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# Synthesis and characterization of $TeO_2/TiO_2$ powders obtained through Te (VI) acid

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The present study is focused on the possibility for obtaining $TeO_2$ containing powders in the $TeO_2$–$TiO_2$ system applying a low temperature wet chemistry method. Telluric (VI) acid ($H_6TeO_6$) and titanium butoxide were used as a new combination of precursors. Two compositions with high $TeO_2$ content (80, 90 mol%) were selected. Yellow coloured powders were obtained and they were characterized by XRD, IR and UV-Vis analysis. The crystallization tendency of the powders in the temperature range 300–600 °C was studied as well. The crystallization process started at heat treatment above 300 °C. Composite powders containing α-$TeO_2$ (paratellurite) and $TiTe_3O_8$ were obtained as final products.

**Key words:** telluric (VI) acid, $TeO_2$, $TiTe_3O_8$.

## INTRODUCTION

Tellurium oxide – based materials have attracted considerable research interest in recent years due to their high refractive index, good non-linear optical properties and electrical semiconductivity appealing for various applications [1–4]. Up to now different methods for synthesis of Te-based materials were applied such as: melt quenching technique, chemical or physical vapour deposition, pulverization, molecular beam epitaxy or laser ablation [5]. It is known that most tellurium-based oxide materials can be synthesized at temperatures below 900 °C. Recently, much attention has been paid on applying the low temperature sol-gel method, which is an attractive alternative to the high temperature melt quenching route. The main disadvantage of this method is using of tellurium alkoxides, which possess high sensitivity to the moisture in air. Up to now, there are a few papers, which reported on sol-gel processing of $TeO_2$ powders and films using $H_6TeO_6$ as a precursor for obtaining Te (VI) alkoxide [4, 6]. Beaudry et al. [7] reported on synthesis of high purity $TeO_2$ powders applying a wet chemistry method, starting from elementary Te and $HNO_3$ as precursors. Several authors successfully prepared tellurium dioxide nanoparticles using different methods [8, 9].

On the other hand the binary $TeO_2$–$TiO_2$ system is very interesting one due to the existence of thermodynamically stable compound $TiTe_3O_8$, which possesses microwave-dielectric properties [10–12]. Up to now it has been synthesized mainly via solid-state reaction method in the temperature range 650–700 °C [12, 13]. However, it is difficult to obtain pure $TiTe_3O_8$ by solid state reaction of $TiO_2$ and $TeO_2$ because the volatilization of $TeO_2$ occurs rapidly at high temperatures [11].

The aim of this study was to verify the possibility for obtaining $TeO_2$ – based powders and $TiTe_3O_8$ compound in the $TeO_2$–$TiO_2$ system using telluric (VI) acid ($H_6TeO_6$) and titanium butoxide as a new combination of precursors. This investigation is an attempt to prepare such powders more readily and less expensively aiming to overcome the problems when using of tellurium alkoxides.

## EXPERIMENTAL

### *Samples preparation*

Two samples with high $TeO_2$ content and nominal compositions $90TeO_2.10TiO_2$ (sample 1, mol%)

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and $80TeO_2.20TiO_2$ (sample 2, mol%) were selected. It is well known that there are problems concerning the high hydrolysis rate of the tellurium alkoxides [4, 14]. In order to overcome this problem we used Te(VI) acid (Aldrich) in combination with Ti butoxide (Fluka AG) and ethylene glycol ($C_2H_6O_2$) (99% Aldrich). The scheme for synthesis is presented in Figure 1. Solutions (A and B) were prepared via dissolving of the precursors in ethylene glycol by means of vigorous magnetic stirring. Thus, white precipitates were obtained and subsequently they were subjected to evaporation at ~60 °C and heating on a hot plate at ~100–150 °C. A stepwise heating of the samples from 400 to 600 °C for 2 hours exposure time in air was performed, until obtaining powders (samples 1 and 2). The calcination temperature was selected on the basis of our previous investigations [15]. As we found earlier, there is no presence of organic constituents above 400 °C. The pH during the experiments was measured to be about 7.

