JOURNAL OF MATERIALS SCIENCE 29 (1994) 6479–6484

Effects of microwave and heating treatments on the crystallographic properties of a potassium acetate powder

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The crystallographic properties of a commercial potassium acetate powder have been analysed before and after various heat treatments. From X-ray diffraction patterns and scanning electron microscopy it is shown that the initial material is constituted by two chemical compounds which are characterized by tetragonal structures. After heating either by means of a microwave monomode, or under a poor vacuum at low temperature (363 and 413 K), one of these compounds disappears. This one is very likely a hydrated form of the acetate. Additionally, infrared and Raman spectra of the potassium acetate have been recorded. The absorption bands have been compared to those of sodium acetate. Moreover, X-ray absorption spectra (recording of the K edge of potassium) corroborates the desorption of water from the powder maintained under high vacuum.

1. Introduction

Alkylation of solid potassium acetate can be easily and efficiently performed in the absence of organic solvent, either using impregnated reactants on to alumina ("dry media" conditions) [1] or solid–liquid phase transfer catalysis (PTC) [2]. At the present time, when coupled to microwave (MW) energy transfer, these methods lead to considerable improvements in yields and experimental conditions [3–5].

However, the crystallographic characteristics of potassium acetate show some differences according to the results reported in previous papers. Hatibuara and Parry [6] have observed between 297 K and the melting point (583 K), three phases which have been classified as monoclinic III (297 K), monoclinic II (348 K), and orthorhombic I (428 K). Such transitions have been also specified by differential scanning calorimetry [7], and thermal and Raman investigations [8]. Another solid-state transition at 500 and 474 K has been reported [9, 10]. Bouaziz and Basset [11], and Nirsha *et al.* [12] have recorded various X-ray patterns relative to CH_3COOK, β-CH_3COOK and hydrated acetates. It is unlikely that such patterns were not indexed. Moreover, comparison of the interplanar spacings leads us to conclude that there are few correlations between them. For example, the two so-called β-CH_3COOK compounds are very different. In the same way, the interplanar spacings calculated from the lattice parameters given by Hatibuara and Parry [6], do not correspond either to those given by Bouaziz and Basset [11], or to those reported by Nirsha *et al.* [12], respectively.

The aim of the present work was to determine the crystallographic properties of a commercial potassium acetate powder before and after treatment by means of a monomode microwave (MW), and heating under a poor vacuum. Additional infrared, Raman and X-ray absorption spectra have been recorded for the first time.

2. Experimental procedure

The fine white powder was obtained from Janssen Chimica (purity 97%). Three thermal treatments were used to study the possible chemical and crystallographic changes of this powder. First, it was exposed at a low power ($P = 60$ W) to the electromagnetic beam of a nearly "focused" monomode MW. The experimental procedure is described in detail in a previous paper [13]. Second, it was annealed under a vacuum of about 20 mm mercury at 363 K; and third, under a vacuum of 1–2 mm mercury at 413 K. Such treatments allow a good solid reactant to be obtained which induces maximum yields for chemical reactions. After exposure to the air, the initial powder is often hydrated, and shows a pasty appearance. The material was analysed before and after treatments by several methods: X-ray diffraction (Debye method), scanning electron microscopy, infrared and Raman spectroscopies, and X-ray absorption spectroscopy (XAS).

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3. Results

3.1. X-ray diffraction and scanning electron microscopy

3.1.1. *Initial powder*

The initial powder is constituted by two kinds of particles as revealed by SEM observations (Fig. 1): some present a near spherical aspect, while others are shapeless and longer in size (up to 1 mm). X-ray diffraction patterns (XDP) show clearly that two different X-ray line systems coexist (Fig. 2). They correspond, respectively, to the smaller grains (continuous lines) and to the larger particles (dotted lines). The crystallographic data are reported in Tables I and II. By using the $\sin^2\theta$ method, it was concluded that the two systems can be indexed according to two tetragonal lattices. These have been specified as T_1 for the smaller grains, and T_2 for the larger particles. They are characterized by the following parameters:

$$\begin{aligned} T_1 \quad a_1 = b_1 &= 1.385 \pm 0.002\,\text{nm}, \\ c_1 &= 1.780 \pm 0.002\,\text{nm}, \\ V_1 &= 3.414\,\text{nm}^3 \\ T_2 \quad a_2 = b_2 &= 1.045 \pm 0.002\,\text{nm}, \\ c_2 &= 2.624 \pm 0.002\,\text{nm}, \\ V_2 &= 2.865\,\text{nm}^3. \end{aligned}$$

