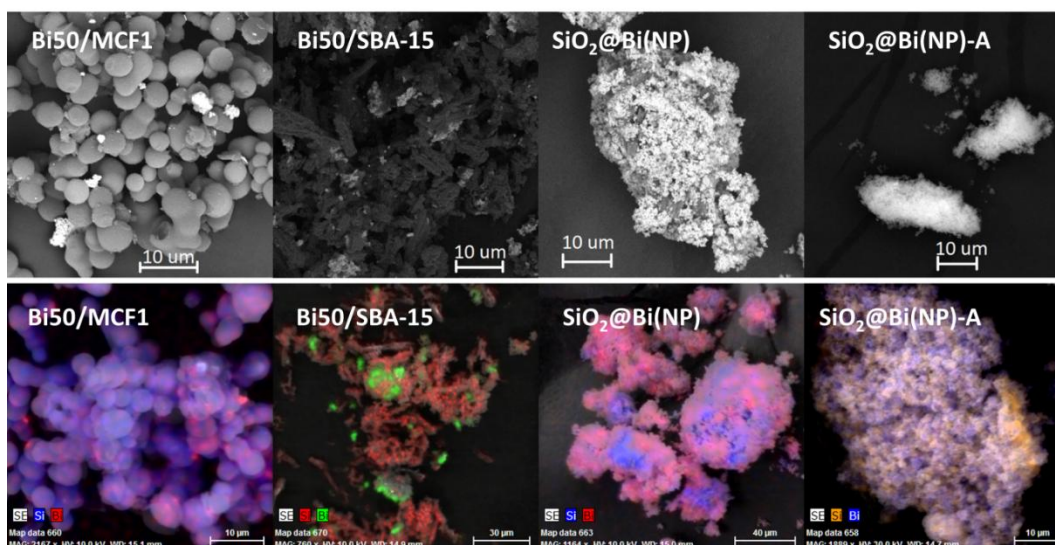


Figure 6: Representative SEM images (top) and EDX mapping (bottom) of Bi50/MCF1, Bi50/SBA-15, SiO₂@Bi(NP) and SiO₂@Bi(NP)-A samples.

From the TEM images of the composite materials with MCF silica matrix, the spongy porous structure with ~30 nm pores can be seen (**Figure 7**). In TEM images obtained in the light field, the dark areas are associated with bismuth impregnated and nanoconfined in the pores (**Figure 7**, E). Nanoconfined bismuth particles were highlighted by STEM-HAADF analysis; they appear as bright spots (**Figure 7**, C, F). The Bi70/MCF1 sample has a higher bismuth content compared to the Bi50/MCF1 sample (**Figure 7D, F**). Small amounts of bismuth nanoparticles can also be observed on the outer surface of the silica matrix.

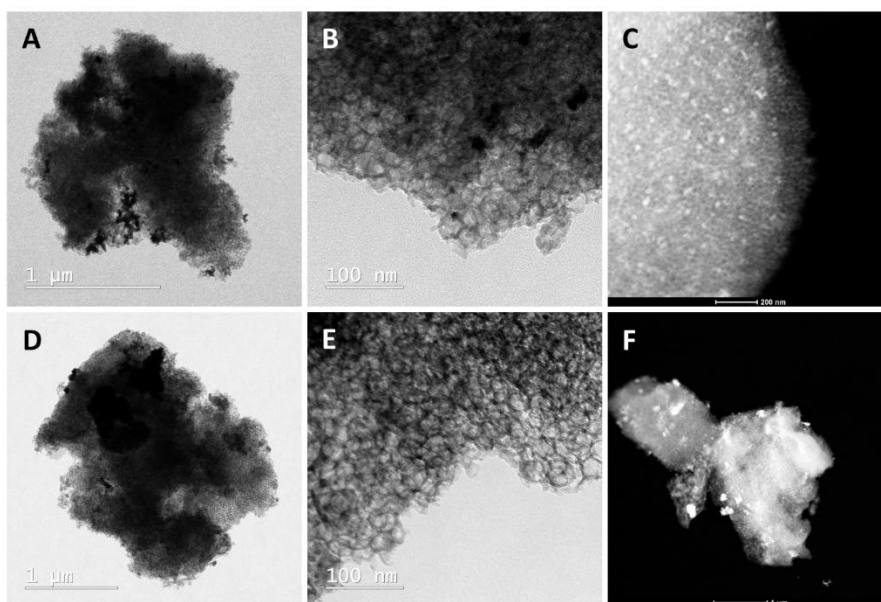


Figure 7: TEM images of samples A, B) Bi50/MCF1 and D, E) Bi70/MCF1, STEM-HAADF analysis of C) Bi50/MCF1 and F) Bi70/MCF1.