### *Samples characterization*

Powder X-ray diffraction (XRD) patterns of the samples were registered at room temperature with a Bruker D8 Advance diffractometer using Cu-Kα radiation. The main short range orders of the powders were determined by IR spectroscopy (Nicolet 320 FTIR spectrometer). The infrared spectra were registered in the range 1600–400 $cm^{-1}$ using the KBr pellet technique on a Nicolet-320 FTIR spectrometer with 64 scans and a resolution of ±1 $cm^{-1}$. The optical absorption of the obtained powders was measured by UV-Vis analysis (Spectrophotometer Evolution 300).

## RESULTS AND DISCUSSION

The XRD patterns of the yellow coloured $TeO_2$/$TiO_2$ powders (samples 1 and 2) are shown in Figure 2. As is seen, the metallic tellurium (ICDD, PDF 78-2312) is found predominantly in the samples up to 400 °C. It is possible this phase to be completely removed by oxidation at temperatures above 450 °C [16]. At this temperature separation of paratellurite (α-$TeO_2$, ICDD, PDF 42-1365) is also registered. With increasing the temperature (up to 500 °C) the paratellurite became a dominant phase and formation of the crystalline $TiTe_3O_8$ (ICDD, PDF 50-0250) phase occurred. With further increasing of the heating temperature (600 °C), all above pointed out crystalline phases were found to be present. In the XRD pattern of sample 1 (90 mol% $TeO_2$), α-$TeO_2$ remains as a main phase, while in the other sample 2 (80 mol% $TeO_2$), $TiTe_3O_8$ is the predominant one (Fig. 2). Probably, this phase ($TiTe_3O_8$) has wide primary crystallization field. Thus, our XRD data

