



INVESTIGATION OF THE STRUCTURAL AND THERMAL PROPERTIES OF MAGNESIUM TUTTON SALT NHMgSOH : AIMING AT AN APPLICATION IN THERMOCHEMICAL ENERGY STORAGE.

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ABSTRACT

The development of heat storage and thermal energy conversion technologies aims to improve the inefficiency of renewable energy systems. In this work, crystalline magnesium-ammonium Tutton salt (NHMgSOH) was successfully synthesized after 25 days by the slow solvent evaporation method. The crystal structure was confirmed by powder X-ray diffraction (PXRD) and refined by the Rietveld method, allowing the precise identification of the structural parameters and the crystal system. Thermal analysis by differential scanning calorimetry (DSC) revealed that NHMgSOH presents a dehydration temperature of ≈ 379 °C. The calculated dehydration enthalpy was 319.41 kJ/mol, resulting in an energy storage density of approximately 1.50 GJ/m³, higher than the minimum recommended criterion (≥ 1.30 GJ/m³). The results demonstrate that NHMgSOH is a promising candidate for detailed investigation, aimed at applications in thermochemical energy storage systems, considering its physicochemical characteristics, high availability of raw material, excellent thermal stability, energy density value and low synthesis cost of hexahydrate salt.

Keywords: Heat storage, Thermal energy, Tutton salt, PXRD, Energy storage, Thermochemical energy storage.

INTRODUCTION

Decarbonizing the global energy supply system is a key priority of the 21st century. The unbridled use of fossil fuels, in addition to intensifying climate change, has stimulated the search for sustainable alternatives based on renewable energy sources, aiming for an energy infrastructure that reduces environmental damage and achieves a balance between energy supply and demand [1]. In this context, solar energy emerges as one of the main alternatives, especially when integrated with thermal storage systems. In this case, it is necessary to develop efficient heat storage systems during periods of high solar availability, capable of meeting high demand through a clean energy transition [2].

Among the technologies under development, sulfated crystals have stood out due to their abundance, economic viability and plurality of applications in diverse research fields [3,4]. Crystals of the Tutton salt family are a class of hexahydrate hydrates, which have gained great prominence in the investigation of thermochemical storage systems [5]. Crystals of the Tutton salt family represent a class of hexahydrate hydrates that have gained significant prominence in the investigation of thermochemical storage systems [5]. These compounds possess a monoclinic structure, with space group P21/a, and have the chemical formula $M_2M'(SO_4)_2(H_2O)_6$, where M is the monovalent cation (Cs^+ , K^+ , NH_4^+ , Rb^+ , Tl^+) and M' is the bivalent cation (Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , V^{2+} , Zn^{2+}) [6].

Hydrated double sulfates have been the focus of many studies, because they have optimal characteristics for a wide range of technological applications. In this context, recent studies seek to select potential thermochemical materials (TCMs) that present high energy densities (≥ 1.3 GJ/m³), sorption temperature (≥ 283 K) and H₂O desorption (≤ 393 K), and high stability rates of multicycle sorption/desorption (≥ 10 cycles) [5]. In a comparative study of 24 double salt hydrates, Kooijman (2022) demonstrated that Tutton-type structure salts presented promising thermal properties for potential thermochemical use [7]. Therefore, the present study aims to investigate the structural and thermal properties of the salt $(NH_4)_2Mg(SO_4)_2(H_2O)_6$, to investigate a possible use as a TCM.

MATERIALS AND METHODS

Crystal synthesis

The Tutton salt $(NH_4)_2Mg(SO_4)_2(H_2O)_6$, herein named NHMgSOH, was crystallized by the slow solvent evaporation method from a saturated aqueous solution. From a molar ratio (1:1) of the reactants $(NH_4)_2SO_4$ and $MgSO_4(H_2O)_7$, they were dissolved in 50 mL of deionized water under constant magnetic stirring at 360 RPM for 5 hours. The final solution was filtered and stored in an oven (308 K) for nucleation. After 25 days, translucent single crystals with whitish coloration were successfully obtained.

