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Efficiency Evaluation of Double Hydrate Salt Mixtures as Low Temperature Thermo Chemical Heat Storage Materials

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Abstract: Recently, thermo chemical heat storage (TES) has gained important attentions, since it offers a high storage capacity with low temperature ensured by thermochemical heat storage materials (TcSM) [1]. The hydrates salt can react, store and release heat during a Charge/Discharge cycle based on hydration/dehydration reactions over different temperature range. Due to their good energy storage density, hydrates salts have been widely developed on different researchs to be used in solar energy storage[2].Blödite, Konyaite and Löweite are double salt with a good behavior as TcSM thanks to their significant reaction enthalpy. However, theirapplications still limited by the problems of reversibility, complexity and the high charging temperature which is supposed to be provided by solar domestic collectors applications. Moreover, it is complicated to predict the purity and the structural stability of these salts during the dehydration and hydration reaction, which affects the storage density and the efficiency of TcSM. In this work, Konyaite-Blödite (MDHS1) and Löweite-Blödite (MDHS2) were synthesized and characterized. Quantitative XRD analysis of mixtures was performed adopting the Reference Ratio Intensity (RIR) method [3]. In addition, an evaluation of (MDHS) is developed taking into account many parameters such as charge temperature, storage density, reversibility and storage performance in order to identify the most promising candidate for domesticheat storage systems. FTIR results confirm good reversibility of hygroscopic behavior at temperature up to 200 °C. Thesemixtures show agood stability behavior, but only MDHS2 offers a good net storage density of 370.8 $KWh.m^{-3}$ and an excellent efficiency of 38%.

INTRODUCTION

The storage of thermal energy drives a change towards the use of renewable energy resources and energy efficiency. It is regarded as promising technology with a variety of applications, including the use of solar thermal energy and waste heat. Effective low-temperature heat storage is important for applications with a time shift between energy supply and energy demand, such as the use of solar thermal energy or combined heat and power(CHP) plants [2].During the thermochemical energy storage (TcES), the energy is stored according to a physico-chemical process that consumes energy during the charging phase (dehydration) and releases it during the discharge (hydration) (Fig.1). In contrast to sensible and latent type, thermochemical storage materials (TcSM) provide ten times higher storage capacity in mass or volume.

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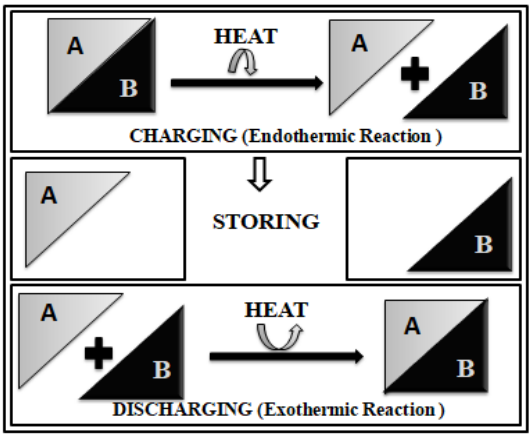

Fig.1: Process of Thermochemical storage

In addition, TcSM such as hydrates salts can store heat for an indefinite time without insulation and are considered as a technology that represents a key to long-term average heat transport and storage, which seems more useful in terms of economy. In this context, the use of the reversible reactions energy to achieve chemical heat storage promises good efficient for short and long term storage with high energy density and relatively low heat losses.

Salt hydrates have growing an attractive interest as potential and long-lasting heat storage materials. These TcSM are loaded by dehydration of the hydrates. Then, the heat is accumulated during the storage phase and the energy is recovered by the hydration reaction. Nevertheless, the use of these salts is limited due to several problems as the reversibility, storage density and the charging temperature which must be suitable with the conditions of the aimed application.Double salts with their high reaction enthalpy are considered as good candidates for thermal energy storage.

The ternary system of Na_2SO_4-$MgSO_4$-H_2O (Fig.2)shows the possible phases and their which can be formed. This system has been investigated by numerous studies [4, 5], but the interactions of these phases in case of the coexistence of such phases or the presence of others hydrates as metastable phasesstill misunderstood [6].