The stabilized shape was determined by optical microscopy by recording images below and over the melting point of bismuth (**Figure 8**). The materials were pressed in the form of pellets, but they were also studied in the form of powders. All materials maintain their circular shape after heating to temperatures higher than that of bismuth melting. In the case of the Bi(P) pellet following the melting of the metal, the pellet shows liquid bismuth leakage in the form of droplets (Figure 8 red arrows). The composites obtained by the impregnation method have a stabilized shape even up to a metal addition of up to 70% (wt.) bismuth. In the material, SiO₂@Bi(NP), obtained by the encapsulation method, in the images at 300 °C, spheres of molten metal can be observed, suggesting that this material has a stabilized shape less stable than those obtained by the impregnation method, but more stable than Bi(P).

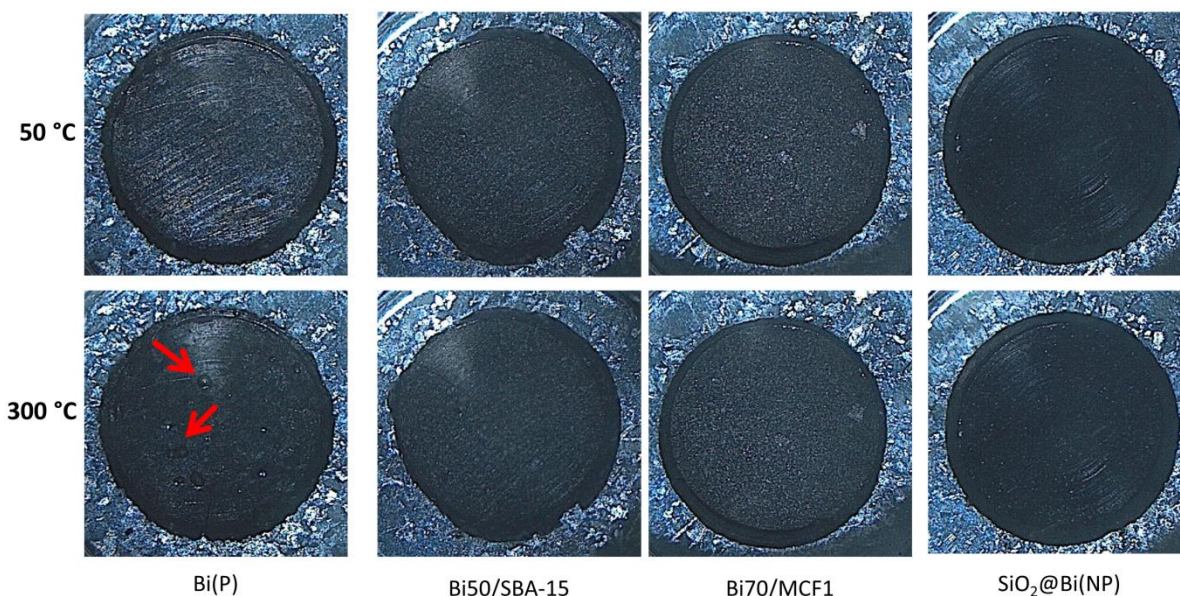


Figure 8: Optical microscopy images at 50 and 300 °C of composite materials in the form of pills. Red arrows indicate the presence of bismuth in liquid form.