The planar indices relative to these lattices are characterized by the same general conditions such as:

$$\begin{aligned} hkl{:}\ l &= 2n; \\ hhl{:}\ l &= 2n; \\ 0kl{:}\ l &= 2n; \\ 00l{:}\ l &= 2n; \\ hk0&{:}\ \text{no conditions}; \\ h00&{:}\ \text{no conditions}. \end{aligned}$$

This leads to conclude that the space group is either 103, or 124, as given by the X-ray International Tables.

Compared to the results reported previously, one can notice that a great part of the interplanar spacings of the β-acetate [12], and those of the so-called hydrated (1.5) acetate [11] can be indexed according to the T_2 cell, and some others with those of the T_1 cell. On the contrary, there are very few correlations between the monoclinic and orthorhombic lattices [6] and the two tetragonal cells.

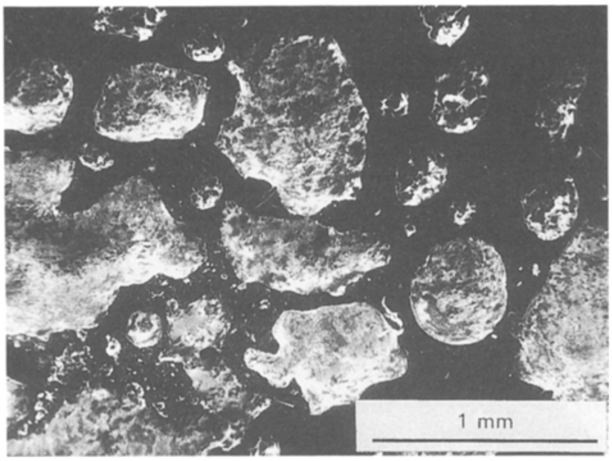

Figure 1 Scanning electron micrograph of the initial potassium acetate powder.

3.1.2. *Microwave and heating treatments*

After either treatment by means of the monomode MW, or heating at a low temperature (363 K) under vacuum, the XDP show that only the presence of the T_1 structure can be indexed (Fig. 3). Comparison of the patterns allows us to conclude that the heating mode leads to a better crystallization of the powder, and that additional X-ray lines, such as (2 2 0) and (5 0 0), can be indexed. SEM observations show that the major part of the grains present a near spherical shape (Fig. 4).

Annealing at higher temperature (413 K) changes the intensity of the X-ray lines of the T_1 structure (Fig. 5). For instance, the (1 1 0) diffraction line becomes very strong in intensity, while the (0 0 4) and (3 2 2) ones are less intense. This implies a change in the texture of the particles. Moreover, compared to Fig. 3, the X-ray lines relative to the (3 0 2) and (4 2 0) crystallographic planes (with interplanar spacings such as 0.408 and 0.3075 nm) are now observed on the pattern. Lastly, three additional faint X-ray lines (indicated by arrows in Fig. 5) can be observed. Their interplanar spacings (d = 1.155, 0.753 and 0.540 nm) do not belong to other known structures.

3.2. Infrared and Raman spectroscopies

To our knowledge no infrared and Raman spectra relative to the potassium acetate have been published

