

HIGH-TEMPERATURE RAMAN SPECTRA IN THERMOANALYTICAL STUDIES ON THE HYDRATES OF MAGNESIUM AND ZINC SULFITE

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ABSTRACT

High-temperature Raman spectra are used for studying the thermal decomposition of $\text{ZnSO}_3 \cdot 2 \text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 6 \text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$.

$\text{ZnSO}_3 \cdot 2 \text{H}_2\text{O}$ dehydrates forming the hitherto unknown $\beta\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$ ($\text{MnSO}_3 \cdot 1 \text{H}_2\text{O}$ type), $\alpha\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$ (in former work [2,6] identified as $\text{ZnSO}_3 \cdot 1/2 \text{H}_2\text{O}$) and ZnSO_3 . $\text{MgSO}_3 \cdot 6 \text{H}_2\text{O}$ is decomposed to $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$ or $\text{MgSO}_3 \cdot 2 \text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$ (and the other lower hydrates of MgSO_3), first to amorphous anhydrous MgSO_3 and then to an unknown crystalline compound. Single crystals of $\text{MgSO}_3 \cdot x \text{H}_2\text{O}$ with $x = 2 \frac{1}{2}$ (hitherto unknown), 2 and 1 were obtained using gel crystallization and hydrothermal techniques. Thermoanalytical data (DTA, TG, DTG, high- and low-temperature X-ray diffraction patterns), IR and Raman spectroscopic data of these hydrates are reported. The crystal data are: $\text{MgSO}_3 \cdot 2 \frac{1}{2} \text{H}_2\text{O}$ ($P4_12_12$, $\text{CoSO}_3 \cdot 2 \frac{1}{2} \text{H}_2\text{O}$ type): $a = 944.4(1)$ and $c = 1025.5(1)$ pm, $Z = 8$, $\text{MgSO}_3 \cdot 2 \text{H}_2\text{O}$ ($P2_1/n$, $\text{ZnSeO}_3 \cdot 2 \text{H}_2\text{O}$ type): $a = 635.9(1)$, $b = 854.7(1)$, $c = 754.4(1)$ pm, and $\beta = 98.72(1)^\circ$, $Z = 4$, $\text{MgSO}_3 \cdot 1 \text{H}_2\text{O}$ ($P2_1/n$, $\text{MnSO}_3 \cdot 1 \text{H}_2\text{O}$ type): $a = 469.9(3)$, $b = 1282.3(10)$, $c = 563.2(4)$ pm, $\beta = 90.26(5)^\circ$, $Z = 4$.

INTRODUCTION

For studying the dehydration and phase relationships of solid hydrates common thermal analytical methods such as DTA, DSC and TG, or high temperature X-ray diffraction patterns are used. However as briefly reported in a previous paper [1], high-temperature Raman spectra have some advantages compared to the usual procedures, for three reasons particularly.

(i) The heating rates can be chosen over a very large range from s to $\text{h } ^\circ\text{C}^{-1}$, whereas for thermal analysis high heating rates and for high-temperature X-ray diffraction patterns low heating rates must be used.

(ii) Thick-walled glass ampoules, suitable for high water partial pressures, can be used as sample holders, not only thin-walled quartz glass capillaries as for high-temperature X-ray measurements.

(iii) Direct information on the compounds formed at each dehydration

stage is obtained, not only DTA peaks or possibly unknown X-ray diffraction patterns.

This paper presents the use of high-temperature Raman spectra for studying the thermal decomposition of hydrated magnesium and zinc sulfites with the aim of obtaining hitherto unknown lower hydrates of these compounds.

