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# ŠTRUKTURÁLNE A MORFOLOGICKÉ VYŠETROVANIE STARNUTIA HYDRÁTU KYSLIČNÍKA WOLFRÁMOVÉHO PRI IZBOVEJ TEPLOTE V ALKALICKOM VODNOM PROSTREDÍ

## STRUCTURAL AND MORPHOLOGICAL OBSERVATIONS ON TUNGSTEN OXIDE HYDRATES AGED AT ROOM TEMPERATURE IN ALKALI CONTAINING AQUEOUS ENVIRONMENT

*V príspevku je analyzovaný proces starnutia zrn kysličníka wolfrámového ( $H_2WO_4 \cdot H_2O$ ) pri izbovej teplote pripravený metódami Freedmana [J. Am. Chem. Soc. 81 (1959) 38 B4.] ([Na] zvyšok < 10 ppm) a Zoherom a Jacobsonom [Kolloidchem. Beih. 28-6 (1929) 167] ([Na] zvyšok < 10 ppm). Porovnávajú sa tieto dve prípravné metódy a charakteristiky starnutia. Zistené boli vretenovité tvary - Zoherov typ zrn má silnú tendenciu k morfolologickej zmene závislej od veľkosti pH obklopujúceho vodného roztoku. Rastrovacía elektromikroskopia (SEM) a Fourierova transformačná interferenčná spektroskopia (FTIR), ktorej štúdie sú prezentované, ukazujú na vysokú štruktúrálnu a morfológickú stabilitu Freedmanovho typu zrn, čo môže byť zmenené prítomnosťou alkalických iónov. Bolo zistené tiež isté vmiešavanie katiónov.*

*The room temperature ageing process of tungsten oxide hydrate ( $H_2WO_4 \cdot H_2O$ ) grains prepared by the methods of Freedman [J. Am. Chem. Soc. 81 (1959) 3834.] ([Na]residual  $\leq$  10ppm) and Zoher and Jacobson [Kolloidchem. Beih. 28-6 (1929) 167.] ([Na]residual  $\geq$  100ppm) has been studied. A comparison between two preparation methods and ageing characteristics is given. It is found that spindle shaped - Zoher type grains have a strong tendency to morphological conversion depending on pH value of surrounding aqueous solution. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) studies have shown that the high structural and morphological stability of Freedman type grains can be altered by presence of alkali ions. Moreover, some incorporation of cations was observed.*

### 1. Introduction

Tungsten oxide hydrates are important basic materials for the tungsten industry involving the production of carbides, hard metals, heavy metals and electronic materials [1]. Due to the wide interest in science and large applicability in modern technology, numerous investigations were made on them. Several decades earlier this compound was successfully nominated as the parent phase for metastable hexagonal tungsten oxide representing an optimal substance in intercalation chemistry [2]. Starting from the same basic material with considerably high level of persistent background chemical impurity (residual sodium) and deliberately added organic residue, besides the hexagonal form another metastable polymorph, the cubic tungsten oxide with enlarged stability range was prepared in our laboratory [4]. In the latest reports new interesting properties came to light of already realized or prospective tungsten compounds, which could be easily synthesized from tungsten oxide hydrates [5]. Localized high critical temperature ( $T_c$ ) superconductivity was found on the surface of sodium doped tungsten oxide by Levi et al, thus initiating a potential candidature for tungsten oxides among superconductive materials which could revolutionize transportation, communications and could have impact

to several branches of industry. All of these observations enhance the necessity to control the alkali content and to establish the role of alkali concerning preparation processes and properties of derivatives. Other up to date applications such as electrochromic, photochromic and gasochromic devices using tungsten oxide as the basic-active material have attracted worldwide interest in recent years [6, 7, 8, 9]. These phenomena are related to color changes induced in selected materials by reversible electro-, photo-, gasochemical processes. The color changes result from the generation of different electronic absorption bands in the visible region, which is correlated to redox states switching. In commercial production for example, electrochromic or photoelectrochromic (electrochromic/solar cell sandwich constructions) windows, variable reflectance (antidazzle) mirrors for automobiles are already realized applications [6]. However, still uncertainty remained relating the mechanism of chromism phenomenon, such as long-term degradation and sensitivity against environmental conditions [8, 10]. Electro-, photo- and gasochromic devices are realized mainly by thin film processing, assuring porous structures and columnar morphologies for insertion host, enhancing ion mobility. Comparing the properties of films with bulk materials (grains in powder form) may result in new, surprising facts [9]. Continuing our study

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on ageing tungsten oxide hydrate grains [11], in this paper we present results on long-term observations of tungsten oxide hydrate grains in aqueous environments containing various alkali ions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  with various concentrations.