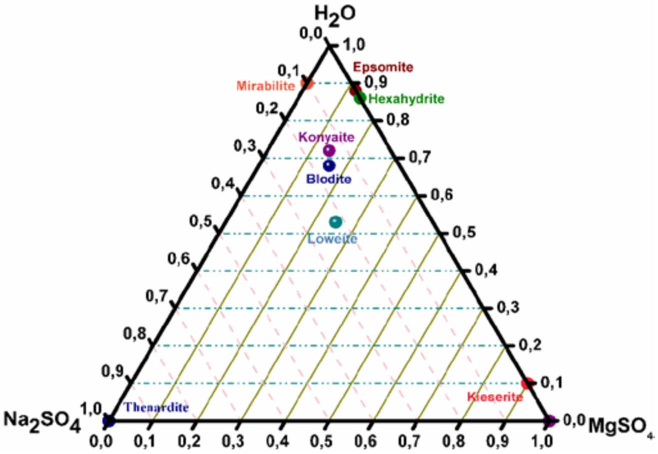

Fig.2: Ternary diagram of Na_2SO_4-H_2O-$MgSO_4$ system

The blöditeNa$_2$Mg $(SO_4)_2.4H_2O$ areactive phase in the presence of parent solution, it is able to coexist with several phases in stable equilibrium like $Na_2SO_4.10H_2O$, $MgSO_4.7H_2O$ and other sodium magnesium sulfate. The crystal structures of blödite were already structurally studied [7]. The thermal behavior of blödite shows a good thermal stability up to 107°C [8].Unlike the Konyaite Na_2Mg $(SO_4)_2.5H_2O$ which revealed spontaneous decomposition by losing one molecule of water to form blödite as described in the following reactions [1, 9]:

$$Na_2Mg(SO_4)_2.5H_2O \rightarrow Na_2Mg(SO_4)_2.4H_2O + H_2O \qquad (1)$$

Blödite salt could be consideredas derived from Konyaite which is as a metastable phase[10].At lower temperature, blödite show a good stability at severe conditions [11] till reaching of 60°C to 80°C to form the Löweite $Na_{12}Mg_7$ $(SO_4)_{13}.15H_2O$ which have a high charging temperature[2], and vanthoffite Na_6Mg $(SO_4)_4$. The coexistence of these phases can take place in an invariant conditions of temperature limits which present the purity problem of these materials since storage or synthesis conditions[12].Even for pure phases, a mixture can be formed spontaneously within a thermochemical storage reactor during the charging phase (hydration reaction) underwater vapor pressure gradient or Temperature. This issue must be taken into account by studying the mixtures performance before using these double salts as TcSM.Only few references about the thermal behavior of mixture of these hydrates for thermochemical storage could be found. The aim of this work is to valorize these compounds as low temperature TcSMfor domestic applications.

In this study, the structural and thermal investigation of the two synthesized mixtures Konyaite-blödite and Löweite-Blöditewereevaluated taking into account the charging temperature, the storage density and the storage efficiency of each MDHS, in order to identify the most promising mixture as TcSM.

MATERIALS AND METHODS

Synthesis

According to the method described by Doesburg[13], Konyaite phase was synthesized from evaporation of an aqueous solution of $MgSO_4$ and Na_2SO_4 with a molar ratio of 1: 1 in a Petri dish at 35 ° C after 20 days the Konyaite crystal was obtained as a first step and kept in ambient air for 30 weeks in order dehydrate it partially to blödite obtaining the mixture MDHS1. A prepared solution of 7:6 molar ratios of $MgSO_4$ and Na_2SO_4 respectively was evaporated at 65 ° C. The obtained compound labeled MDHS2.

X-ray Powder diffraction (XRD)

X-ray powder diffraction data of the synthesized material was produced using Bruker D8 Advance X-ray diffractometer with a LYNXEYE detector using copper radiation (λ=1.5418 Å) was used and θ-2θ geometry. Data were collected at room temperature with a step size of 0.1° and counting time of 8s per step. The experimental patterns were identified and indexed using X'Pert Highscore software and COD.2018 database. Quantitative Analysis, using RIR (reference intensity ratio) was undertaken on MDHS1 and MDHS2.