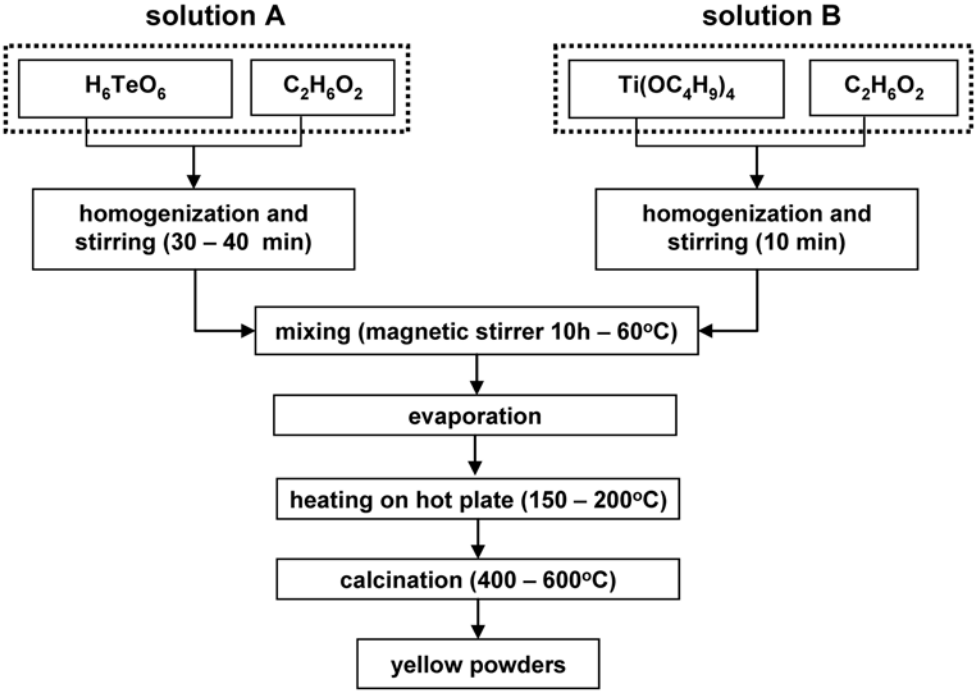

**Fig. 1.** Scheme for the low temperature synthesis of $TeO_2/TiO_2$ powders

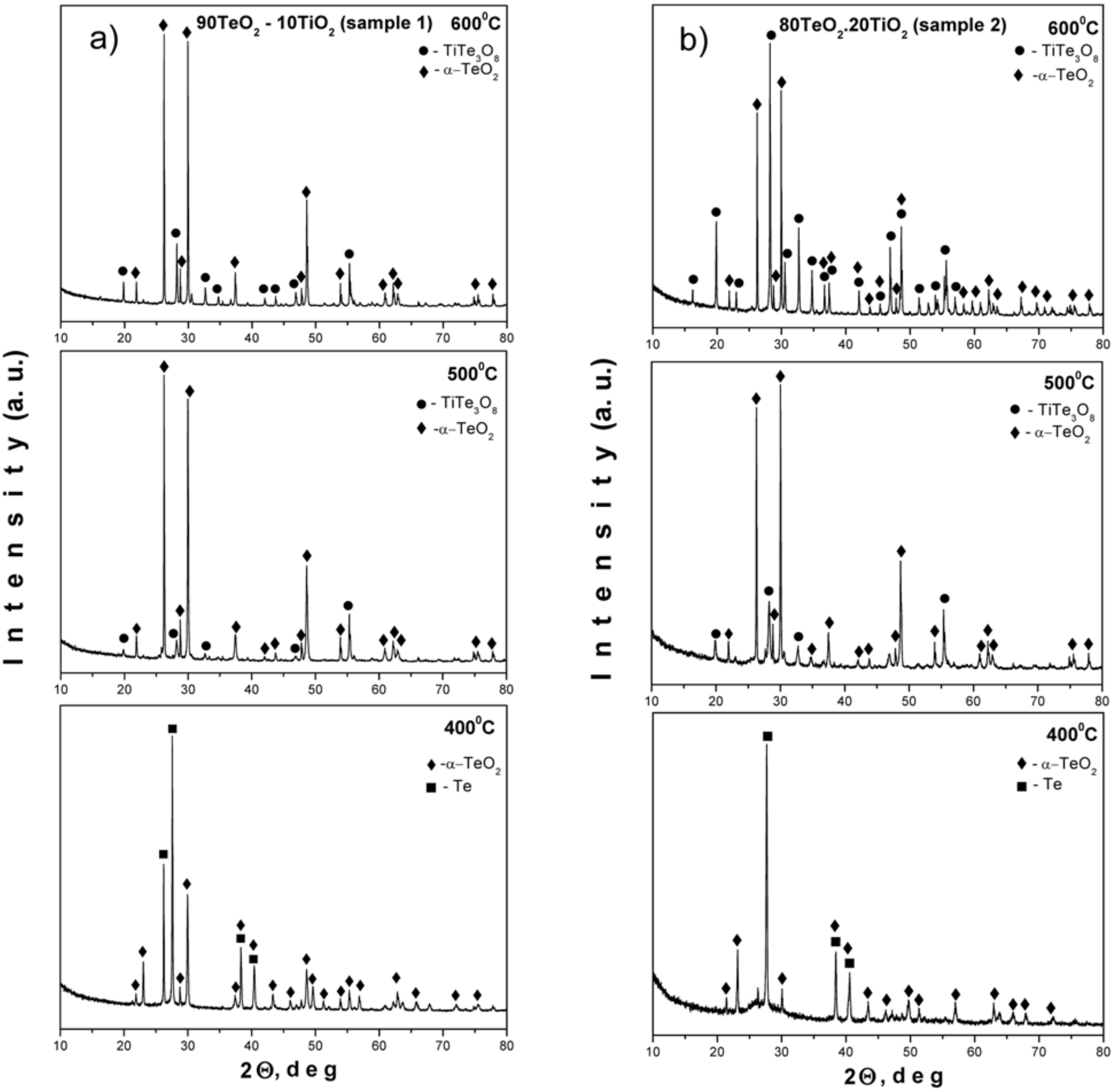

**Fig. 2.** XRD patterns of samples: a) $90TeO_2.10TiO_2$ (sample 1) and b) $80TeO_2.20TiO_2$ (sample 2)

are in good accordance with those obtained by other authors [2, 3, 17], who established formation of these phases using other precursors but at similar heating temperatures. By the way, for comparison XRD patterns of elementary tellurium, $TeO_2$ and $H_6TeO_6$ (JCPDS 70-1524) are shown as well (Fig. 3).

The phase transformations during the heat treatment were monitored also by IR spectroscopy. All IR spectra of the calcinated at different temperatures samples 1 and 2 are shown in Fig. 4a, b. At low temperatures (200 °C) characteristic bands in the range 1500–800 $cm^{-1}$ were observed. Generally, they may be attributed to the C-OH stretching vibrations of $C_2H_6O_2$ and Ti butoxide [18]. The residual organic groups disappeared above 200 °C. At 400 °C the IR spectra of both samples are characterized by wide absorption bands in the range 770–460 $cm^{-1}$, which could be assigned to the vibrations of Me–O (Me = Ti, Te) complexes [19–21]. The IR spectra at 500 °C of both samples are very similar and vibrations at 770, 670-650, 630, 480-460 $cm^{-1}$ were observed. The increase in the temperature (up to 600 °C) led to some changes in the IR spectra. The IR spectrum of sample 1 is typical for the crystalline $TeO_2$ [19].