## 2. Experimental method

*Zocher (Z) type preparation.* A typical Z preparation is presented in Table 1.  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was dissolved in deionized water (70 g/l) and the solution was cooled to 5 °C. 1N hydrochloric acid solution (18 % in excess of equimolar reaction) cooled to the same temperature was added to the solution in several doses. The mixture was stirred (120 rpm, blade:  $52 \times 30 \text{ mm}^2$ ) for 1.5 hr in an ice bath and for 0.5 hr at room temperature. The precipitate was separated by centrifuging (5000 rpm). Washing of the precipitate was carried out by addition of water to the precipitate at room temperature followed by stirring and keeping the solid particles dispersed in the liquid. At the end of a washing step the mixture was centrifuged. Several washing steps were applied. After each washing step samples from the centrifuge were dried in exsiccator at room temperature and passed for investigations. The washing conditions were varied by the variation of the volume of the washing liquid, the stirring time and the duration of the washing steps, the effective time while the precipitate was contacted with the washing liquid. After each washing step samples with their mother liquids were collected to ageing analysis. In the case of Z preparations duration of one and two month was chosen for ageing observations. Properly cleaned polythene, or Teflon laboratory vessels and tools, deionized water ( $2 \mu\text{Scm}^{-1}$ ) and analytical grade reagents were used for the experiments.

*Freedman (F) type preparation.* Tungstic acid hydrate samples were prepared following the preparation route of Freedman [12] for comparison (Table 1). Washing of these precipitates was carried out by 0.1N HCl solution on filter. Stirring and centrifuging were

not used for the preparation of these samples. For long-term ageing investigations the tungsten oxide hydrate gels were mixed with water or alkali tungstate solutions and allowed to stay under solutions in polypropylene containers. The following alkali tungstates were deliberately added to solutions: potassium tungstate ( $\text{K}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ), sodium tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ), lithium tungstate ( $\text{Li}_2\text{WO}_4$ ) and ammonium metatungstate ( $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot 2 \cdot 6\text{H}_2\text{O}$ , with  $\text{WO}_3$  %: 91.3%,  $\text{NH}_3$  %: 3.35 %). The suspensions in containers were regularly re-mixed by hand shaking. Four months and 24 months ageing times were chosen for the F suspensions at room temperature.

*Characterization of samples.* The pH values of the washing liquids were also determined. The procedures of the sodium analysis have been described earlier [16]. X-ray powder patterns were recorded at room temperature in a Guinier focusing camera using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154051 \text{ nm}$ ). Infrared absorption spectra were taken by BOMEM MB-102 FT-IR spectrophotometer equipped with DTGS detector, at a resolution of  $4 \text{ cm}^{-1}$ , in the range of  $400\text{-}4000 \text{ cm}^{-1}$ ; 2 mg/g KBr pellets were used. The morphology of the solid products was studied by scanning electron microscopy with a JEOL-25 microscope. Samples of the strongly adhering powder for SEM have been prepared by controlled dispersing of the powder in deionized water [13]. Droplets of the mixture were poured on conductive specimens and after drying covered with a layer of sputtered gold.

## 3. Results and discussion

Evolution of morphology of Z type particles during ageing process is presented in Fig. 1. Spindle shaped morphology of  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$  particles (Fig. 1a) do not represent the final stage of morphology conversion. On longer interaction with liquid (long term ageing at room temperature) fine microsteps develop around the edges of the spindle shaped particles which finally transform

Table 1  
Summary of the preparation conditions for typical Z and F type grains. The concentration of Na is determined by atomic absorption spectroscopy, crystallographic structure by Guinier patterns and FTIR measurements [13]; drying: in exsiccator at room temperature.