II.7. Mesoporous silica - Bismuth phase change materials obtained by nanocasting

In the previous chapter, the study of the influence of the mesoporous silica matrix type and its porosity on the thermal properties of Bi-containing composites obtained by impregnation in aqueous solution followed by reduction was presented. Although the composites obtained by impregnation from the solution led to high enthalpy values, the presence of a significant fraction of nanoconfined metal inside the mesopores of the MCF matrix was not observed. However, the properties of PCMs can be changed by changing the method of obtaining them. In this part of the thesis, the study of the influence of different synthesis methods and the degree of metal loading on the properties of shape-stabilized PCMs is presented. Casting-type syntheses (nanocasting) have been successfully used in other studies to obtain nanoconfined oxide phases in the pores of mesoporous material [18, 19]. The casting method ("nanocasting") consists of loading the mesoporous matrix with a molten hydrated salt in the presence of a hydrophobic solvent [20]. The hydrophilic surface of silica promotes the adsorption of hydrated metal salt, which is

converted into the corresponding oxide by heat treatment. In this study, molten bismuth nitrate pentahydrate (p.t. $\sim 30^\circ\text{C}$) and toluene or n-heptane were used as hydrophobic solvents. The resulting oxides were reduced with an aqueous solution of sodium borohydride. Also, for comparison, a sample was obtained by reducing with hydrogen gas. The synthesis parameters (time, temperature, solvent) were investigated to optimize the thermal storage properties of the resulting composites. They have been characterized in terms of energy storage capacity, stability in air or after being subjected to several thermal cycles, and shape stability. The results show that stabilized shape PCMs containing both intergranular phase and nanoconstrained metal phases could be obtained. As for the stabilized form, the best results were obtained for nanocomposites with 50% wt. Bi. The short reaction time and low temperatures led to the best results in terms of nanoconstrained metal phase.

As in the case of the other composites presented in the previous chapters, the thermal reliability was evaluated by performing 50 heating-cooling cycles, and each 5th cycle was recorded, these being shown in **Figure 9**. All materials obtained by solvent impregnation show a small variation in melting enthalpy following the 50 cycles, which indicates good thermal reliability. The sample obtained by H_2 reduction shows an increase in enthalpy during the first 15 cycles after which it stabilizes. This variation is most likely due to the variation of nanoconfined phases in mesopores that eventually aggregate with each other.

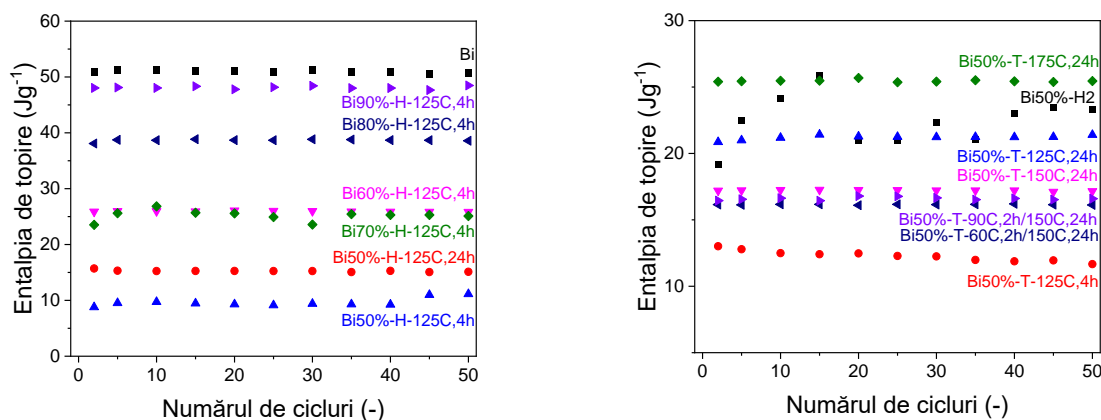


Figure 9: Thermal reliability of materials

II.8. Phase change materials based on mesoporous silica and stearic acid or bismuth