In the system $\text{MgSO}_3 \cdot x \text{H}_2\text{O}$, hydrates with $x = 6, 3,$ and 2 have been definitely characterized so far [2–4]. The existence of a monohydrate was reported by Szendrei and Ho-Tun [3]. In the system $\text{ZnSO}_3 \cdot x \text{H}_2\text{O}$, a relatively large number of hydrates are known, namely compounds with $x = 3, 2 \frac{1}{2}$ (three forms $\alpha, \beta,$ and γ), 2 and 1 [2,4,5]. In the literature [2,5,6] the monohydrate was reported to be a semihydrate. From structural analysis [4], however, it was found that this hydrate is really $\text{ZnSO}_3 \cdot 1 \text{H}_2\text{O}$, in the following called $\alpha\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$ [4].

The thermal decomposition of the hydrates of MgSO_3 and ZnSO_3 was investigated several times in the literature [2–6]. The results obtained, however, are not in good agreement, and the reason for this is discussed in ref. 5.

In this paper we confirmed all hydrates discussed including $\text{MgSO}_3 \cdot 1 \text{H}_2\text{O}$ and obtained the hitherto unknown $\text{MgSO}_3 \cdot 2 \frac{1}{2} \text{H}_2\text{O}$ and $\beta\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$. Furthermore, the thermoanalytical, X-ray, IR and Raman spectroscopic data of these compounds are presented.

EXPERIMENTAL

Starting materials

The hydrated sulfites used for the high-temperature Raman studies were prepared in the usual way [2,5] by crystallization from aqueous $\text{M}(\text{HSO}_3)_2$ solutions, at room temperature in the case of $\text{MgSO}_3 \cdot 6 \text{H}_2\text{O}$, at $85\text{--}95^\circ\text{C}$ for $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$, at $\sim 100^\circ\text{C}$ for $\text{MgSO}_3 \cdot 2 \frac{1}{2} \text{H}_2\text{O}$ and at $65\text{--}85^\circ\text{C}$ for $\text{ZnSO}_3 \cdot 2 \text{H}_2\text{O}$.

Preparation of single crystals

Single crystals of $\text{MgSO}_3 \cdot 2 \frac{1}{2} \text{H}_2\text{O}$ (and of $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$), distorted octahedra of up to 1 mm diameter, were obtained by a gel crystallization technique using silicic acid gels. A layer of 4 M MgCl_2 solution (at lower MgCl_2 concentrations the ternary $\text{Na}_2\text{Mg}(\text{SO}_3)_2 \cdot 2 \text{H}_2\text{O}$ [7] and $\text{NaMg}_2\text{OH}(\text{SO}_3)_2 \cdot 1 \text{H}_2\text{O}$ [8] are formed) was added to the gel saturated with 1.5 M Na_2SO_3 solution. Crystallization occurs at $85\text{--}95^\circ\text{C}$ within 24 h. Details are given elsewhere [9].

$\text{MgSO}_3 \cdot 2 \text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 1 \text{H}_2\text{O}$ were prepared from higher hydrates

in small thick-walled glass ampoules placed in a steel bomb. Monoclinic prisms (up to 1 mm diameter) of the dihydrate were obtained within 48 h from $\text{MgSO}_3 \cdot 6 \text{H}_2\text{O}$ without excess water at 150–160°C, and needles (up to 0.15 mm in length) of $\text{MgSO}_3 \cdot 1 \text{H}_2\text{O}$ from $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$ at 180°C within 4 h (see also Szendrei and Ho-Tun [3]). Higher temperatures and longer crystallization times should be avoided because of possible disproportionation of the sulfite, forming elemental sulfur and H_2S . Anhydrous MgSO_3 was prepared by heating of $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$ in an argon stream at 180°C.

Apparatus and technique

The high-temperature Raman spectra were recorded with a Coderg T 800 triple monochromator Raman spectrometer (resolution $< 4 \text{ cm}^{-1}$) excited by 488.0 and 514.5 nm radiation from an Ar^+ ion laser and analysed with the usual right-angle geometry. The samples were heated in closed or open glass tubes of 2 mm diameter, i.e., under their own vapour pressure, in air and in a vacuum of 1 Pa, using a Coderg model CRN 2 variable temperature cell. The spectra were recorded discontinuously, with heating rates from 2 to 50°C h^{-1} and isothermal measuring steps.