Sample	Precipitation conditions			Washing conditions			Product of preparation		
	Quantity of starting $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ [g]	Temperature of precipitation [°C]	Number of washing steps	Volume of washing liquid [ml]	Stirring	Centrifuging, 5000 rpm	Time of interaction in one step [h]	XRD Guinier	[Na] in solid [ppm]
Z	10.5	5	5	600	mechanical, 120 rpm, 15 min	3 min	~ 1	$\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$	200
F	16.5	25	3 by 0.1N HCl on filter	2000	none	None	0.12	$\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$	< 10

Samples Z were prepared similarly to the method reported by Zocher [14]; Sample F1 was prepared following the method of Freedman [12]

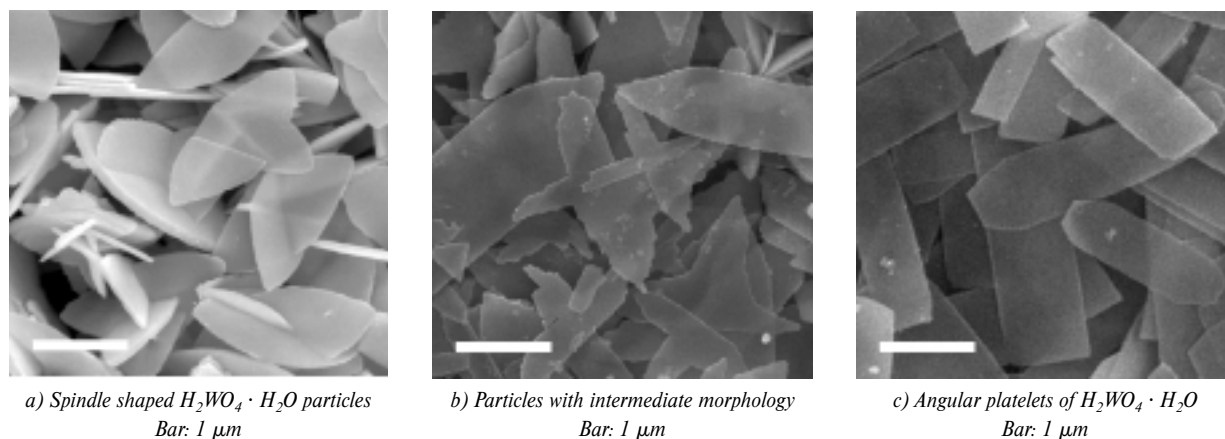


Fig. 1

into angular platelets as it was earlier observed [23] and studied by us in details [3,13]. Particles of  $H_2WO_4 \cdot H_2O$  with deteriorated spindles and intermediate morphology are shown in Fig. 1b. In Fig. 1c well-developed angular platelets represent the final morphology of  $H_2WO_4 \cdot H_2O$  observed after one month in aqueous ambient at room temperature. In earlier reports [3, 11] the pH values were identified, which accurately have described the ranges for morphological changes of Z, type particles. Shape conversions occurred in a pH band from 2.9 to 3.6 during one month ageing, and an enlarging tendency for pH band was observed from 2.8 to 4.9 in the case of two month ageing process [11].

Details about F type particles ageing characteristics can be followed in Table 2. Adhered irregularly shaped submicron grains of freshly prepared F preparation are shown in Fig. 2a. Similar to Z type particles well developed rectangular platelets can be observed after two month ageing in alkali ion free aqueous ambient (Fig. 2b). After 4 and 24 months of ageing on infrared spectra of the un-doped sample a structural conversion, dehydration of  $H_2WO_4 \cdot H_2O$  to  $WO_3 \cdot H_2O$  can be followed (Fig. 3). Room temperature

FTIR absorption bands assignments of the ageing products are presented in Table 3. At ageing of the grains in ammonium tungstate solution the transformation of the grains into new phase(s) are shown in Fig. 2d. After 4-month contact at room temperature between tungsten oxide hydrate grains and  $NH_4^+$  solution a peak at  $1400\text{ cm}^{-1}$  has appeared (Fig. 4b). This peak can be observed after 24 months contact at the same concentration as well (Fig. 4c). A change (breaking of bonds) in  $W = O$  and  $W - O - W$  bonds at lower vibrations than  $1200\text{ cm}^{-1}$  can also be noticed (Table 3.) Moreover, in the case of sample with higher concentration (Fig. 4d) even after 4 months aging one can observe a strong peak at  $1400\text{ cm}^{-1}$ . In this case the vibration changes below  $1200\text{ cm}^{-1}$  -presenting degradation of material- are more clearly shown. We found the peak at  $1400\text{ cm}^{-1}$  evolved in the case of  $S_1/[Li^+]$  sample as well, but with lower intensity than presented in the  $NH_4^+$  case. In solutions with  $Na^+$  and  $K^+$  only a small peak is developing at  $1400\text{ cm}^{-1}$  and the degradation of crystalline phase is more pronounced. According to reference [17], we assign this peak at  $1400\text{ cm}^{-1}$  with modes of adsorbed  $OH^-$ , the pair of this vibration being overlapped with stronger vibrations of struc-