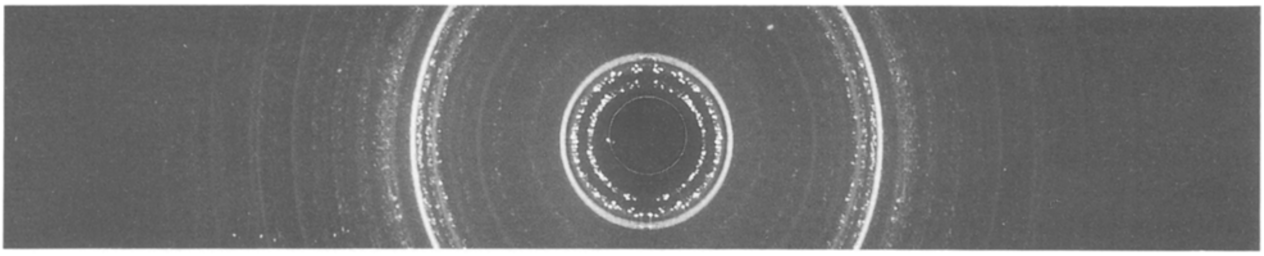

Figure 2 X-ray diffraction pattern of the initial powder characterized by two kinds of lines relative to the (———) T_1 and (· · · ·) T_2 tetragonal structures.

TABLE I CH_3COOK: tetragonal T_1 structure

d ($h k l$) (nm)	Int.[a]	$h k l$
1.385	w +	100
0.982	w +	110
0.891	vs	002
0.491	vw	220
0.447	m	004
0.383	w +	320
0.355	m +	322
0.336	w	410
0.323	s	402
0.2975	m	006
0.288	m	324
0.284	vw	116
0.276	vw	500, 430
0.2705	w +	404
0.2635	w +	432
0.2525	w +	424
0.2445	w +	440
0.237	w +	530
0.2305	w +	600
0.2245	w +	406
0.222	w +	008, 602
0.2185	m –	620
0.216	m –	540
0.210	w	542
0.204	w	614
0.198	m	318
0.1945	m	526
0.1895	w +	720
0.1825	w	606
0.1775	m	0010
0.1735	vw	508, 438
0.171	w	810, 740
0.168	w	820, 743
0.162	m	660

[a] Visualized intensities.

TABLE II CH_3COOK: tetragonal T_2 structure (probably hydrated form)

d ($h k l$) (nm)	Int.[a]	$h k l$
1.316	vs	002
1.058	vs	100
0.830	w	102
0.660	m	004
0.650	w	112
0.526	w	200
0.4925	m	114
0.437	vw	006
0.415	vw	204
0.402	m	106
0.378	w	116
0.3595	s	222
0.336	s	302
0.328	s	008
0.323	w	312, 224
0.313	w	108
0.3085	w	304
0.2985	m	314
0.293	m	320
0.286	m	322
0.284	m	226
0.2785	m	208
0.268	w	324
0.2625	m	0010
0.2565	w	410
0.252	w	412
0.2485	m	330
0.237	m	420
0.230	m	2110
0.227	m	406

[a] Visualized intensities.

previously. Only from these can one determine the absorption bands by comparison with those given for sodium acetate [14, 15]. The experiments were carried out on the initial material. The infrared spectrum reported in Fig. 6, has been recorded at 293 K on a Perkin–Elmer 1730 JRFT spectrophotometer. A disc was prepared such as the initial potassium acetate powder be suspended in KBr, and then pressed at several tons. The spectrum shows that between 400 and 1600 cm^{-1} the main absorption bands can be compared with those of sodium acetate. So, according to Kaklana *et al.* [14] the vibrational assignments should be listed such as:

$1575\ cm^{-1}$: $\nu_{as}(CO)$, $\gamma_{in}(COO)$;

$1410\ cm^{-1}$: $\delta_{as}(CH_3)$, $\nu_s(CO)$;

$1340\ cm^{-1}$: $\delta_s(CH_3)$, $\nu(C\text{–}C)$;

$1020\ cm^{-1}$: $\gamma_{in}(CH_3)$, $\nu_{as}(CO)$;

$922\ cm^{-1}$: $\nu(C\text{–}C)$, $\delta(COO)$, $\nu_s(CO)$;

$660\ cm^{-1}$: $\delta(COO)$, $\nu(C\text{–}C)$;

$465\ cm^{-1}$: $\gamma_{in}(COO)$, $\gamma_{in}(CH_3)$;

$1050\ cm^{-1}$: $\pi(CH_3)$, $\pi(COO)$;

$620\ cm^{-1}$: $\pi(COO)$, $\pi(CH_3)$.