In previous chapters, the results on high-temperature phase-change composites based on silica with disordered pore network structure (MCF) or silica with hexagonal pore structure (SBA-15) were presented. The influence of the pore network geometry of mesoporous silica can have significant implications on the nanoconstraint of the active energy storage phase and the achievement of the stabilized form. FDU-12 is a type of ordered mesoporous silica having a 3D arrangement of mesopores in a cubic spatial group [21]. FDU-12 silica is made up of larger mesopores called "cells," interconnected with smaller pores called "windows" [22]. The size of

the pores can be adjusted by varying the temperature and salt content in the synthesis. To date, mesoporous silica FDU-12 has been investigated by our group only as a matrix for the molten salts $\text{NaNO}_3\text{:KNO}_3$, 1:1 mol [23]. In order to study the influence of the matrix on the properties of the final composite material, two types of phase-change substances were chosen, an organic one, stearic acid, and an inorganic one, bismuth. Stearic acid, $\text{n-C}_{17}\text{H}_{35}\text{COOH}$, was chosen as the representative PCM with good heat energy storage properties (enthalpy of 205–215 Jg^{-1} , melting point of 69°C) [24]. Bismuth was chosen because of its good thermal energy storage properties. This is the first study on the possibility of using mesoporous silica with cubic symmetry pore network FDU-12 as a matrix for stearic acid, an organic PCM, and bismuth as an inorganic PCM. Thus, PCM composite materials with stabilized shape were obtained, for which the thermal and physico-chemical properties were determined. The effects of nanoconfinement of the active phase of thermal energy storage in the mesopores of the matrix and in the intergranular space were quantified using the Gibbs-Thompson equation.

The thermal properties of the active thermal energy storage agents, as well as of the composite materials were determined by DSC, performing heating-cooling cycles. To avoid errors, the second cycle was considered for determining melting point and enthalpy. Stearic acid presents a single endothermic phenomenon, which is attributed to its melting, and composite materials containing this active agent of thermal energy storage present several thermal events. In the case of composite materials, the melting and crystallization of stearic acid can be observed at the same temperatures as those of stearic acid, this phase being the macroscopic phase and is located between the silica particles. On the other hand, the stearic acid found in the silica mesopores has a lower melting temperature than that of the macroscopic phase and at the same time a pronounced hysteresis between crystallization and melting. The melting of the nanoconstrained phase can be observed in the form of two overlapping effects from the second heating cycle, the first effect being attributed to particles from small mesopores and the second to larger particles from larger mesopores. The crystallization of the stearic acid nanoconfined phase occurs at about 25°C. The difference between the melting and solidification points is similar to that of other phase-change materials based on mesoporous silica with hexagonal pores and stearic acid or lauric acid [214, 215].

Both stearic acid and silica composite materials - stearic acid exhibit good thermal reliability evidenced after 50 heating-cooling cycles. All values are found in the standard deviation of the initial melting enthalpy, suggesting that no changes occurred during the experiment. In the case of the silica composite material FDU-12-Bi, the same behavior was observed. Moreover, no significant changes in the melting point and peak shape attributed to the phase transition were observed during the 50 heating-cooling cycles, suggesting that the composite materials obtained exhibit good thermal reliability.

III. Conclusions

The doctoral thesis contains the results obtained in five studies to obtain and optimize the characteristics of phase change materials containing mesoporous silica matrix and eutectic mixture of salts, bismuth, or stearic acid. Thus, in order to obtain composite materials with phase change and stabilized shape, both inorganic and organic substances were used as an active phase of thermal energy storage. The mesoporous silica matrices used to obtain the composite materials showed an ordered structure of the pore network with hexagonal (SBA-15) or cubic (FDU-12) or disordered (MCF) symmetry. Also, MCF and SBA-15 silica was doped with Al with the formation of aluminosilicates to study the influence of surface acidity on the properties of shape stabilized phase change composite materials.

The active phases of inorganic thermal energy storage used were: the eutectic mixture NaNO_3 - KNO_3 , the eutectic mixture of NaCl - NaBr - Na_2MoO_4 and metallic Bi which led to the obtaining of high temperature phase change composite materials. Stearic acid was also used, which is an organic substance with a low temperature phase change.

The Al doping of mesoporous silica matrices led to the obtaining of 7 types of mesoporous materials, which were used to obtain phase-change composite materials with eutectic mixture of NaNO_3 - KNO_3 , with stabilized shape and thermal stability up to 550 °C. Aluminosilicate composites - mixture of alkaline nitrates exhibit two phase transitions, one determined by the nanoconfined phase in the mesopores of the mesoporous matrix that melts at a lower temperature and exhibits hysteresis and one associated with the intergranular phase, which behaves similarly to the macroscopic phase and does not exhibit subcooling. Composite materials containing mesoporous aluminosilicate with a high aluminum content retain their thermal energy storage capacity at a rate of 90% after 50 heating-cooling cycles. The melting temperature of the nanoconfined phase depends on the diameter of the particle, determined using the Gibbs-Thompson equation. It has been observed that the enthalpy of this phase is lower than that of the macroscopic phase due to the surface tension and adsorption of the mixture on the surface of the silica, in the form of an amorphous layer.