Infrared Spectroscopy

The FT-IR spectra were recorded by Fourier transform infrared spectroscopy (FT-IR, Tensor27, and Bruker, Germany) in the range of 400-4000 cm^{-1} at ambient temperature. Samples were mixed with KBr and pressed to be a pellet before analysis. Then the spectra are processed using the Win-IR software. For the hygroscopic behavior reversibility method, MDHS1 and MDHS2 materials were heated at 200 °C with a rate of 5 °C / min.Then, the rehydration test of the dehydrated samples was performed at 60°Cunder water vapor for 90min.

Raman Spectroscopy

The Raman spectra were recorded in the range from 400 to 3400 cm^{-1} with a Thermo Scientific DXR2 spectrometer. The samples were placed under the achromatic objective with a microscope resolution of x50. The laser power on the sample was kept bellow 5.54 mW to avoid any heating or dehydration effects of the powder sample.

Thermal Analysis

Thermal analyses were carried out in STA 449 F3 Jupiter (Netzsch, Germany) with SiC-furnace (maximal temperature 1550ºC) using alumina crucibles. For subsequent data analysis the Netzsch software Proteus 6 was utilized. 20 mg of sample were placed in an alumina crucible with a volume of 100 µL.Thermal analyses were carried out without holding times in temperature range between room temperature and 400ºC with a heating rate of 10ºC/min. All experiments were performed at atmospheric pressure in air with a gas flow of 60 mL/min. STA provides information on reaction-enthalpy, mass-change, reaction-time, onset-temperature and reaction-temperature.

RESULTS AND DISCUSSION

Structural Studies

Fig. 3 shows the X-ray diffraction patterns of the mixtures. The identification and indexation of the prepared salts were carried out using the X'Pert Highscore software and the COD.2018 database. The corresponding profile matching was in good agreement with the isotypic structure data and the cell parameters of the double salts which are illustrated in the Table.1. These results were obtained by the matching profile using the quantitative analysis (Reference intensity ratio) RIR method [3, 14, 15].

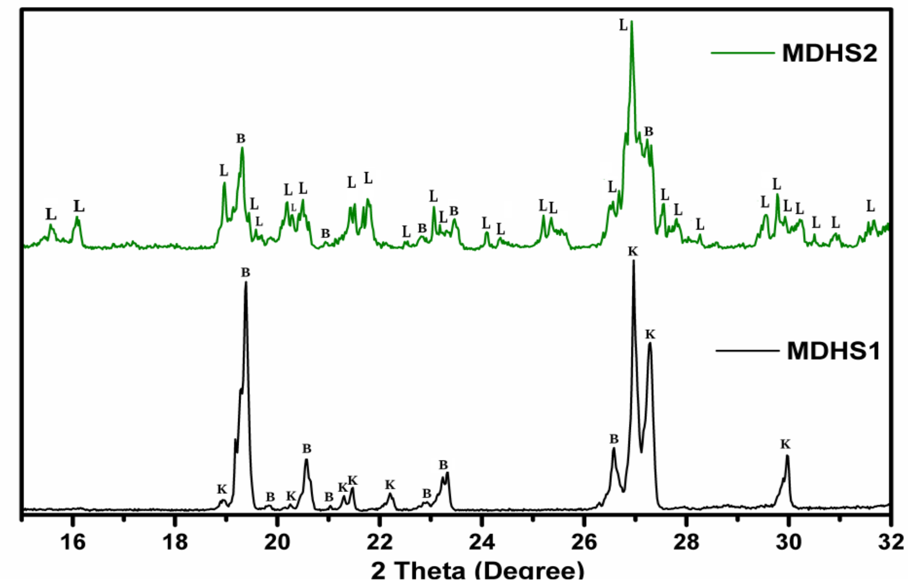

Fig.3: X-ray Powder Diffraction Patterns of MDHS1 and MDHS2

Table 1: Space Group and Cell Parameters of Double Hydrate Salt, Blödite, Konyaite and Löweite