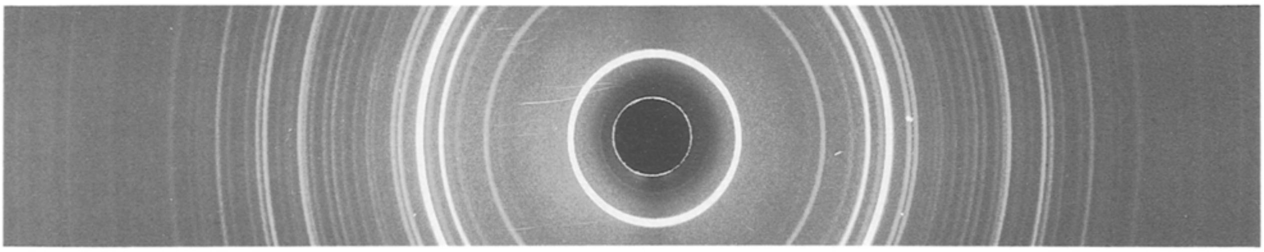

Figure 3 X-ray diffraction pattern of the pure T_1 lattice (powder heated at 363 K).

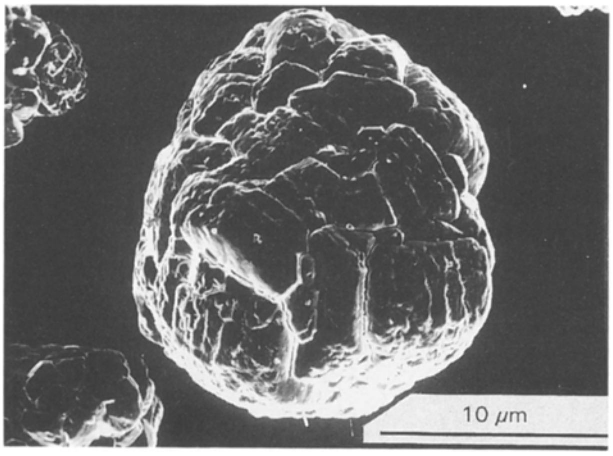

Figure 4 Scanning electron micrograph of the powder after MW treatment.

Beyond 1600 cm^{-1}, three absorption bands are attributed to H_2O (or the OH group) at 1650 and 3400 cm^{-1}; and to CO_2 at 2280 cm^{-1}. One can also notice that the broad H_2O band (between 2800 and 3650 cm^{-1}) does not allow the absorption bands due to the CH_3 stretching modes (as ν_{as}, and ν_s, respectively) to be resolved.

The Raman spectrum of the untreated powder has been recorded using a Jobin–Yvon T 800 (Laser Ar II) apparatus (excitation wavelength 488 cm^{-1}, power 100 mW, spectral resolution 4 cm^{-1}). The spectrum (Fig. 7) has been compared with that given for sodium acetate [15] which reveals 14 absorption bands between 0 and 3000 cm^{-1}. In this way, the bands localized at 2980, 2940, 1435, 1340 and 1015 cm^{-1} can be attributed to the CH_3 methyl group, those at 1590, 650, 620 and 470 cm^{-1} can be expressed according to the COO and CO groups, and the intense band at 920 cm^{-1} is relative to the C–C stretching mode. The lower absorption bands at 520 and 110 cm^{-1} should be attributed to the potassium ionic group. It can be remarked that in spite of the change in the ionic radius between sodium and potassium, there are few divergences between the two spectra.

3.3. X-ray absorption spectroscopy

X-ray absorption spectroscopy has been used to record the potassium K edge which is located beyond