Summary of ageing conditions for F type particles. Samples  $S_1/[Li^+]$  and  $S_1/[Na^+]$  dissolved in the alkali tungstate solutions after a few days.

Table 2

Sample	$H_2WO_4 \cdot H_2O$ g	Added alkali tungstate solution		pH immediately after mixing	pH after 2 months
		Volume ml	Concentration of alkali ion, N		
$S_{undoped}$	0.72	76		2.34	2.23
$S_1/[NH_4^+]$	0.72	50	0.095	2.49	2.59
$S_2/[NH_4^+]$	0.72	28	0.017	2.12	2.00
$S_1/[K^+]$	0.72	50	0.095	6.88	6.28
$S_2/[K^+]$	0.72	30	0.016	3.61	3.92
$S_1/[Na^+]$	0.72	50	0.097	6.42	6.22
$S_2/[Na^+]$	0.72	30	0.016	3.61	4.42
$S_1/[Li^+]$	0.72	50	0.095	5.96	6.33
$S_2/[Li^+]$	0.72	30	0.016	3.31	5.06

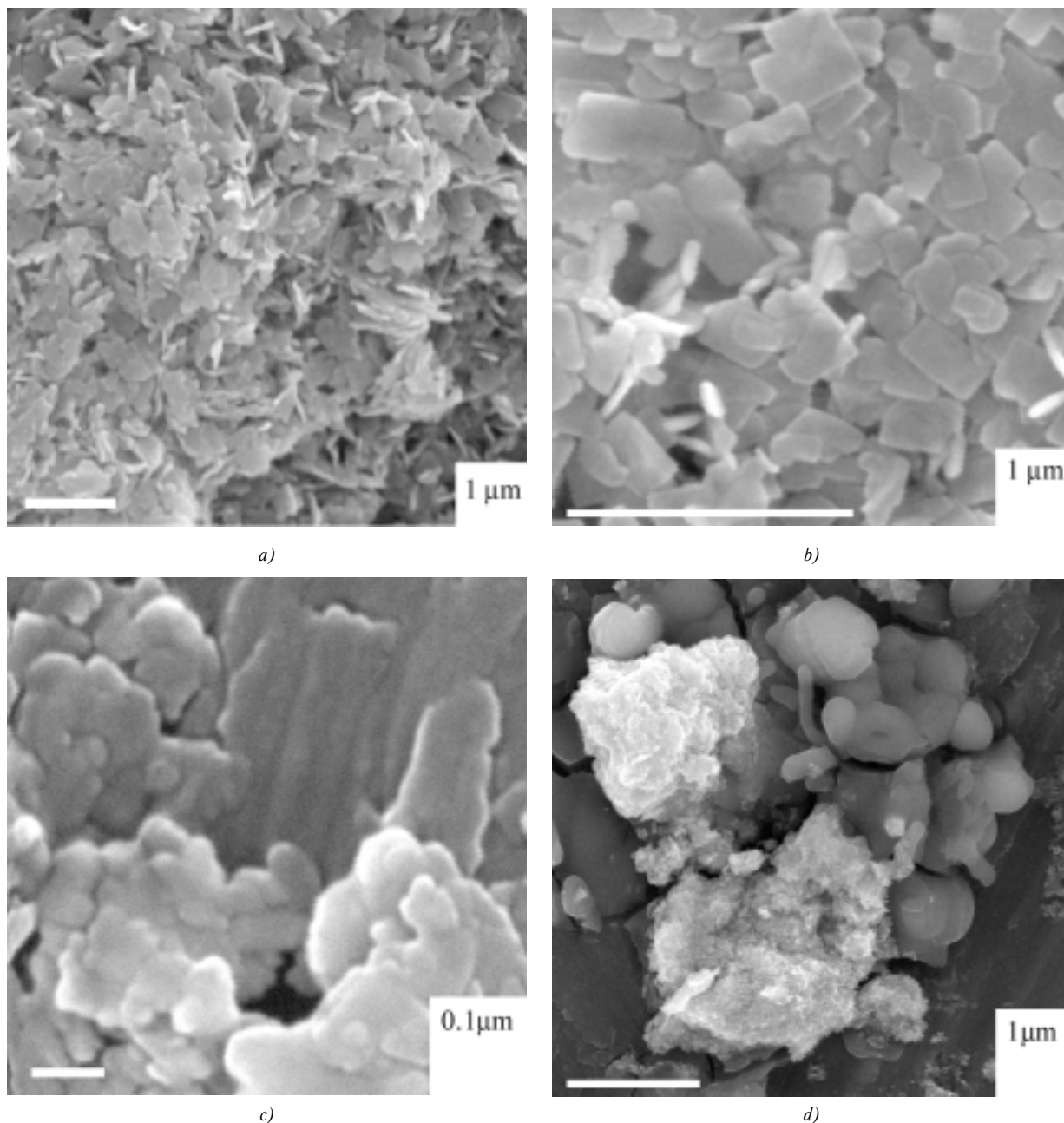


Fig. 2.

tural water in our case (in the range of  $3000-3600\text{ cm}^{-1}$ ). On the basis of IR spectroscopic measurements we consider that this peak is an indicator for the presence of alkali ions in solution. In this regard is interesting to recall some of the discussions about several ion insertion studies [8,18,19]. J-G. Zhang et al. [18] considered the following ion-exchange reaction at  $\text{Li}^+$  insertion in  $\text{WO}_3$  films, for small  $x$  values in  $\text{Li}_x\text{WO}_3$ :  $(\text{W} - \text{OH}) + \text{Li}^+ \rightarrow (\text{W} - \text{OLi}^+) + \text{H}^+$ . They found a diffusion coefficient for  $\text{Li}^+$  higher in the presence of humidity than in dry environment. In agreement with our observations, their IR measurements also showed