DOUBLE SALT	**Blödite**	**Konyaite**	**Löweite**
Crystal System, SG, Z	Monoclinic, $P2_{1/a}$, Z= 2	Monoclinic, $P2_{1/c}$, Z= 4	Rhombohedral, R-3, Z=3
a (Å)	11.081	5.7860	18.8660
b (Å)	8.258	24.0100	18.8660
c (Å)	5.538	8.0610	13.4340
β (°)	100.20	91.410	90.000
V (Å^3)	498.7	1115.69	4140,91
D_{cal} (g.cm^{-3})	2.22	2.11	2.36

After the estimation of the absence of the formation of the amorphous species, blödite hydrates was chosen as an internal reference, the obtained results reveal that the mixture MDHS1 consists (% wt: 52.0% Konyaite and 47.9% blödite) and (% wt: 70.3% Löweite and 29.6% blödite).

These results prove the presence of blödite in both mixtures, which confirm the good stability of this hydrate, and its capability of the simultaneous presence with other types of hydrates [12].Moreover, the conditions of synthesis and storage could affect the form of these hydrates. Konyaite dehydrates partially after the exposure in ambient conditions for 30 weeks after the synthesis time and coexists with blödite. These results prove the strong relationship that exists between the two hydrates, but it may also be due to the fact that the two phases precipitate almost under the same conditions while respecting the stoichiometric formula[12, 16]. The limiting experimental conditions of synthesis of MDHS2 imposed by the forbidden zone of Löweite and blödite hydrates play an important impact on the purity of the final compound as well as its physical and thermal properties[12]. In addition, each hydrate is characterized by this zone which defines its required experimental conditions to obtain a double hydrates salt with high degree of purity, the thing that is strictly difficult to control. Therefore, it is essential to study the impact of mixing on the thermal behavior of double hydrates salt for thermochemical storage.

The most important bonds of double sulfate salts are referred to the sulfate ion (SO_4^{2-}), there are four normal Raman and FTIR active modes of vibration: ν_1 symmetric stretching, ν_2 symmetric bending, ν_3 asymmetric stretching, $\nu_4$asymmetric bending[17]. The Raman stretching modes usually appear at the 900-1200 cm^{-1} and the bending modes appear at 400-650 cm^{-1}region. Moreover, the FTIR spectra (Fig.4) of MDHS1 and MDHS2 have typically bonds in shape and relatives intensities, can be attributed to different regions : <400cm^{-1}, 500-700 cm^{-1}, 700-850 cm^{-1}, 1000-1250 cm^{-1}, 1550-1700 cm^{-1}, 2050-2390 cm^{-1}, 2800-3600 cm^{-1}, and >3600 cm^{-1}. The similarity of the mixtures spectra belongs to the identical chemical compositions. However, each difference in position, intensity and shape of bonds includes interested structural informations, water clusters and type of hydrogen bonding in the framework. MDHS2 spectrum show a peak above 439cm^{-1}belong to ν_2(S-O), while a medium bonds at 615, and 613cm^{-1}can be attributed to ν_4(S-O) symmetric bend for MDHS1 and MDHS2 respectively. The both mixtures, two similar small bonds at 719 and 829cm^{-1}referred to the wagging and rocking in plan stretch of O-H.

