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THERMAL AND SPECTROSCOPIC STUDY OF DEHYDRATION OF LITHIUM FORMATE MONOHYDRATE SINGLE-CRYSTALS

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Abstract

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) of lithium formate monohydrate ($LiHCOO{\cdot}H_2O$) were performed in the temperature range 300–700 K. The DSC/TG measurements show that the dehydration process to anhydrous lithium formate (LiHCOO) is complex and occurs in two stages. The data are correlated to the structure and to the arrangement of the molecules in the crystal, including the hydrogen-bonding. Infrared transmittance and Raman spectra of this crystal are reported and commented on.

Keywords: DSC, hydrogen-bond, IR, lithium formate monohydrate, Raman spectroscopy

Introduction

The thermal behaviour of various formate compounds has been already investigated by a number of researchers. Friedlin and Bulanova [1] reported that the salt decomposes between 513 and 533 K; according to Ray and Sinnarkar [2], decomposition occurs at 463 K. The thermal behaviour of some hydrated crystals has been studied as a function of temperature by means of IR spectroscopy [3–5]. Shishido and Masuda [6] carried out a wide-ranging study on a series of metal formates by thermogravimetric and gas-chromatographic techniques. We earlier characterized several modifications of lithium formate monohydrate (LFMH) [7] by Raman spectroscopy. The present study is undertaken with the use of thermogravimetric (TG) and differential scanning calorimetry (DSC) techniques. Furthermore, IR transmittance spectra of LFMH single-crystals are reported.

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Experimental

The single-crystals studied were prepared according to the methods described in references [7] and [8], i.e. by dissolving lithium hydroxide in formic acid solution in equimolar proportions (1:1). The detailed descriptions of the thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) methods are to be found in reference [8]. The curves were recorded with increasing temperature in both DSC and TG scans. The temperature range of interest in the present case was 300–700 K. The samples of different masses were scanned with a heating rate of 2, 3, 5 or 10 K min^{-1}. Anhydrous salts were obtained by heating the corresponding hydrates to 440 K. The IR transmittance spectra were recorded in the region 400 to 4000 cm^{-1} on a Mattson 3000 FTIR spectrometer, using KBr pellets containing a fine LFMH powder obtained from the grown single-crystals. The Raman spectra were recorded on a SPEX double monochromator spectrometer, using the 5145 Å line of an argon ion laser (400 mW). The sample was mounted in a furnace whose temperature was controlled by a thermocouple with a precision of ±5 K.

Results and discussion

The TG(%) curve of 20 mg sample for a scanning rate of 3 K min^{-1} is shown in Fig. 1. The curve is characterized by three steps. The first, between 336 and 384 K, corresponds to a mass loss of about 4%. The second occurs between 394 and 463 K, and the mass loss is about 21%. The total mass loss is therefore about

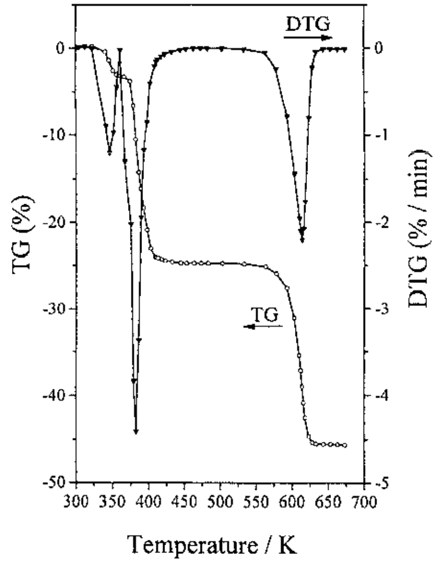

Fig. 1 TG (%) and DTG (%/min) curves of LFMH (m=20 mg, V=3 K min^{-1})

25%, which corresponds well to the mass percentage of the water molecules in the formula unit. The crystal becomes progressively anhydrous in the temperature range 330 to 470 K. The last step, between 580 and 660 K (Fig. 1), corresponds to the destruction of the crystal. The overall loss was 45% of the initial mass.