Characterization techniques

The crystal structure of NHMgSOH was solved from X-ray diffraction (PXRD) using a PANalytical Empyrean powder diffractometer with $CuK\alpha$ radiation ($\lambda = 1.5418$ Å) and operating at 40 kV/40 mA. The diffractogram was collected in the 2θ angular range between 5 and 50°, with an angular step of 0.02° and an acquisition time of 2 s. The initial parameters were accessed from file 43309, found in the Inorganic Crystal Structure Database (ICSD). Subsequently, the Rietveld method, using the GSAS/EXPGUI II software [8], was applied using several least squares cycles until the quality parameters of the PXRD pattern reached the best data correlation. A differential scanning calorimetry (DSC) measurement was performed on a DSC 60 thermal analyzer (Shimadzu, Tokyo, Japan), under a heating rate of 10 K/min, in the temperature range of 300–773 K under a nitrogen atmosphere (100 mL/min), with a powder sample weighing ≈ 2.44 mg (conditioned in an aluminium crucible). The reversibility test was performed under ambient conditions, with a sample exposure to 433 K for complete salt dehydration. After dehydration, the rehydration profile was investigated at $\approx 58\%$ RH (relative humidity), atmospheric pressure and temperature of 300 K, simulating an open system configuration.

RESULTS AND DISCUSSION

Crystal structure

The NHMgSOH crystal was successfully obtained after a period of 25 days, presenting a translucent coloration and well-defined faces (Fig. 1). Fig. 2(a) shows the XRD pattern under ambient conditions refined by the Rietveld method.



Fig. 1 – NHMgSOH crystal.

The experimental patterns were compared with the theoretical pattern of the structure $[(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_6]$ attached to file number 43309 of the ICSD database [9]. NHMgSOH, shows a good correlation with the theoretical data. At an ambient temperature of 300 K, this double salt crystallizes in a monoclinic system, with space group $P2_1/a$, with two formulas per unit cell ($Z=2$). The cell parameters obtained (Table 1), associated with the excellent convergence indices ($R_{wp} = 9.97$, $R_p = 7.87$ and $S = 1.82$) make this system belong to the isomorphic crystallographic family of Tutton salts.

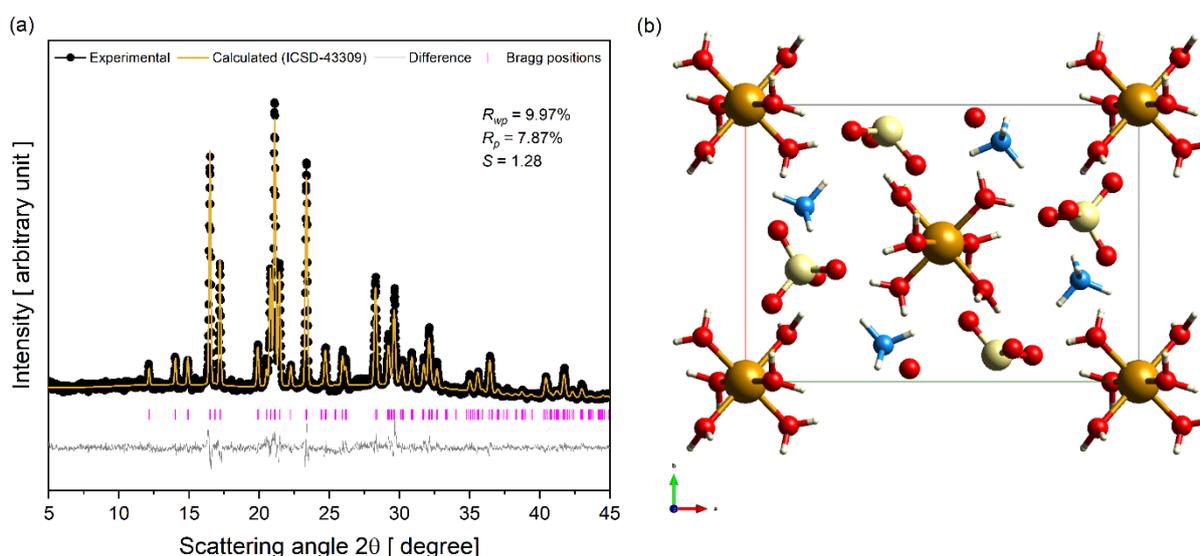


Fig. 2 – a) NHMgSOH PXRD pattern refined by the Rietveld method at 300 K; (b) Unit cell with monoclinic symmetry along the bc axis demonstrating the hydrogen bonds formed by H_2O molecules in ammonium and sulfate fractions.