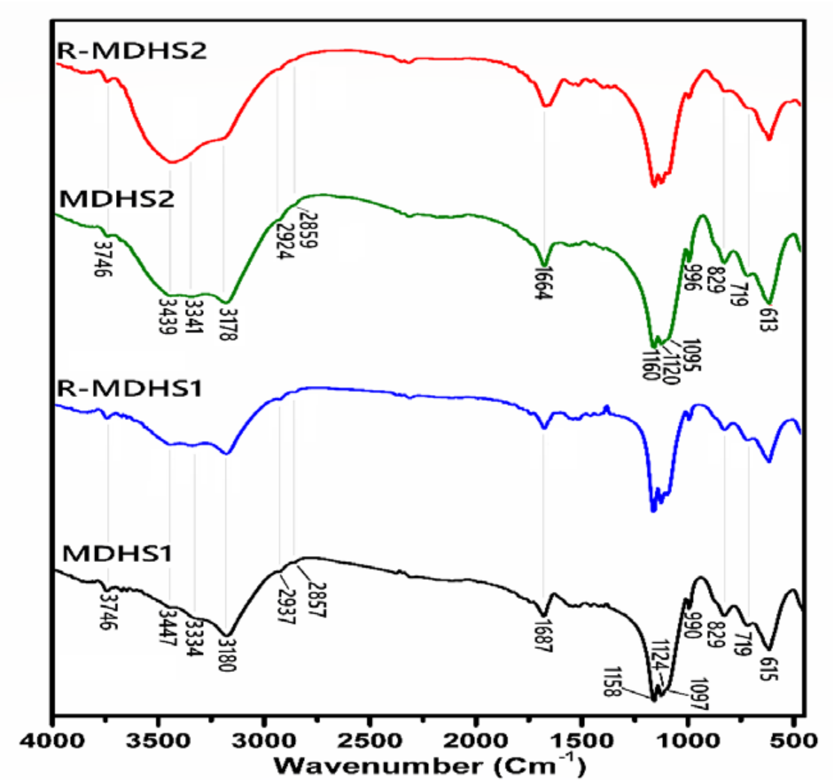

Fig.4: FTIR spectra of MDHS1 and MDHS2 and Rehydrated mixtUres

The absorption features at 990, 996cm^{-1}(which appear as a shoulder on the strongest bonds) can be explained by ν$_1$ symmetric of sulfate ions of Konyaite-Blödite and Loweite-Blödite mixture respectively. Three more intense bonds at 1097, 1124, 1158 cm^{-1}for MDHS1 and 1095, 1120, 1160 cm^{-1}for MDHS2 belong to ν$_3$(S-O) asymmetric stretching. The waters crystallization provides vibration at 1687 MDHS1and 1664cm^{-1}for MDHS2 [18]. Moreover, weak bonds between 2050-2390 cm^{-1}resulted of the water clusters interaction. These similarities could be affected to the presence of blödite hydrate in both phases. However, a large characteristic in plan bend and in plan stretch frequencies of O-H bonds at 3180, 3334, 3447 cm^{-1}and 3178, 3341, 3439 cm^{-1}for MDHS1 and MDSHS2 respectively, while smaller intensities bonds at 3746 cm^{-1}could be attributed to O-H stretch. R-MDHS1 and R-MDHS2 show a good reversibility respecting to the characteristic O-H bonds. Although both mixtures showed a good reversibility of their hygroscopic behavior, which is very important and may justify the reversibility of the reactions involved during the charge / discharge phase, but the FTIR analysis remains limited and insufficient to show their structural reversibility, which is very important for the TcSM cycling parameter which is not taken into account in our evaluation.