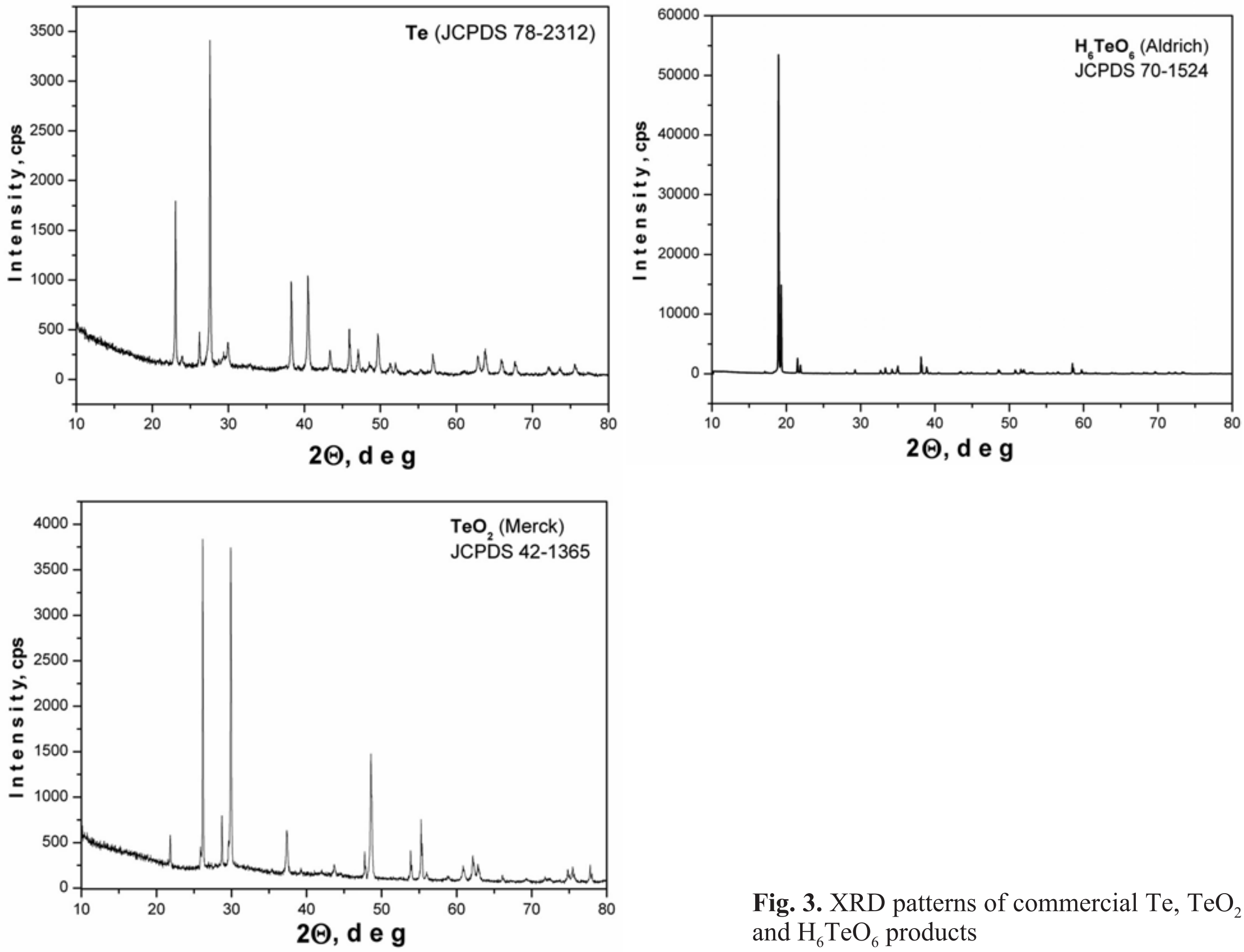

**Fig. 3.** XRD patterns of commercial Te, $TeO_2$ and $H_6TeO_6$ products

Intensive bands at 770 cm$^{-1}$ ($\nu^s$) and 670 cm$^{-1}$ ($\nu^{as}$) with a shoulder at 630 cm$^{-1}$ ($\nu^s$) were registered, which may be related to the stretching vibrations of $TeO_4$ groups (Fig. 4a). The IR spectrum of the other sample 2 is more close to that of the crystalline $TiTe_3O_8$ phase (Fig. 4b) [19]. The data obtained by IR spectroscopy are in good accordance with the XRD data.

The optical absorption spectra of the investigated samples are presented in Figure 5. As is seen from