Table 1 – Crystallographic parameters of the NHMgSOH crystal obtained by means of refined PXRD patterns in comparison with the literature.

Crystal	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	$\alpha=\gamma$ [°]	β [°]	<i>V</i> [Å ³]
ICSSD – 43309	9.383 (15)	12.669(20)	6.220(5)	90	107.05(10)	706.89
NHMgSOH	9.333 (2)	12.626(5)	6.215(0)	90	107.10(0)	700.03

Fig. 1(b) illustrates the projection of the unit cell for magnesium Tutton salt, composed of three distinct molecular units, where we have a hexahydrate complex, where the Mg metal is in one centre of a sphere coordinated by six water molecules [Mg(H₂O)₆] forming a slightly distorted octahedron, linked to a sulfate group [SO₄]²⁻ and an ammonium group [NH₄]⁺, via hydrogen bonds of the type O5–H5···O3 and N1–H3···O1, respectively, responsible for conferring thermal and structural stability to the crystal lattice [6].

Thermal analysis

To be applied as a thermochemical energy storage device, the crystal was investigated by means of a DSC thermal study. The DSC thermogram, in the temperature range between 300 and 773 K, is shown in Fig. 2. From the DSC curve, it was possible to stipulate the dehydration temperature, and the reaction enthalpy values (ΔH_r), obtained from the area under the dehydration peak of NHMgSOH. The crystal presents a dehydration temperature centered at ≈ 379 K and an enthalpy of 319.41 kJ/mol.

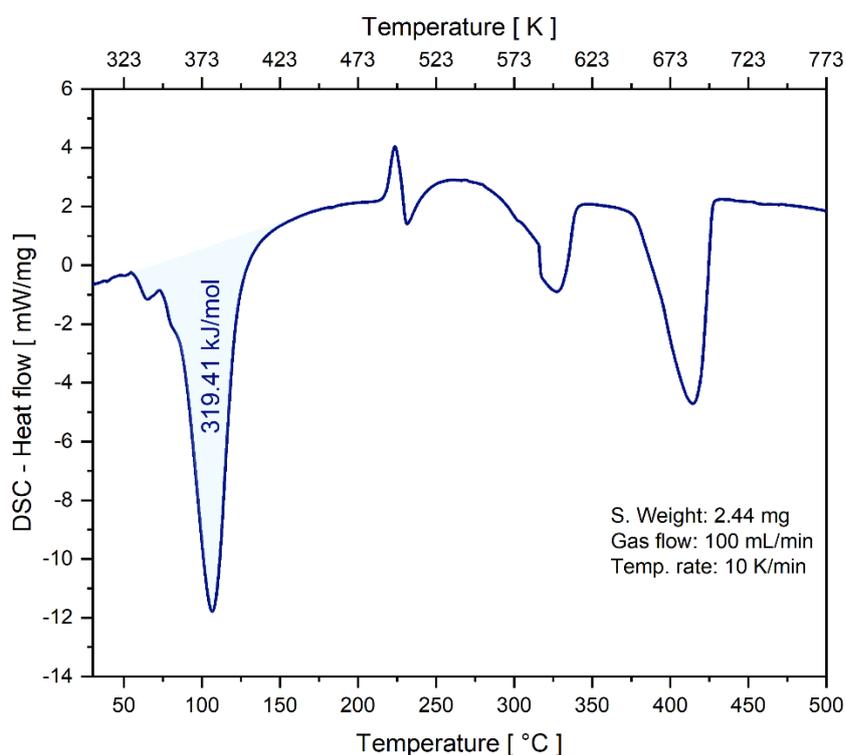


Fig. 2 – DSC spectrum for the Tutton salt NHMgSOH.

The volumetric density was measured using equation (1), where ΔH_r corresponds to the molar enthalpy of the reaction; M_s the molar mass of the hydrate and ρ_s the density of the compound [5]:

$$\Delta H_{r,v} = \frac{\Delta H_r}{M_s} \rho_s \quad (1)$$

Table 3 presents the thermal data extracted for NHMgSOH. The Mg salt meets all the requirements studied by Kooijman (2022). Therefore, considering its promising thermal properties, the crystal qualifies as a possible TCM.