DTA, TG and DTG measurements were made in an argon stream and in a vacuum of 1 Pa with the thermobalance Linseis L 81. High- and low-temperature X-ray diffraction patterns were obtained using an Enraf–Nonius Guinier Simon camera. X-ray single crystal data were obtained with a Huber precession camera. Unit cell dimensions were refined by the least-squares method from Guinier powder data, with SiO_2 as an internal standard. The IR spectra of polycrystalline samples were recorded with a Perkin–Elmer model 283 spectrophotometer using both Nujol mulls and KBr discs. Details of the techniques used are given elsewhere [1,5].

RESULTS AND DISCUSSION

Thermal analysis and high-temperature Raman studies

The high-temperature Raman spectra of $\text{ZnSO}_3 \cdot 2 \text{H}_2\text{O}$ are shown in Fig. 1. The obtained spectra show that dehydration occurs firstly to the hitherto unknown $\beta\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$, then to $\alpha\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$ (or to mixtures of α - and $\beta\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$), and finally to anhydrous ZnSO_3 , that is the modification reported in ref. 2. DTA, DTG and high-temperature X-ray studies on the dehydration of $\text{ZnSO}_3 \cdot 2 \text{H}_2\text{O}$ resulted in the formation of $\alpha\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$ and ZnSO_3 , see ref. 2, in which $\alpha\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$ [4] was wrongly assumed to be a semihydrate. $\beta\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$ is isotypic with $\text{MnSO}_3 \cdot 1 \text{H}_2\text{O}$ [2,4] and $\text{MgSO}_3 \cdot 1 \text{H}_2\text{O}$, as shown by the Raman spectra. Because this hydrate has only been found as an intermediate of the thermal decomposi-

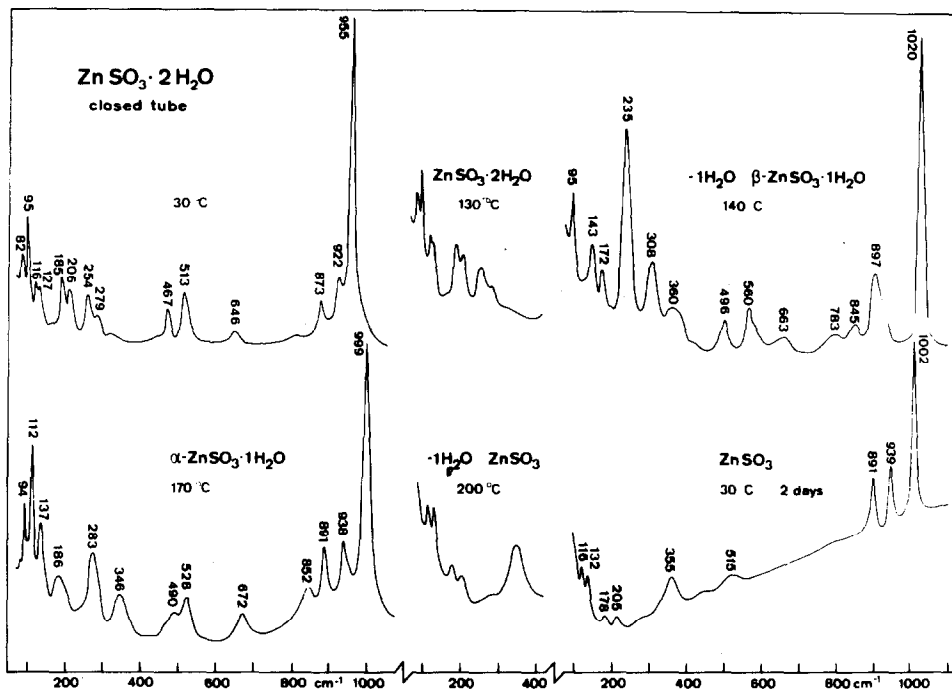


Fig. 1. High-temperature Raman spectroscopic measurements on $\text{ZnSO}_3 \cdot 2 \text{H}_2\text{O}$ (dehydration, phase transition and rehydration studies). The quoted wavenumbers are taken from room temperature spectra in all cases.

tion of $\text{ZnSO}_3 \cdot 2 \text{H}_2\text{O}$, we assume that $\beta\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$ is metastable compared to $\alpha\text{-ZnSO}_3 \cdot 1 \text{H}_2\text{O}$.