Composite materials with SBA-15 mesoporous silica in which no swelling agent was used in synthesis show a decrease in enthalpy due to high surface tension. The addition of the swelling agent leads to a decrease in enthalpy which presents a variation inversely proportional to the amount used.

The storage of thermal energy in phase change composite materials based on aluminosilicates is a promising strategy, the most suitable material being the SBA-15 type containing 10% wt. Al and 10% nanoconfined phase. It exhibited up to 80% of the thermal energy storage capacity of the nitrate mixture.

For the composite materials with phase change based on ternary eutectic mixture NaCl - NaBr - Na_2MoO_4 , mesoporous silica MCF was used, and the mass content of eutectic mixture was 70%, 80%, 85%, and 92.5%.

These materials exhibited thermal stability up to 650 °C and exhibited stabilized form. The ternary eutectic mixture was found nanoconfined in the pores of the mesoporous matrix, but

also in the intergranular space. Sodium molybdate has particles smaller than the size of the pores, being nanoconfined in the pores of MCF silica.

An 80% eutectic mixture content in the composite material resulted in an enthalpy of 148.34 Jg^{-1} for the optimized sample.

Also, the possibility of using Bi as an active phase of thermal energy storage in mesoporous silica matrix was studied. Thus, two types of silica were studied, MCF and SBA-15, in composite materials there being at least 50% wt. metallic Bi. Two methods were used to obtain composite materials, impregnation and encapsulation. The encapsulation method leads to the production of smaller Bi particles.

In composite materials, Bi was found both in the pores and in the intergranular space, and the presence of secondary phases, Bi_2O_3 and precursor of unreacted Bi, was also identified. The impregnation method led to the production of composite materials with a higher Bi content, which led to higher thermal energy storage capacities than in the case of composite materials obtained by the encapsulation method.

Composite materials exhibit a stabilized shape at temperatures higher than the melting temperature of Bi, and good thermal reliability after 50 heating-cooling cycles. The impregnation method leads to obtaining large diameters of Bi particles (200-500 nm), while the encapsulation method leads to obtaining small particles (40-50 nm).

A content of 70% of Bi in the composite material led to the obtaining of composite materials with enthalpy similar to that of Bi particles, which can be explained based on the protection offered by the mesoporous matrix against Bi oxidation.

The optimization of the synthesis parameters and the amount of Bi was performed by using several synthesis methods and by varying the temperature and time parameters. The method of casting (nanocasting) has been investigated to obtain materials loaded with Bi precursor. Metallic Bi was obtained either by reduction in an aqueous medium with sodium borohydride or by reduction by H_2 .

It was observed that lower values of the material production temperature, as well as shorter impregnation times, led to the production of smaller metal particles of about 30 nm for the reduced hydrogen gas sample and for the sample obtained by impregnation in toluene at 125°C , 4 h. The particle size increases with the increase of the impregnation time, over 100 nm for an impregnation time of 24h.

The composite materials thus obtained have a stabilized shape and good thermal reliability after 50 heating-cooling cycles. The best properties were the composite material obtained by impregnation in toluene at 125°C , 4 h, which presented 72% of the theoretical melting enthalpy associated with the Bi content. The molding process (nanocasting) proved to be suitable for obtaining phase change and shape-stabilized materials based on Bi.

The last experimental study consisted of obtaining phase change materials based on mesoporous silica with cubic pore network (FDU-12). A composite material with a stabilized shape based on stearic acid was obtained, by separating the excess of stearic acid, with an

enthalpy of 99 Jg^{-1} . Bi-based composite with a content of 50% wt. Bi showed stabilized form and a melting enthalpy of 21.9 Jg^{-1} . Both organic and inorganic PCM exhibit a decrease in the melting temperature of the active storage phase nanoconfined in the space between the silica particles. The organic PCM additionally exhibits a nanoconfined stearic acid phase in the mesopores of silica, with lower melting temperature and stearic acid particle diameters of 6.5 nm.