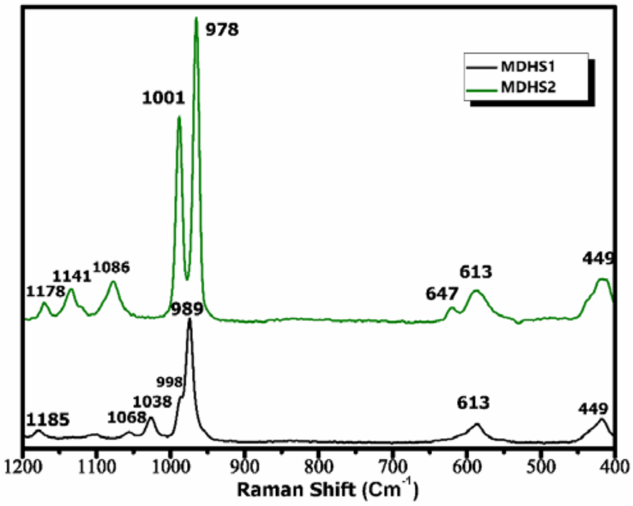

Fig.5: Raman Spectra of Crystals of MDHS1 and MDHS2

Raman spectrum of mixtures (Fig.5) show large different between the two compounds which can be explained by the interaction of the similar sulfate oscillators and the diverse polyhedra arrangement in the pure doubles hydrates framework. In addition, the coexistence of mixtures hydrates produce a typical interaction, the unlike coordination environment of the metal (II) ions, and the differences in the unit cell volumes. The characteristic bonds at 989, 998 Cm^{-1} for MDHS1 and 978, 1001 $Cm^{-1}$for MDHS2 belong to ν_1 symmetric stretching of sulfate ions. The results obtained in this study were closely different to other studies[16] carried out by others authors that confirm the impact of mixture factor on Raman frequencies.

Thermal Investigations

TG-DSC measurements of the dehydration of MDHS1 and MDHS2 (Fig.6) have been reported. The decomposition of MDHS1 shows a total mass loss of m_{exp} = 21.04% while the empirical formula of pure Konyaite hydrate shows a mass loss of m_{cal} = 25.53%. This can be explained by the partial decomposition of Konyaite to form the MDHS1 mixture. The TG of pure Löweite involves m_{exp} = 14.06% [19] compared to m_{exp} = 18.02% for the MDHS2, this difference is especially normal considering the presence of blödite as a second hydrate in the mixture.

The dehydration process of $Na_2Mg(SO_4)_2{\cdot}5H_2O$ produce several hydrates depending usually to rate of decomposition and relative humidity, it can be described as Konyaite→ Blödite→ Löweite →Thenardite + Hexahydrate[9]. In our case, blödite produced by the decomposition of Konyaite respecting to the reaction (1) occurs two major endothermic stepwise in the temperature interval of 128–230ºC describing by reaction (2) and (3) successively, thus forming an anhydrous salt. The first step indicates a mass loss of m_1= 9.7% and a strong endothermic effect centered at 156°C with ΔH_1=332.2J/g, while the second one at 230°C resumes a mass loss of m_2=11.4%, and ΔH_2=272.7J/g). The total MDHS1 enthalpy of dehydration has value of 604.9 J/g.

$$15Na_2Mg(SO_4)_2.4H_2O \rightarrow 2Na_{12}Mg_7(SO_4)_{13}.15H_2O + Na_6Mg(SO_4)_4 + 30H_2O \quad (2)$$

$$2Na_{12}Mg_7(SO_4)_{13}.15H_2O + Na_6Mg(SO_4)_4 \rightarrow 6Na_2Mg_2(SO_4)_3 + 3Na_6Mg(SO_4)_4 + 30H_2O(3)$$

Pure Blödite dehydrates to form Löweite which is subsequently decomposed at lower temperatures than pure synthesized Löweite, the difference between the two hydrates can be well understood taking into account that the blödite expands during its dehydration, forming Löweite phase which is often characterized by weak hydrogen bonds, which promotes a rapid increase in the thermal movements of the molecules of water in the structures. Nevertheless, the coexistence of blödite with Löweite has no effect on its thermal behavior, which shows the good stability of these hydrates as TCMs.