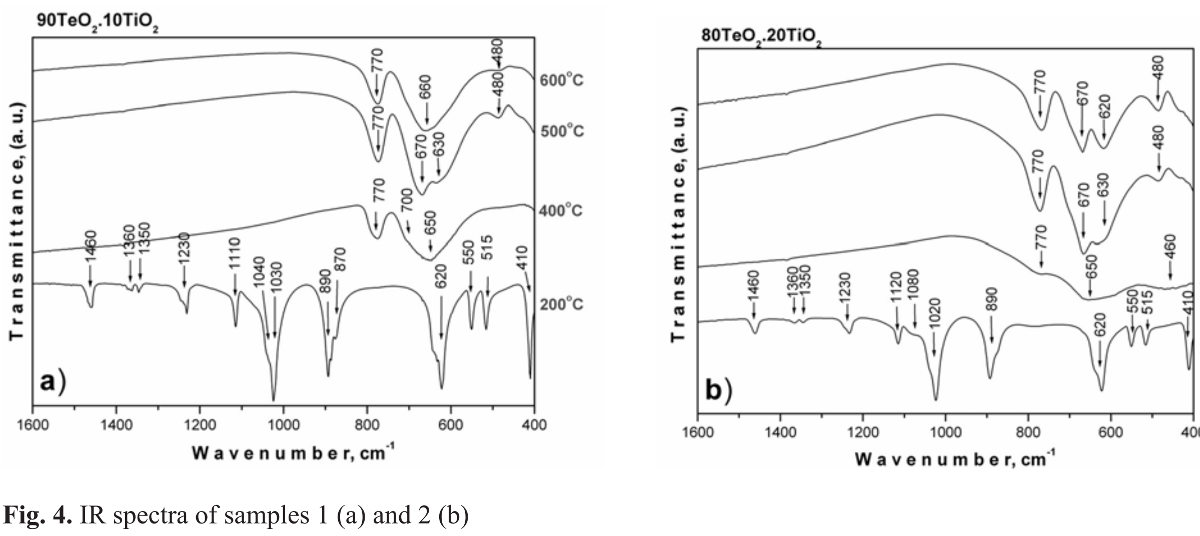

**Fig. 4.** IR spectra of samples 1 (a) and 2 (b)

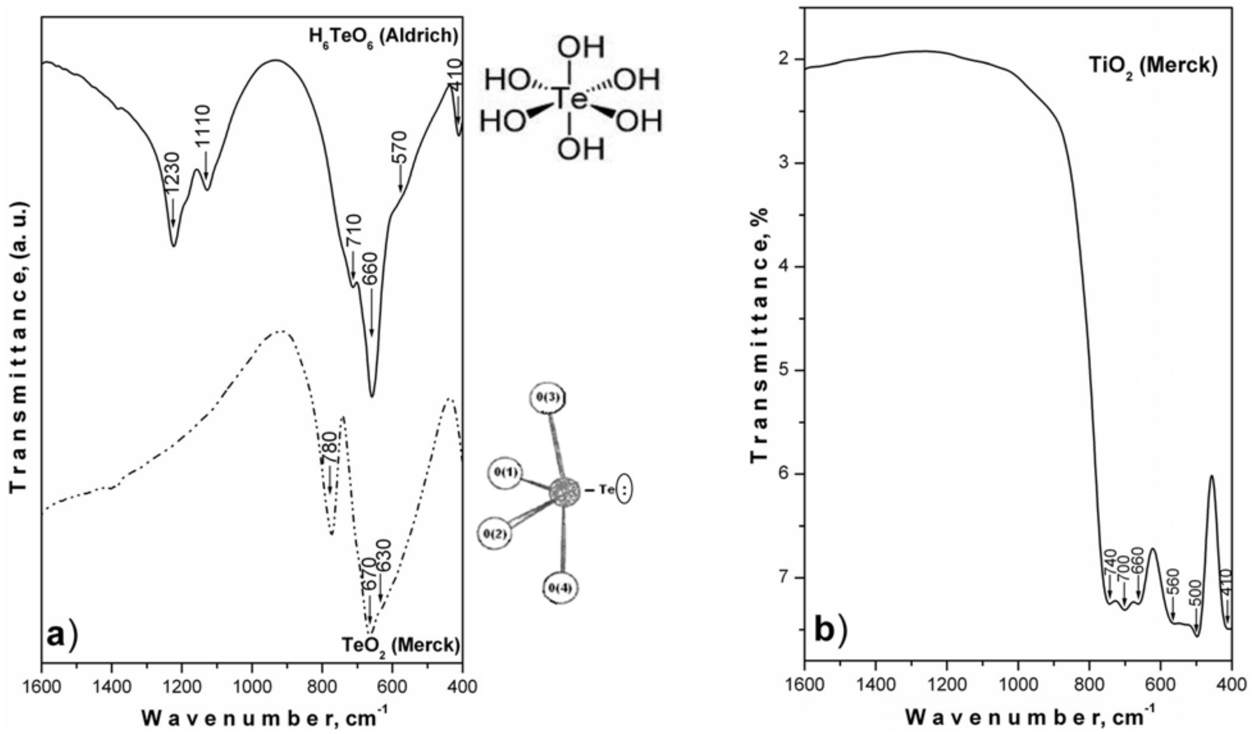

**Fig. 5.** IR spectra of: a) $TeO_2$ and $H_6TeO_6$; b) $TiO_2$

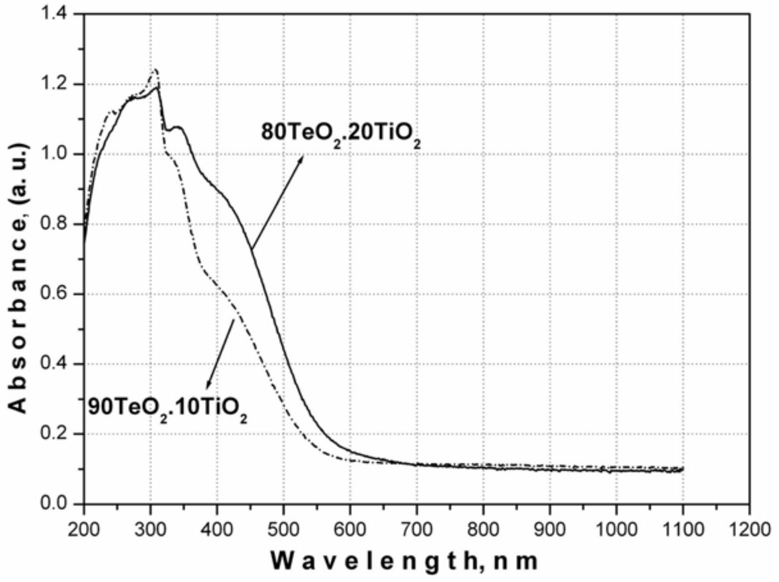

**Fig. 6.** UV-Vis absorption spectra of the investigated powder samples heated at 600 °C

the figure the sample containing lower $TeO_2$ content (80 mol%) exhibited more intensive absorbance in the UV spectra than those containing 90 mol% $TeO_2$. The absorption spectra were used to determine the optical band gap ($E_{opt}$) of both samples. For sample 1 $E_{opt}$ is 3.45 eV, while for sample 2 it is 3.43 eV. According to Weng and Hodgson [3] similar powder compositions (containing 80, 90 mol% $TeO_2$) exhibited optical band gap value about 3.3 eV. Our values are higher than these obtained for the $TeO_2$/$TiO_2$ thin films (~3.29 eV) [14] but lower than the value of melted bulk tellurite glass (~3.79 eV).

## CONCLUSIONS

Yellow coloured powders were obtained using a low temperature wet chemistry method. The crystallization tendency of the powders in the range 300–600 °C was studied. The crystallization process started at heat treatment above 300 °C and mixtures containing α-$TeO_2$ and $TiTe_3O_8$ were obtained