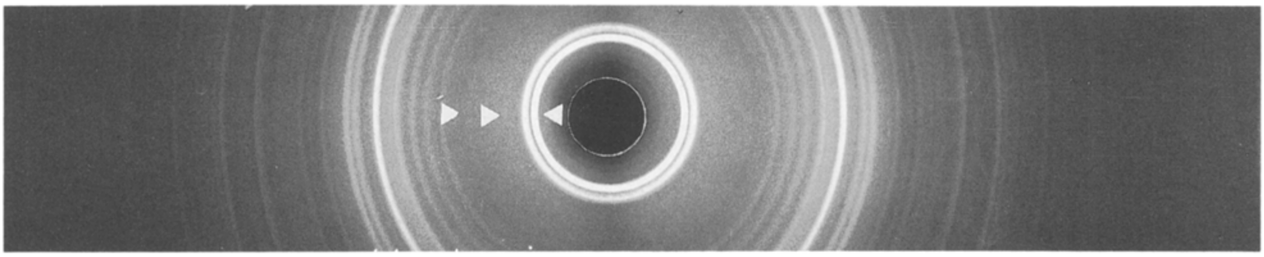

Figure 5 X-ray diffraction pattern of the heated (413 K) powder. Arrows indicate the lines which do not correspond to the T_1 structure.

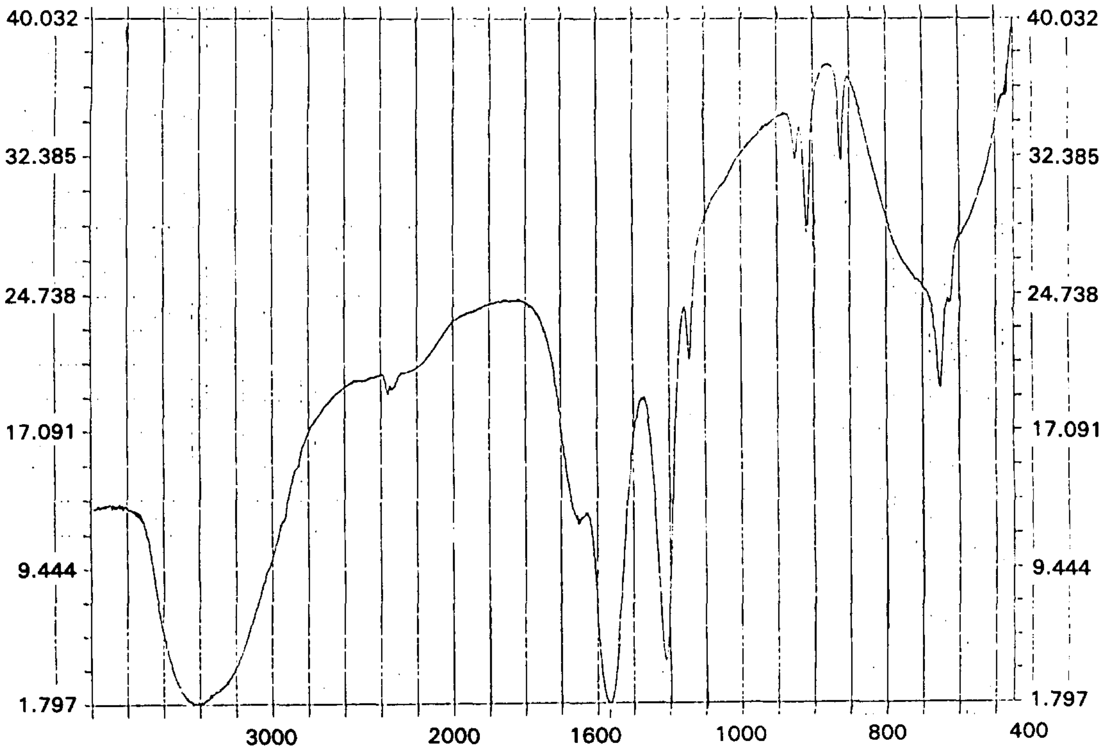

Figure 6 Infrared spectrum relative to the untreated material.

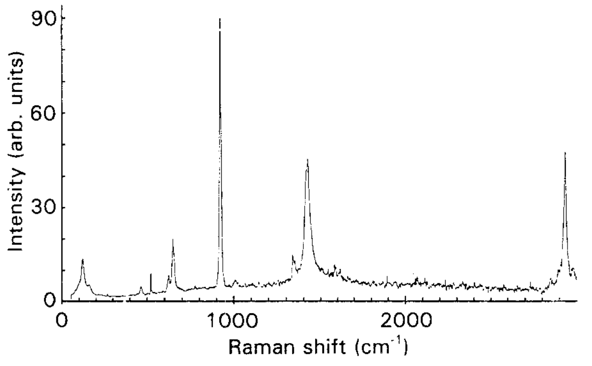

Figure 7 Raman spectrum relative to the initial powder.