The silica composite material FDU-12 - stearic acid showed thermal stability up to 160°C , and the silica type FDU-12-Bi up to 271°C , in the oxidizing atmosphere. FDU-12 silica can be used to obtain materials with thermal energy storage with both organic and inorganic storage active phase.

IV. Perspective

This doctoral thesis is a study in the field of phase change materials. It is therefore proposed to use this study as a starting point for obtaining phase-change materials that can be used at industrial level. For this, it is necessary to obtain a simpler process of obtaining phase change materials, as well as a low production cost. Also, in addition to the use of more environmentally friendly reactants, it is also necessary to optimize the production process to minimize energy consumption.

Phase change materials can also be structured at a macroscopic level, so their manufacture through technologies such as 3D printing can lead to better control of their properties and easier integration into various devices with complex geometries.

Another direction that may result from the study within the doctoral thesis is the use of materials of natural origin, with a high abundance, or even the recovery of some waste to obtain phase change materials.

Another perspective is represented by the study of the possibility of recovering and recycling these materials, after they lose their thermal properties.

V. List of publications

1. R.-A. Mitran, S. Ioniță, **D. Lincu**, D. Berger, C. Matei, *A Review of Composite Phase Change Materials Based on Porous Silica Nanomaterials for Latent Heat Storage Applications*, *Molecules* 26(1) (2021) 241.
2. **D. Lincu**, S. Ioniță, O.C. Mocioiu, D. Berger, C. Matei, R.A. Mitran, *Aluminum doping of mesoporous silica as a promising strategy for increasing the energy storage of shape stabilized phase change materials containing molten NaNO_3 : KNO_3 eutectic mixture*, *Journal of Energy Storage* 49 (2022) 104188.
3. **D. Lincu**, S. Ioniță, B. Trică, D.C. Culita, C. Matei, D. Berger, R.-A. Mitran, *Bismuth-mesoporous silica-based phase change materials for thermal energy storage*, *Applied Materials Today* 29 (2022) 101663.
4. R.-A. Mitran, **D. Lincu**, D. Berger, C. Matei, *FDU-12 cubic mesoporous silica as matrix for phase change materials using bismuth or stearic acid*, *Journal of Thermal Analysis and Calorimetry* (2022).

5. S. Ionita, **D. Lincu**, O.A. MOCIOIU, R.-A. MITRAN, C. MATEI, D. BERGER, Optimization of shape – stabilized phase change materials containing *NaCl – NaBr –Na₂MoO₄ and mesoporous silica*, U.P.B. Sci. Bull. 85(4) (2023).
6. **D. Lincu**, S. Ioniță, M. Deaconu, F. Papa, B. Trică, C. Matei, D. Berger, R.-A. Mitran, *Optimizing nanocasting techniques for stable bismuth-mesoporous silica composites in thermal energy storage application*, *Sustainable Materials and Technologies* 42 (2024) e01157.

VI. List of conference participation

1. **Daniel Lincu**, Simona Ionita, Mihaela Deaconu, Ana-Maria Brezoiu, Raul-Augustin Mitran, Cristian Matei, Daniela Berger. Phase change materials based on porous silica. ECerS Conference for Young Scientists in Ceramics - 14th Edition, Novi Sad, Serbia. **2021**.
2. **Daniel Lincu**, Raul-Augustin Mitran, Simona Ionita, Mihaela Deaconu, Cristian Matei, Daniela Berger. Mesoporous silica-based phase change materials for thermal energy storage. PRIOCHEM "Priorities of Chemistry for a Sustainable Development", Bucharest, Romania. **2021**.
3. **Daniel Lincu**, Raul-Augustin Mitran, Simona Ionita, Mihaela Deaconu, Florica Papa, Cristian Matei, Daniela Berger. Mesoporous silica–metal composites for thermal energy storage. 20th International Balkan Workshop on Applied Physics and Materials Science, Universitatea Ovidius, Constanta, **2022**.

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