depending on composition and heating temperature. The observed crystalline phases are in different quantity depending on the $TeO_2/TiO_2$ ratio. According to the IR results, the organic constituents existed below 400 °C and characteristic bands for α-$TeO_2$ and $TiTe_3O_8$ were observed at 600 °C. The obtained powders would be promising candidates for optical applications.

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# СИНТЕЗ И ХАРАКТЕРИЗИРАНЕ НА $TeO_2/TiO_2$ ПРАХОВЕ, ПОЛУЧЕНИ ОТ Te (VI) КИСЕЛИНА

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(Резюме)

Настоящото изследване е фокусирано върху възможността за получаване на $TeO_2$ прахове в системата $TiO_2$–$TeO_2$ прилагайки един ниско температурен метод. Телурова (VI) киселина и титанов бутоксид са използвани като една нова комбинация от прекурсори. Като обекти на изследване бяха подбрани два състава с високо съдържание на $TeO_2$ (80, 90 mol%). Получени са жълти прахове, които са характеризирани с РФА, ИЧ и УВ-Вис спектроскопия. Изследвана е кристализационната тенденция на праховете в интервала 300–600 °С. Установено бе, че кристализационния процес започва при нагряване над 300 °С. Композитни прахове съдържащи α-$TeO_2$ (парателурит) и $TiTe_3O_8$ са получени като крайни продукти.