High-temperature X-ray diffraction patterns show that $\text{MgSO}_3 \cdot 6 \text{H}_2\text{O}$ dehydrates in two stages to $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$ and amorphous anhydrous MgSO_3 , and $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$ in one stage to amorphous MgSO_3 . This was confirmed by DTA, TG and DTG [2,3,10]. Low-temperature X-ray diffrac-

TABLE 1

d -Spacings of the unknown compound formed by thermal decomposition of amorphous anhydrous MgSO_3

d_{exp}	I/I_0	d_{exp}	I/I_0
4.96	10	1.864	5
3.34	100	1.742	2
3.23	100	1.670	20
2.63	30	1.626	10
2.31	10	1.612	30
2.07	10	1.457	2
2.04	10	1.316	10

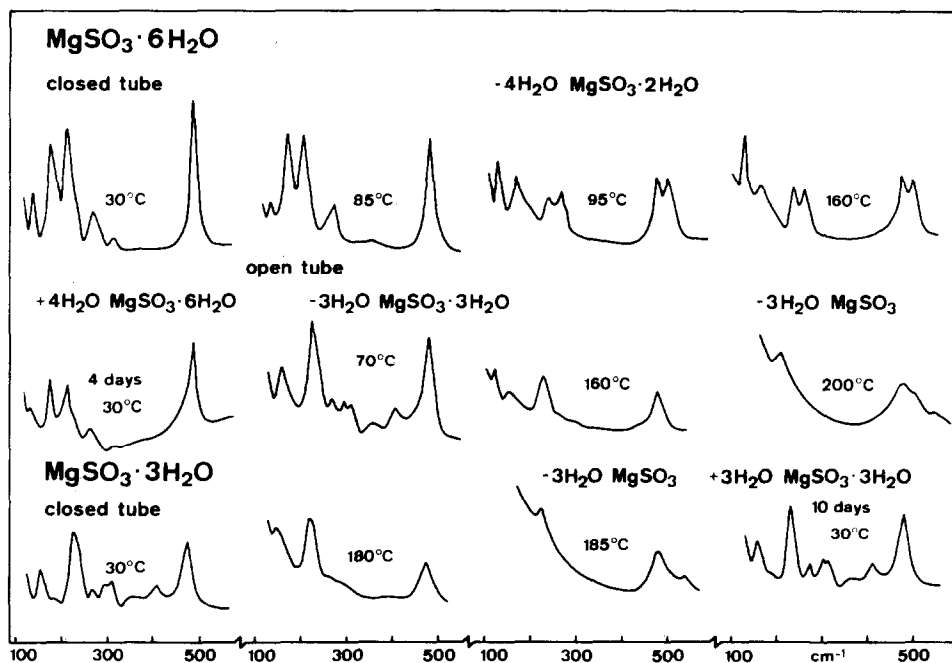


Fig. 2. High-temperature Raman spectroscopic measurements on $\text{MgSO}_3 \cdot 6 \text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$ (see Fig. 1). The complete spectra in the region $100\text{--}1200 \text{ cm}^{-1}$ are given in Fig. 4 and ref. 2, respectively.

tion patterns of $\text{MgSO}_3 \cdot 3 \text{H}_2\text{O}$ [11] indicate a phase transition, to a low-temperature modified hydrate, below -100°C . Amorphous MgSO_3 , the last dehydration product of all hydrates, decomposes further above 400°C to an unknown crystalline compound (for d -spacings see Table 1), see also Saeki et al. [12]. Under vacuum SO_2 is lost, forming MgO .