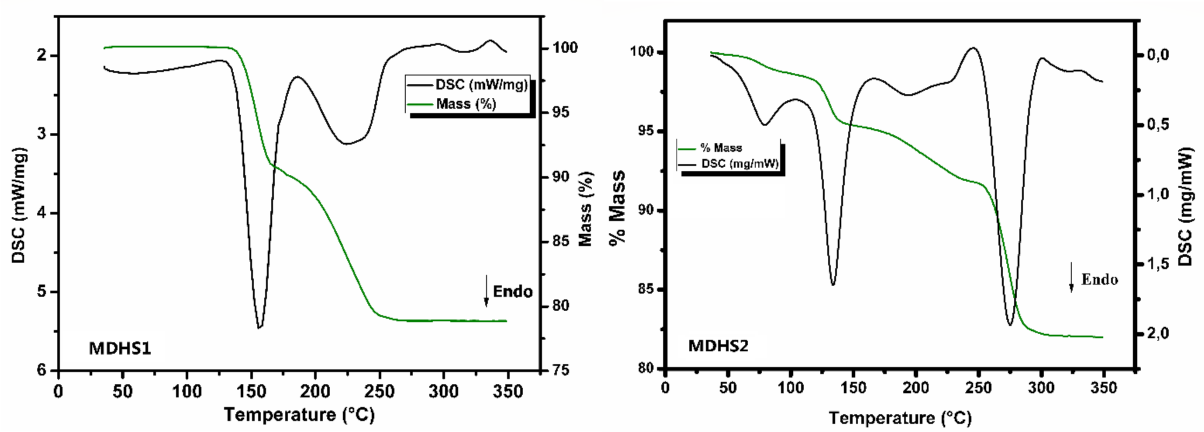

Fig.6: TG- DSC curves of MDHS1 and MDHS2

TG curves of MDHS2 show a mass loss in three major stages, the fourth is perhaps due to exposure of the sample to moist air that evaporates around 50°C-100°C. $MDHS_2$ Blödite decomposes in two stages at 110°C and 168 °C successively resulting mass loss of m_1 = 3.02% and m_2 = 3.66% respecting to the same reaction reported for MDHS1 against the Löweite decomposes at higher temperatures of 245°C with m_3 = 9.83%. These results are slightly similar to those reported Löweite thermal behavior[19]. The dehydration of $MDHS_2$ consists of a total endothermic effect which results global reaction enthalpy of ΔH =583.5J / g.

Storage Efficiency Evaluation of MDHS1 and MDHS2 as TcSM

In order to evaluate these mixtures, theoretical calculations based on experimental results as well as thermal approaches used to evaluate salts for thermochemical storage have been reported and the same applied conditions have been estimated [20]. The storage density was calculated (Table.2) taking into account the composition of the mixtures. The charging temperature of the mixtures remains acceptable above 100 °C which can be easily reached by a solar collector. A charging temperature of 60 ° C is required for a domestic hot water system (DWH), and a good reversibility during the hydration of the mixtures at this temperature has been recorded, which shows their ability to discharge at this temperature.

Table 2: The Calculated Parameters for MDHS1 and MDHS2

Mixture	**MDHS1**	**MDHS2**
ΔH_r (KJ. mol^{-1})	207.3	863.8
$\Delta H_{r,m}$ (KWh. Kg^{-1})	0.168	0.161
$\Delta H_{r,v}$ (KWh. m^{-3})	365.73	370.85
ΔH_{net} (KJ. mol^{-1})	28.93	328.63
η (%)	0.14	0.38

An important dehydration enthalpy was recorded by MDHS2 compared to MDHS1 (207.37KJ/mol) which presents results not sufficient for such application, $MgSO_4.7H_2O$ (335.7KJ/mol)[21], and $SrBr_2.6H_2O$ (337.0KJ/mol)[22]which are among the salts the most promising in thermochemical storage. In addition, MDHS2 offers an increase in net storage volume density of +54.23% over $SrBr_2.6H_2O$ that reveals a density value of 128 Kwh.m^{-3}[20]. These results show that the use of MDHS2 as TcSM offers a significant reduction in the storage volume that will be beneficial for a domestic application. An excellent efficiency of about 38% has been achieved for MDHS2, which makes the latter a good candidate one of the most promising salt in thermochemical storage.

CONCLUSION

In this paper, structural study of the MDHS1 and MDHS2 mixtures was reported using XRD which showed good matching results, FTIR and Raman spectrum spectroscopy confirm the good structural stability even in the case of the coexistence of these hydrates. Further,a good reversibility of mixtures hygroscopic behavior at 60 °C was carried out which shows their ability to be easily discharged at this temperature under reasonable water vapour pression. TG-DSC results show good thermal stability of these materials as well as charging temperature at around 100 ° C which corresponds to the intended application. A gain of + 54.23% was recorded by MDHS2 in terms of net storage volume density compared to the most hydrates $SrBr_2$ used in conventional thermochemical systems and an excellent efficiency of 38% was achieved which makes of MDHS2 one of thebest low temperature candidate TcSM for domestic applications.

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