3600 eV. The experimental method was described in detail in a previous paper [16]. The main improvement is that, at the present time, the recorded peaks are standardized with regard to the incident beam, and therefore it is proportional to the absorption coefficient. Thus it permits a comparison, in fact, of the height of the peaks. Each spectrum is recorded for about 8 min, and for the same sample a time of 1 min is required between each recording. Moreover, during each experiment the incident beam and the sample remain in a fixed position, which allows the same area to be analysed. The K edge of potassium has been recorded for two different samples (Fig. 8a–d). Before

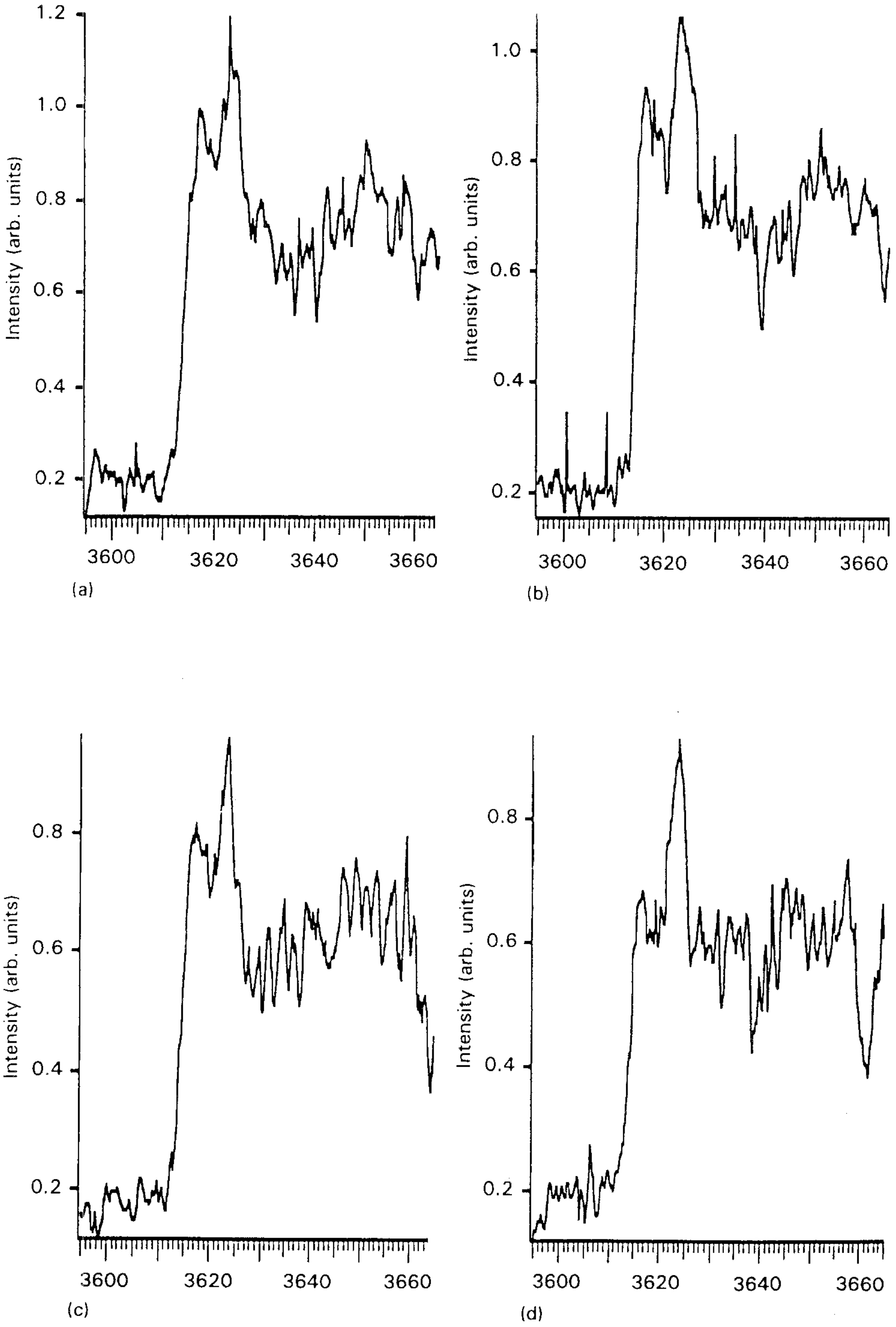

Figure 8 X-ray absorption spectra showing the evolution of the K edge of the potassium under the X-ray beam impact and as a function of thermal treatment: (a) initial powder (maintained 3 days under high vacuum); (b) same area after the powder had been subjected for 9 min to the X-ray beam; (c) powder treated under MW energy transfer; (d) same area after the powder had been subjected for 9 min to the X-ray beam.

exposure to the X-ray beam they were maintained for 3 days under vacuum (about 1.33×10^{-5} Pa). The first material relates to the untreated powder (Fig. 8a and b), and the second refers to the powder heated by means of the MW (Fig. 8c and d). The K edge is constituted by two sharp peaks located at 3617 and 3624 eV (error 0.2 eV), and by a broad peak of which the maximum is localized at about 3650 eV. From these spectra the following remarks can be made. First, during the experiment (i.e. as the X-ray radiation increases) the spectra clearly evolve. Second, the background is always intense. Third, the first peak (at 3617 eV) decreases in intensity and becomes more and more narrow (Fig. 8b and d). It appears also less intense and narrower for the powder treated by means of the MW. The same remark can be made for the broad peak (at 3650 eV) which becomes more and more intermingled with the background (Fig. 8d). Fourth, the higher peak (at 3624 eV) also decreases in intensity and seems to be directed towards a maximum close to 1.0 on the arbitrary unit scale (Fig. 8d). All these observations are probably linked either to the gettered water inside the matrix (intense background), or to desorption of water and OH^- radicals (decreasing peak intensity).