The high-temperature Raman spectra of the magnesium sulfite hydrates are shown in Fig. 2. The dehydration of the hexahydrate and the trihydrate takes place in the main as found by thermal analysis, discussed above. In the case of $\text{MgSO}_3 \cdot 6 \text{H}_2\text{O}$, however, both the trihydrate and the dihydrate were found as dehydration products, but never the other lower hydrates discussed in the following.

Dehydration experiments performed in closed glass tubes show that anhydrous MgSO_3 is hygroscopic (contrary to anhydrous ZnSO_3 , see Fig. 1) and reacts, after cooling to ambient temperature, with the lost water forming the initial hydrate. This behaviour indicates that the hydrates of MgSO_3 can also be prepared by rehydration of the anhydrous sulfite with stoichiometric amounts of H_2O , as found for the hydrates of alkaline earth halides [13] and hydroxides [1].

Characterization of the lower hydrates of magnesium sulfite

$\text{MgSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ crystallizes in the tetragonal $\text{CoSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ type [2,5] (space group $P4_12_12-D_4^4$, $Z = 8$) with $a = 944.4(1)$ and $c = 1025.5(1)$ pm, $\text{MgSO}_3 \cdot 2\text{H}_2\text{O}$ in the monoclinic $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}$ type [5,14] (space group $P2_1/n-C_{2h}^5$, $Z = 4$) with $a = 635.9(1)$, $b = 854.7(1)$, $c = 754.4(1)$ pm and $\beta = 98.72(1)^\circ$, $\text{MgSO}_3 \cdot 1\text{H}_2\text{O}$ (and $\beta\text{-ZnSO}_3 \cdot 1\text{H}_2\text{O}$) in the monoclinic $\text{MnSO}_3 \cdot 1\text{H}_2\text{O}$ type [2,4] (space group $P2_1/n$, $Z = 4$) with $a = 469.9(3)$, $b = 1282.3(10)$, $c = 563.2(4)$ pm and $\beta = 90.26(5)^\circ$. The quality of the Guinier patterns of $\beta\text{-ZnSO}_3 \cdot 1\text{H}_2\text{O}$ was too poor to calculate unit cell dimensions.

The IR and Raman spectra of the lower hydrates and of the amorphous anhydrous MgSO_3 are given in Figs. 3 and 4. From recent studies [8,11] it is shown that in both the SO stretching ($850\text{--}1100\text{ cm}^{-1}$) and the SO_3 bending region H_2O rotatory modes, i.e. H_2O librations, can appear. This fact was not considered in former work, see, for example, refs. 2 and 15, in which it