In another experiment (m=28 mg, V=5 K min^{-1}), we obtained the following values in the temperature range between 300 and 440 K: first loss 9%, and second loss 17%; this variation in the percentages did not affect the final overall mass loss (25%) (Fig. 2).

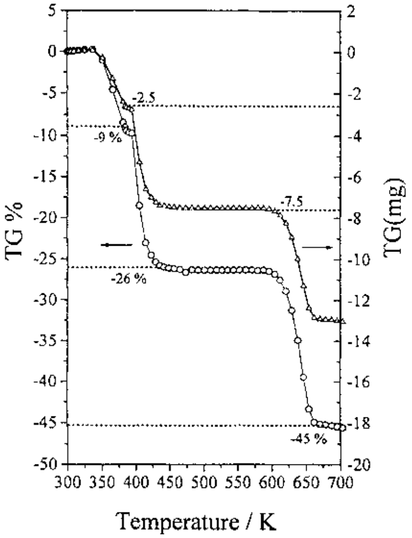

Fig. 2 Mass loss curve (%, mg) of the LFMH sample (m=28 mg, V=5 K min^{-1})

The dehydration of the compound was confirmed by performing DSC in the same temperature range. Figure 3 reports the DSC curve details for two scanning rates and three masses. It can be seen that the number of endothermic peaks (300–440 K) decreases as the mass of the sample is increased (Fig. 3a; V=3 K min^{-1}, m=2.3, 10.7 or 11 mg). The peak at around 495 K appears with increasing mass. The endothermic peak at around 548 K is assigned to the fusion of the substance (Fig. 3b; m=11 mg, V=3, 5 or 10 K min^{-1}). The positions of the peaks increased with increasing mass of the sample. It may be recalled that the peaks at 495 and 548 K (Fig. 3a, b) are situated in the region where there is no loss in mass (Figs 1 and 2).

Figure 4a, b reveals important changes in the Raman spectra in the X(ZX)Z and X(YY)Z polarizations. The first change (313 to 329 K) takes place where no thermal anomaly is observed in Figs 1–3. However, the modifications observed in the Raman spectra in the temperature range between 329 and 369 K and between 401 and 491 K were related to dehydration of the sample in a previous paper [7]. Our TG results showed that the mass loss (25%) corresponds to the mass percentage of the water molecules, and our DSC measurements (Fig. 3, b) re-

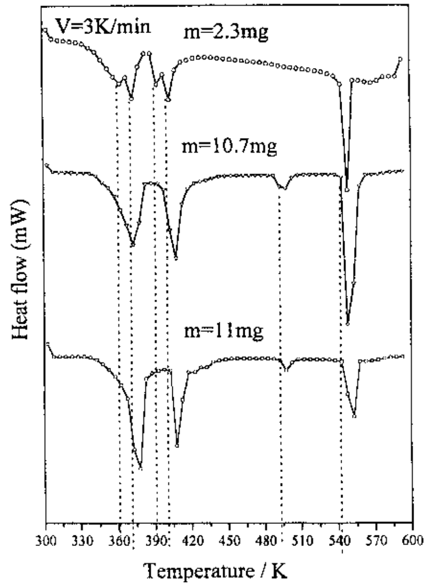

Fig. 3a DSC curves for V=3 K $\min^{-1}$ and three masses, m=2.3, 10.7 and 11 mg

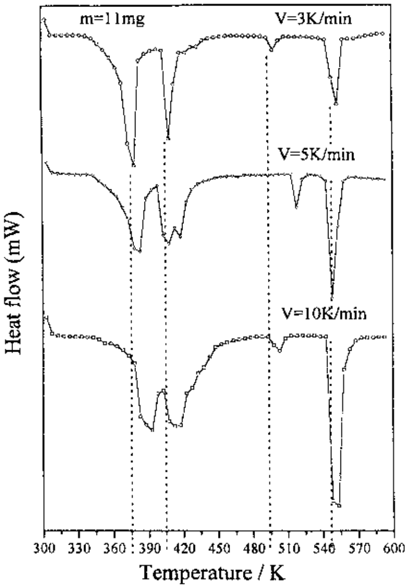

Fig. 3b DSC curves for m=11 mg and three scanning rates, V=3, 5 and 10 K $\min^{-1}$

vealed two peaks, at 373 and 405 K, which could correspond to the breaking of the hydrogen-bonds. The assignment of the observed peaks (a, b, c, d, e, f, g) was discussed earlier [7, 8].