Table 3 - Thermal parameters of NHMgSOH.

Crystal	T _{peak} (K)	ΔH _{exp} (KJ/mol)	ΔH _{exp} (KJ/H ₂ O mol)	ΔH _v (GJ/m ³)
NHMgSOH	379	319.41	53.24	1.50

Dehydration-rehydration studies of the hexahydrate phase

The study of multiple cycles was not explored in the present work. Instead, an analysis of the structural reversibility in a complete dehydration-rehydration cycle, as a function of time for NHMgSOH, was performed. Initially, the sample was subjected to a controlled dehydration process in an industrial furnace, with gradual heating from 300 K to 400 K, a temperature sufficient to promote complete dehydration without the release of NH₄ molecules. The dehydration was confirmed by the XRD analysis shown in Fig. 3(a), which showed an amorphous character, with the absence of diffraction peaks corresponding to the hexahydrate phase.

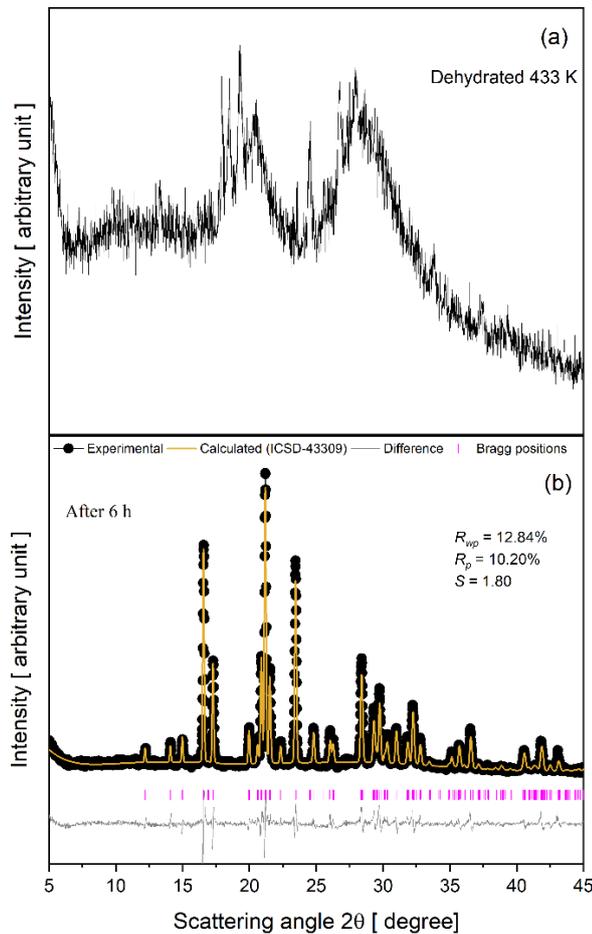


Fig. 3 – DRXP patterns as a function of temperature 433 K. (a) 0 hours; (b) 6 hours.

After dehydration, the sample was cooled to 300 K (after 1 h at ambient conditions) and measured again by XRD. The XRD data were recorded after 6 h, as shown in Figure 3(b). The final analysis showed complete structural reversibility, where the convergence shown between the rehydrated sample and the ICSD chart – 43309 suggests that the crystal returns to its hexahydrate phase.

CONCLUSION

In this study, the crystal NHMgSO_4 , belonging to the Tutton salt family, was successfully grown by slow solvent evaporation. The crystal structure of the salt was confirmed by powder X-ray diffraction (XRD) associated with Rietveld refinement. Thermochemical analyses reveal exceptional thermal properties for application as TCM, with enthalpy values of 319.41 kJ/mol and energy density of 1.50 GJ/m³, meeting the predefined criteria for the selection of optimal TCMs. Although a complete cyclability study (10 cycles) was not performed, the results demonstrated complete structural reversibility in only 6 hours after total dehydration, a characteristic that positions NHMgSO_4 as an extremely promising candidate for practical applications in thermal energy storage.

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