a peak at  $1400\text{ cm}^{-1}$ , but discussions about it were not given. Papaefthimiou et al. constructed an efficient electrochromic (EC) device with significant contamination of  $\text{H}_2\text{O}$  and  $\text{OH}^-$  shown in their IR and XPS (X-ray photoelectron spectroscopy) measurements. They note that diffusion coefficient is high in presence of  $\text{OH}^-$  radicals during  $\text{Li}^+$  intercalation process. The irreversibility of this process however (when most of the exchangeable  $\text{OH}^-$  radicals are exhausted) may lead to degradation of EC device. Not surprisingly, we found in ageing products the  $1400\text{ cm}^{-1}$  peak well developed in the case of  $\text{Li}^+$  which has the smallest ionic radius,

Room temperature FTIR absorption bands assignments of the ageing products, drying: in exsiccator at room temperature.

Table 3

Assignations Sample	$\nu$ HOH (H <sub>2</sub> O)	$\delta$ HOH (H <sub>2</sub> O)	$\nu$ W = O	$\nu$ O-W-O	$\delta$ O-W-O	W-OH (W-OHNH <sub>4</sub> )	Reference
S <sub>undoped</sub> 4 month ageing	3536 3374 3177	1605	1005 940 910	682 630	425 377		
S <sub>undoped</sub> 24 month ageing	3424	1626	945	665	-		[17]
S <sub>1</sub> /[NH <sub>4</sub> <sup>+</sup> ] 4 months ageing	3549 3409 3195	1630	1010 947 922 918	785 721 671	(426)	<b>1406</b>	[17, 20, 21]
S <sub>2</sub> /[NH <sub>4</sub> <sup>+</sup> ] 4 months ageing	3549 3407 3204	1630	1009 947 926	719 659	466	<b>1410</b>	[17, 20, 21]
S <sub>2</sub> /[NH <sub>4</sub> <sup>+</sup> ] 24 months ageing	3557 3434 3208	1636	1010 954 951	681	(466)	1410	[17,20,21]