In this last case, possible variations in the chemical bonds could change the appearance of the peaks as increasing and decreasing slopes, and half-height width for instance. As no previous results have been published, the interpretation of the spectra will be made by comparison with other chemical species, such as KF.

4. Discussion

The commercial potassium acetate used for our experiments presented three main characteristics. First, the initial powder is formed by two species of particles characterized by two tetragonal structures. Such lattices do not correspond to those (monoclinic and orthorhombic) given by Hatibuara and Parry [6]. Second, the vanishing of the so-called T_2 phase after either MW energy transfer, or heating under vacuum, indicates that this solid phase corresponds to a hydrated form of acetate. It can be compared to the CH_3COOK, $1.5H_2O$ form reported by Bouaziz and Basset [11]. The fact that the infrared spectrum shows a broad absorption band at 3400 cm^{-1}, relative to the presence of water (or OH group), corroborates such a hypothesis. In the same way, XAS experiments show clearly that in spite of a preliminary out-gassing under high vacuum, the powders desorb water on impact of the X-ray beam. Third, for higher annealing temperature (413 K), a new structural transition occurs. But, once again, the interplanar spacings do not correspond to those given previously for other materials. Therefore, one can expect that annealing at higher temperature could change the crystalline characteristics, and could induce new chemical reactivities. In conclusion, it is thought that either MW treatments at low power (60 W), or heating at low temperature (363–373 K), allow a potassium acetate powder to be obtained which is characterized by a lower water ratio, and which induces better reactivity with other solid reactants, for example, alumina.

Acknowledgements

The authors thank Mrs G. Attard (IUT, Orsay, France) for the recording of the IR spectra, Dr B. Piriou (CNRS, Laboratoire PCM, Ecole Centrale de Paris, France) for the Raman Spectra, Dr P. Tremblay and Mrs M. Helmer (Laboratoire des Sciences de la Terre, Université Paris-Sud, Orsay) for scanning electron microscopy experiments, and Drs R. Karnatak and J. M. Esteva (Laboratoire de Chimie-Physique et LURE, Université Paris-Sud, Orsay) for X-ray absorption spectroscopy recordings.

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Received 13 October 1993
and accepted 10 May 1994