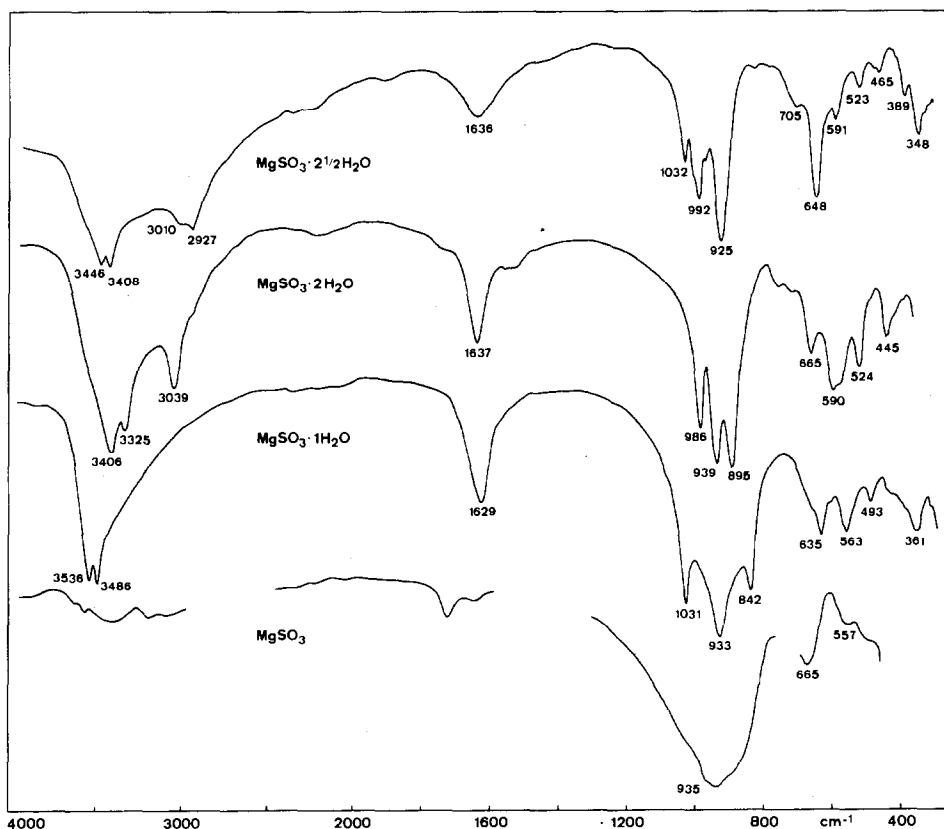


Fig. 3. Infrared spectra of $\text{MgSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 2\text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 1\text{H}_2\text{O}$ (KBr discs) and amorphous MgSO_3 (Nujol) (Perkin-Elmer 283) (for IR spectra of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ see ref. 2).

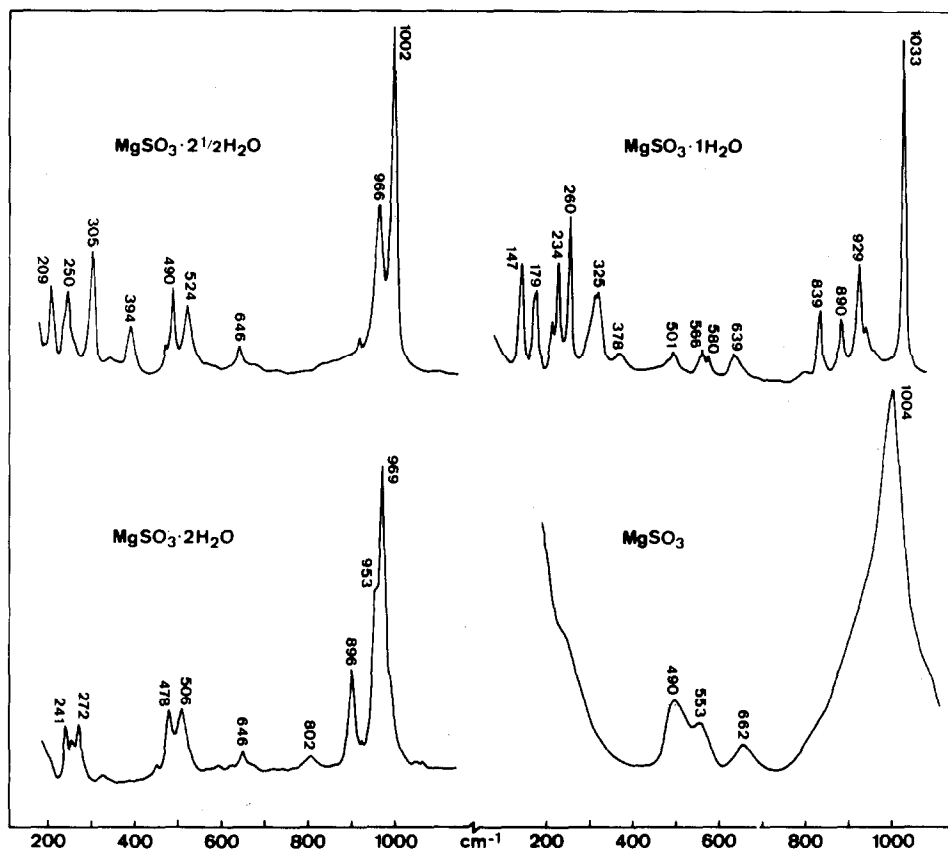


Fig. 4. Raman spectra of $\text{MgSO}_3 \cdot 2\frac{1}{2} \text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 2 \text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 1 \text{H}_2\text{O}$ and amorphous MgSO_3 (Coderg T 800, 488.0 nm).

was assumed that only the bending modes of the sulfite ion may coincide with H_2O librations.