Figure 5 shows the temperature dependence of the fitting parameters of peaks 1 and 2 (Fig. 3a, b). The curves were reproduced by using Gaussian functions. It can be seen, as discussed above, that the fitted parameters (position, heat

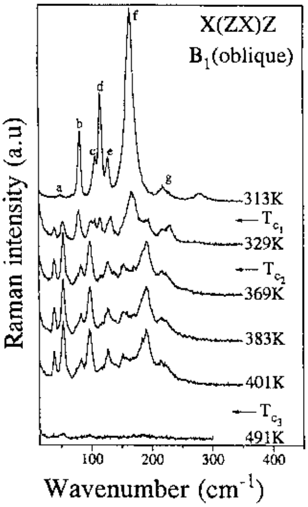

Fig. 4a LFMH high-temperature Raman spectra in the B_1[X(ZX)Z] oblique modes in the region 25 to 350 cm^{-1}

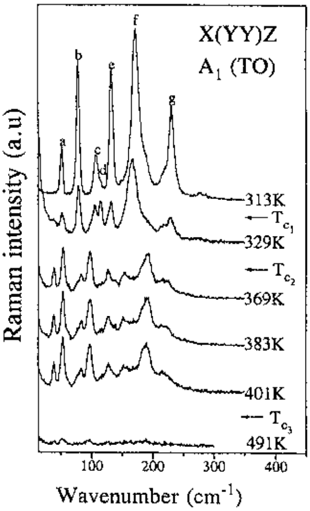

Fig. 4b LFMH high-temperature Raman spectra in the A_1[X(ZX)Z] transverse optical modes in the region 25 to 350 cm^{-1}