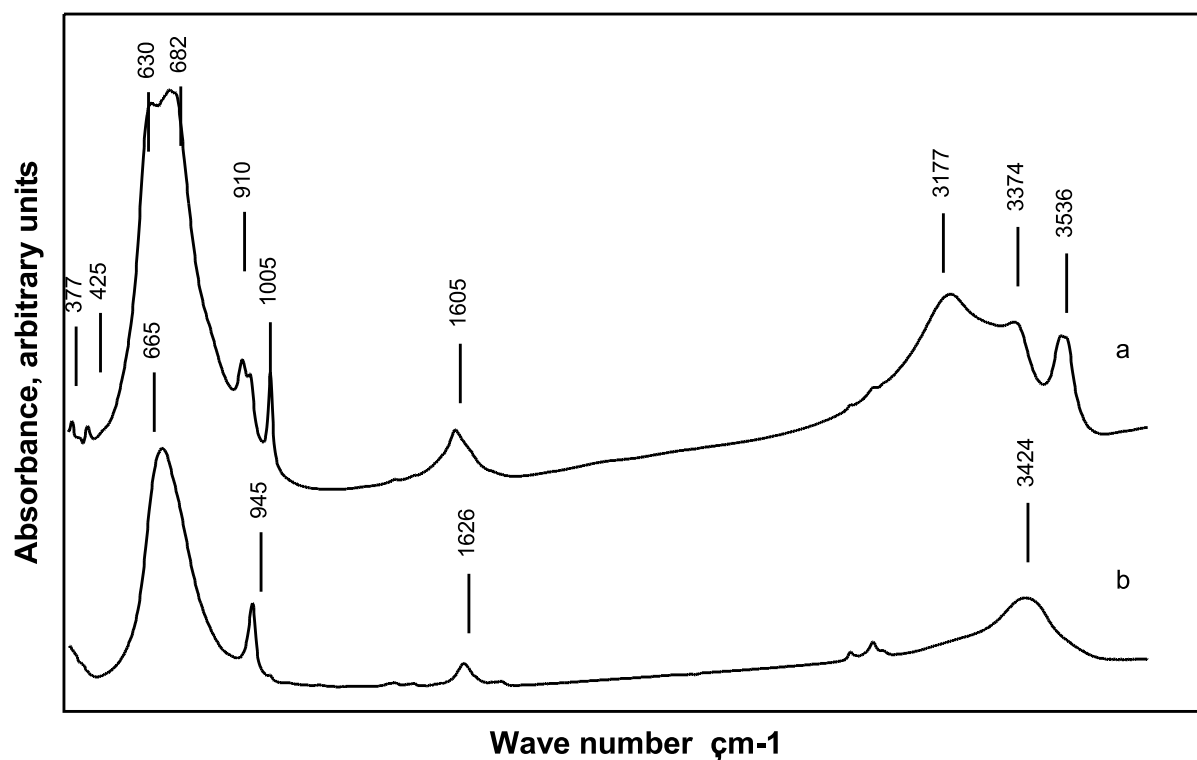


Fig. 3.