The DTA and TG results of $\text{MgSO}_3 \cdot x \text{H}_2\text{O}$ with $x = 2\frac{1}{2}$, 2, and 1 are given in Fig. 5. Dehydration of these lower hydrates occurs in one stage forming amorphous anhydrous MgSO_3 , as shown by high-temperature Raman spectra and high-temperature X-ray diffraction patterns. The relatively low dehydration temperature of $\text{MgSO}_3 \cdot 1 \text{H}_2\text{O}$ compared to the higher hydrates presumably indicates that this compound is less stable than the other hydrates of MgSO_3 . The decomposition of anhydrous MgSO_3 takes place as discussed above.

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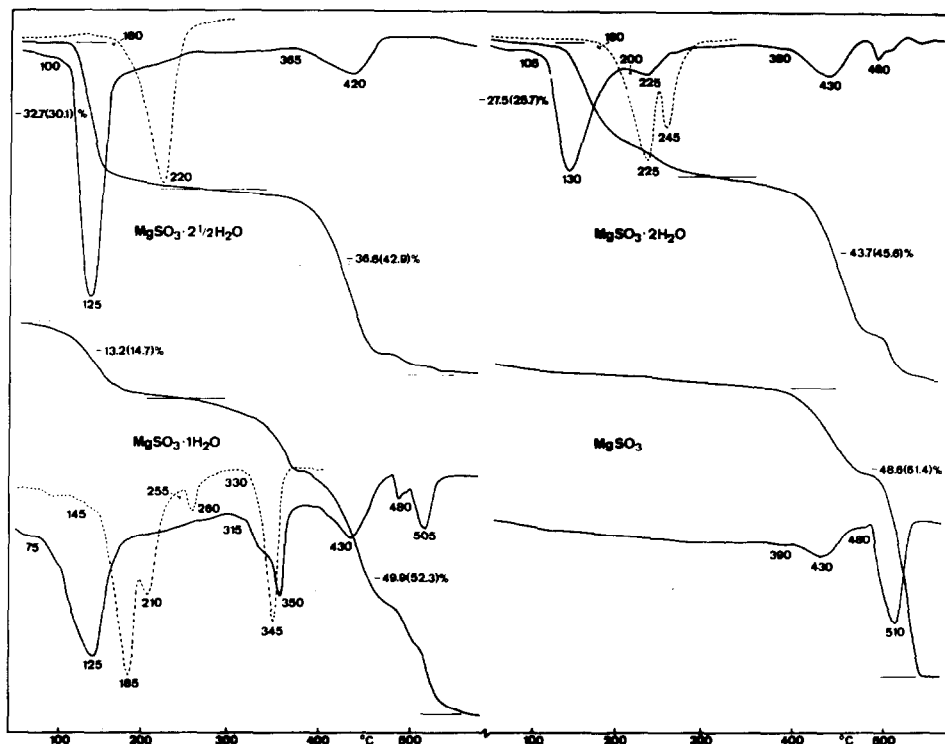


Fig. 5. DTA and TG diagrams of $\text{MgSO}_3 \cdot 2 \frac{1}{2} \text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 2 \text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 1 \text{H}_2\text{O}$ and amorphous MgSO_3 (vacuum, 1 Pa, heating rate 1°C min^{-1} , —; argon stream, heating rate 5°C min^{-1} , - - - -); weight loss (in parentheses) calculated for loss of the whole water of crystallization and sulfur dioxide, respectively.

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