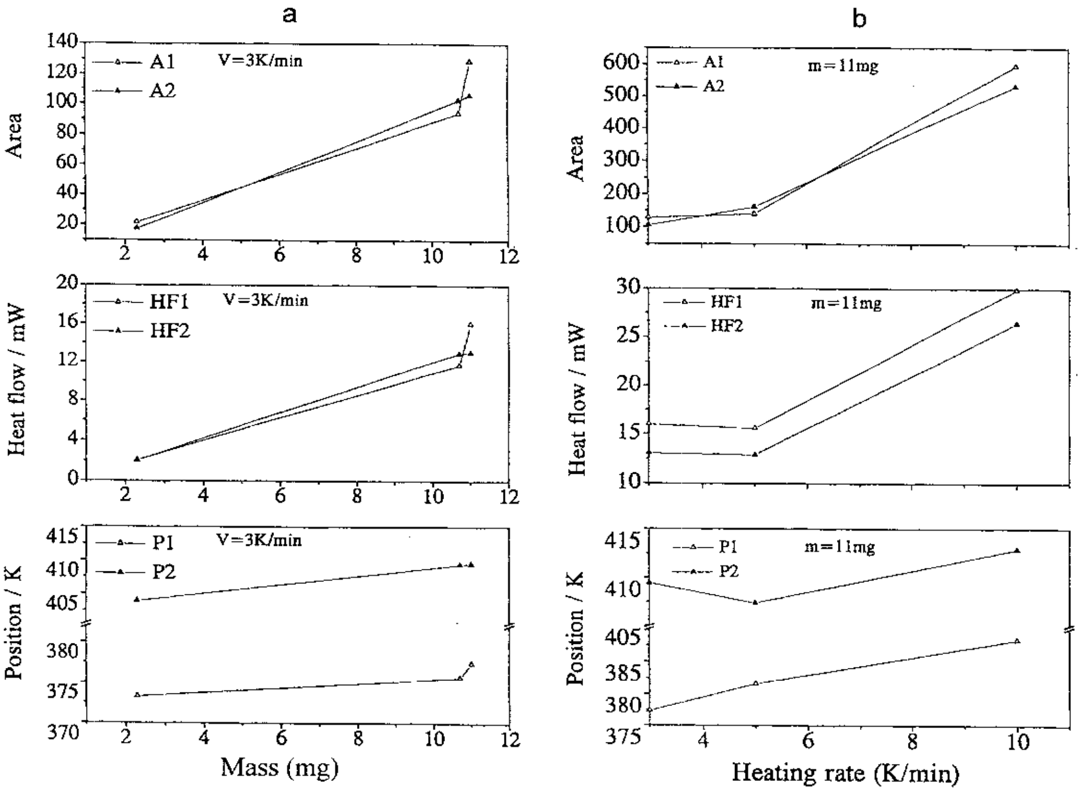

Fig. 5(a+b) Temperature dependence of the position, heat flow intensity and area of thermal peaks 1 and 2

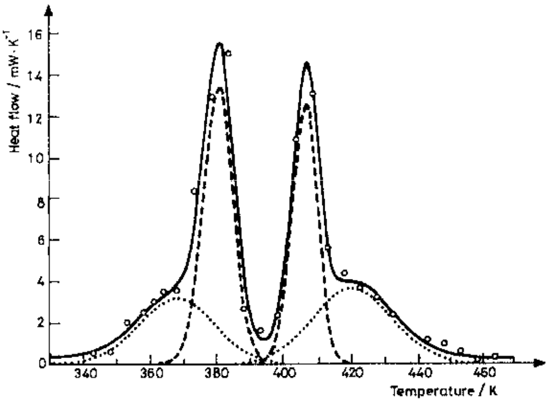

Fig. 6 The DSC (m=6.9 mg, V=5 K min^{-1}) fitted peaks corresponding to the dehydrated compound

flow amplitude and peak area) increase when either the sample mass or the heating rate is increased. Furthermore, in Fig. 6, for the case of m=6.9 mg and V=5 K min^{-1}, we fit the DSC curve, again with the use of Gaussian functions. The

Table 1 Assignment of the IR wavenumber (cm^{-1}) of LFMH at room temperature

IR wavenumbers	Relative intensity of lines*	Assignment**
428	s	H_2O liberation
478	sh	H_2O liberation
636	s	H_2O liberation
677	s	H_2O liberation
796	s	ν_3 (A_1)
820	sh	H_2O liberation
1069	vvw	ν_6 (B_1)
1371	vs	ν_2 (A_1)
1383	vs	ν_5 (B_1)
1590	vvs	ν_4 (B_1) and H_2O bending
1679	sh	H_2O bending
2760	m	$2\nu_2$ or $2\nu_5$
2864	s	ν_1 (A_1)
3000	vb	$\nu_1+\tau(HCOO^-)$ or $\nu_4+\nu_5$
3109	s, b	$O_w–H\cdots O_f$
3398, 3458	s, b	$O_w–H\cdots O_w$

* m – medium; s – strong; vs – very strong; vvs – very very strong; vvw – very very weak; sh – shoulder; b, – broad and vb – very broad

** ν_1 to ν_6 internal modes of the formate ions; O_w: water oxygen atom; O_f: formate oxygen atom fitting parameters (position, heat flow amplitude and peak area) allow determination of the energy of the hydrogen-bonds [8]:

For the peaks in the temperature range 330–395 K: $\Delta H_1 = 6.3\pm1.0$ kcal mol^{-1}.
For the peaks in the temperature range 395–450 K: $\Delta H_2 = 5.9\pm1.0$ kcal mol^{-1}.