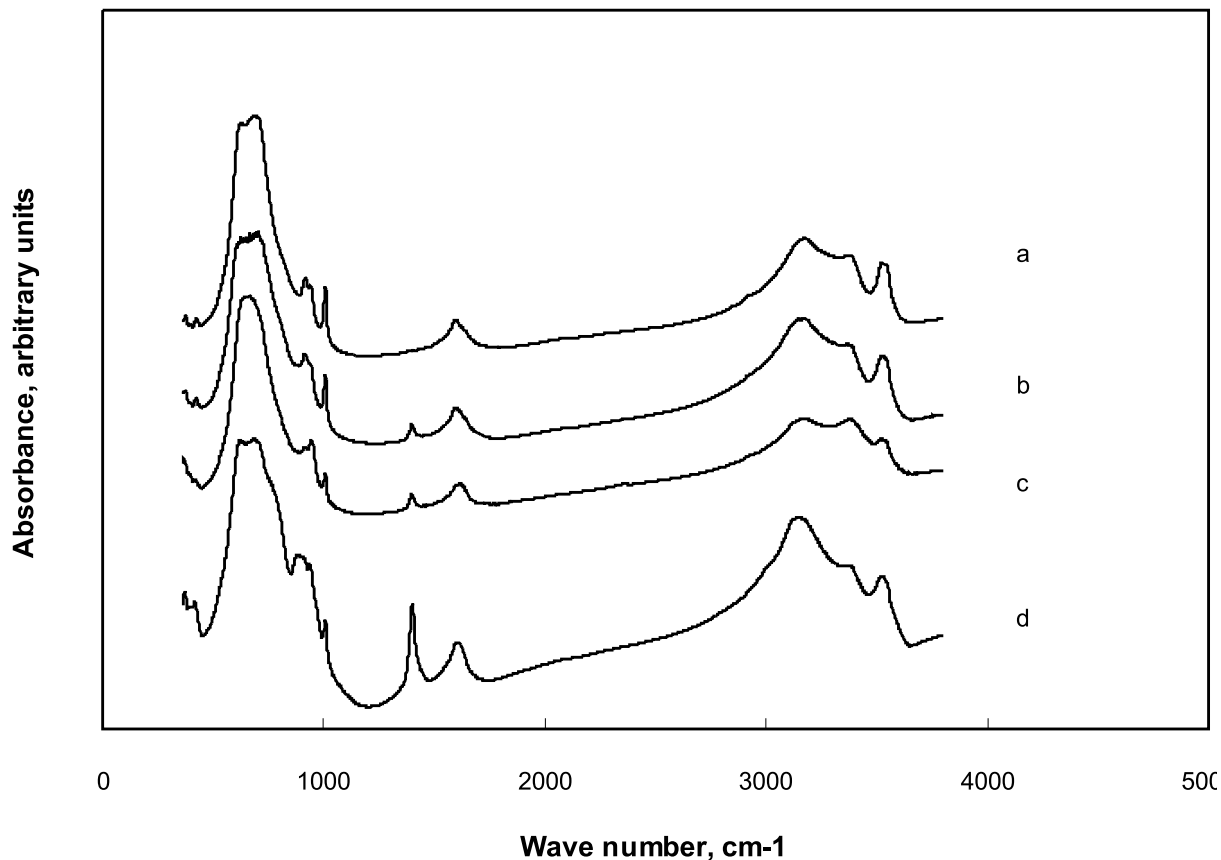


Fig. 4.

60(+1) pm. In the case of  $\text{NH}_4^+$  that has ionic radius larger than  $\text{Na}^+$  – 95(+1) pm and  $\text{K}^+$  – 133(+1) pm we should consider the role of large amount of proton species chemically present on neighboring places close to tungsten-oxygen octahedral units ( $\text{WO}_6$ ). In our opinion this fact could explain the increasing peak intensity with increasing ion concentration (Fig. 4). Judeinstein and Livage [24] have recently measured a lithium diffusion coefficient 10-100 times greater for  $\text{WO}_3$  monohydrate than for anhydrous  $\text{WO}_3$ . The authors assumed that water molecules were strongly involved in the ionic conduction mechanism (e.g.  $\text{Li}^+$  ions in  $\text{WO}_3 \cdot \text{H}_2\text{O}$  remain close to the water molecules in the interfoliar space, whereas the whole oxide is affected in the anhydrous oxide). Cheng et al. and Gui et al. have published IR data for ammonium tungstate compounds  $(\text{NH}_4\text{OH})_x \cdot \text{WO}_3$  ( $0.13 < x < 0.33$ ) and  $(\text{NH}_4)_{0.25}\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$  revealing a well-developed peak at  $1400 \text{ cm}^{-1}$ . Summarizing the presented literature data and our FTIR results it can be concluded that ageing at room temperature in alkali solutions resulted in incorporation of alkali ions into the tungstate structure,  $\text{NH}_4^+$  represents the most relevant case in our examinations.

#### 4. Conclusions

Zocher and Freedman type acidic precipitation of tungsten oxide hydrate grains have been performed. Considerable differences have been found between Z and F type preparations. High morphological and structural stability of F type grains can be altered by the presence of alkali ions in solution. The grains develop into a more regular shape in un-doped low pH ambient. In the presence of cations the preservation of the grain shape, the intergrowth of grains and the full recrystallization depend on the chemical character (and concentration) of the cation. On long-term observations a peak at  $1400 \text{ cm}^{-1}$  is developing on IR spectra. Compared with literature this peak should be assigned with  $\text{W} - \text{OH}$  vibration, but taking into consideration the insertion processes more likely with  $\text{W} - (\text{OHNH}_4)$  vibration. The important role of  $\text{OH}^-$  radicals should be underlined.

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