The total heat which transforms the compound towards an anhydrous state is therefore ΔH=12.2 kcal mol^{-1}. This value is in agreement with the 13 kcal mol^{-1} given in the literature [9]. In accordance with the literature [10, 11], we attribute $\Delta H_1 = 6.3$ kcal mol^{-1} to the breaking of the hydrogen-bond HB_1 ($O_w \cdots O_f$) (of length ≅2.714 Å), and ΔH_2=5.9 kcal mol^{-1} to the breaking of the hydrogen-bond HB_2 ($O_w \cdots O_w$) (of length ≅2.987 Å), where the index *w* means a water oxygen atom and the index *f* means a formate oxygen atom.

Table 1 lists the wavenumbers and their respective assignments [7] from the IR spectra in the range 400–4000 cm^{-1}, recorded on an LFMH sample at room temperature (Fig. 7). When the crystal was heated between 300 and 420 K, the crystallization water was removed from the lattice (Fig. 1), but the corresponding IR spectra still showed the presence of water vibration bands (3000–3600 cm^{-1}) (Fig. 7). For this reason, we recorded a TG curve in the temperature range between 300 and 420 K, up to dehydration of the sample. Then, after 24 h in air with normal ambient humidity, a new TG curve of the previously anhydrous sample showed that there was no loss in mass between 300 and 420 K. However, the corresponding IR spectrum of the salt still exhibited intense bands relating to water.

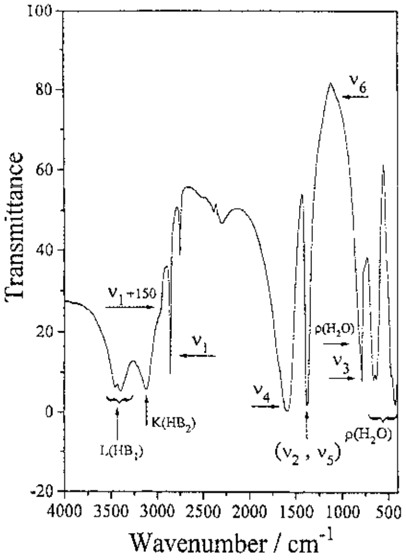

Fig. 7 Percentage IR transmittance spectrum of LFMH in the region 400 to 4000 cm^{-1} at room temperature

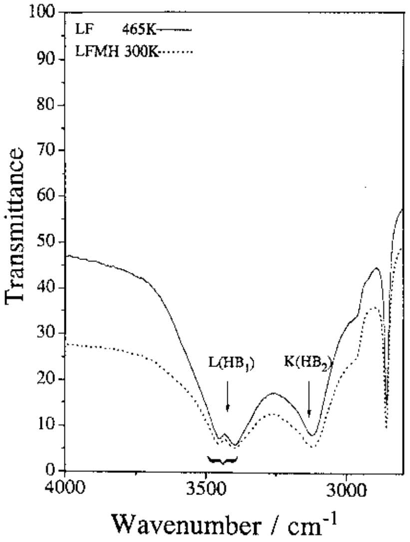

Fig. 8 IR transmittance of the 'anhydrous' salt LFMH in the region 2750 to 4000 cm^{-1}

Figure 8 presents the IR spectra of the two crystals, one at room temperature (300 K) and the second at 465 K. The bands denoted L(HB_1) and K(HB_2) relate to the water molecule hydrogen-bonds. The present study confirms the rehydration of the salt, but the origin of the intensity of the bands is still not clear. In general, our results are in agreement with earlier observation on other formates [4, 12].

Conclusions

We have used DSC and TG in the temperature range 300–700 K to study the thermal behaviour of LFMH, correlated to the Raman and IR spectra. The major results of the study may be summarized as follows:

1 – The dehydration is complex and occurs in two stages in the temperature range 300–470 K.

2 – The samples undergo fusion at ≅548 K, before their decomposition (580–650 K).

3 – Analysis of the DSC curves (Fig. 6), allows determination of the energy of the hydrogen-bonds; this compares favourably with the literature values.

4 – The TG and DSC results were in good agreement with the high-temperature Raman spectra with respect to the dehydration of the samples.

5 – We have obtained evidence of rehydration of the anhydrous sample, detected by IR transmittance spectroscopy.

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