

## Synthesis and crystallization of gels in the $\text{TiO}_2\text{--TeO}_2\text{--ZnO}$ system

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Transparent and monolithic gels were obtained in the ternary  $\text{TeO}_2\text{--TiO}_2\text{--ZnO}$  system. The gel formation region is situated between 10–100 mol%  $\text{TiO}_2$ , up to 65 mol%  $\text{TeO}_2$  and up to 90 mol%  $\text{ZnO}$ . Tellurium alkoxides, the telluric (VI) acid ( $\text{H}_6\text{TeO}_6$ ) along with zinc acetate and titanium butoxide were used as a combination of precursors during the synthesis. The phase transformations of the gels in the temperature range 200–700 °C were investigated by XRD method. It was established that above 200 °C composites were obtained and they contain an amorphous phase and different crystalline phases:  $\text{TiO}_2$  (anatase),  $\alpha\text{-TeO}_2$ ,  $\text{TiTe}_3\text{O}_8$ ,  $\text{ZnTeO}_3$ ,  $\text{ZnTiO}_3$  и  $\text{Zn}_2\text{TiO}_4$  depending on composition and heating temperature. The IR results showed that the short range order of the amorphous phases which are part of the composite materials consist of  $\text{TiO}_6$ ,  $\text{ZnO}_4$  and  $\text{TeO}_4$  structural units.

**Key words:** sol-gel, telluric (VI) acid, crystallization.

### INTRODUCTION

It is well known that amorphous tellurite materials possess good physical and chemical properties which make them good candidates for new optical devices due to their high refractive index, high dielectric constant, wide band infrared transmittance and large third order non-linear optical susceptibility [1]. Pure  $\text{TeO}_2$  is well known conditional network-former although it does not form glass alone, even at high cooling rates [2]. Binary and multicomponent  $\text{TeO}_2$ -based glasses were studied and summarized in El-Mallawany's book [1]. The sol-gel method is an attractive alternative to the melt quenching method that may be used to extend application of new tellurite compositions. Powders and films in the  $\text{TiO}_2\text{--TeO}_2$  and  $\text{TeO}_2\text{--PbO--TiO}_2$  systems were reported in several papers irrespective of the high hydrolysis rate of the Te (VI) alkoxides [3–5]. It was established that sol-gel derived tellurite coatings and glasses exhibit greater resistance to devitrification than melt quenched glasses [3–5]. On the other hand,  $\text{TiO}_2$ -based materials have always been of primary research interest for materials chemistry.

This interest is mostly driven by the unique properties of  $\text{TiO}_2$  and its ability to create high surface area structures suitable for photo catalysis and sensors [6].  $\text{ZnO}$  is an intermediate oxide and in the past years it is the preferred one for obtaining of transparent glass-ceramics applying conventional melt-quenching method. These materials combine the unique properties of  $\text{ZnO}$  as well as its good network formation ability.

As mentioned above the binary  $\text{TiO}_2\text{--TeO}_2$  system is of special interest, as it has been shown that  $\text{TiO}_2$  inhibits structural changes of the Te polyhedra and maintains a continuous glass network [7, 8]. Moreover, it was found that the addition of  $\text{TiO}_2$  increases the thermal stability of  $\text{TeO}_2$ -based glasses by replacing Te-O-Te linkages by more rigid Te-O-Ti ones [9]. The glass forming tendency in the binary  $\text{ZnO--TeO}_2$  system was also studied and the corresponding glasses were found to be stable [10]. Structural investigations on the  $\text{TeO}_2\text{--ZnO}$  binary glasses were also reported [11–15]. Recently, the structure of the binary  $(100-x)\text{TeO}_2\text{--}x\text{ZnO}$  glass was studied using EXAFS data [16]. Several investigations on the refractive index and the optical band gap for binary and ternary zinc tellurite glass system have been published [17–20]. A large number of investigations are devoted to the sol-gel productions of composite materials in the binary  $\text{TiO}_2\text{--ZnO}$ .

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Coupled semiconductor photocatalyst of  $\text{TiO}_2/\text{ZnO}$  has been investigated to enhance the photodegradation efficiency of  $\text{TiO}_2$  catalyst by a number of researchers and its effect for improving photocatalytic efficiency was reported [21–22]. The results showed that the photocatalytic activity of  $\text{ZnO}/\text{TiO}_2$  coupled photocatalysts was higher than that of the single phase [23].

Up to now the thermal, optical and structural properties of glasses in the ternary  $\text{TiO}_2\text{-TeO}_2\text{-ZnO}$  system have been studied by Kabalci et al. [24] as well as by N. Ghribi et al. [25]. But there is no data for gel formation in this ternary system.

The main purpose of this paper is to study the gel formation tendency in the three-component  $\text{TiO}_2\text{-TeO}_2\text{-ZnO}$  system, to identify the phases and structural evolution of the gels upon heating as well as to verify the compatibility of the structural units in the amorphous phase.

were used. Telluric acid ( $\text{H}_6\text{TeO}_6$ ) is selected to overcome the problem with the high hydrolysis rate of tellurium (VI) alkoxide that has been reported in several papers [26–28]. The precursor solutions were subjected to 5–30 min intensive stirring at room temperature in order to achieve complete dissolution. No direct addition of water was made to the precursors' solutions. Sol-gel hydrolysis reaction was acquired from absorbed atmospheric moisture. The measured pH is 4–5 depending on composition. The gelation time for the investigated compositions was from 1 to 5 min. The aging of gels was performed in air for several days (~ one week) to complete the processes. The obtained gels were subjected to the stepwise heating from 200 to 700 °C in air. The heat treatment at 200 °C was performed in order to hydrolyze any unreacted OR groups. Further increasing of temperatures (300–700 °C) was conducted to verify the phase and structural transformations of the gels. Selected gels, containing a constant  $\text{TiO}_2$  amount (40 mol%) were subjected to more detailed phase analysis (Figs. 4 and 7, Table 1).

## EXPERIMENTAL

### Samples preparation

The scheme for sol-gel synthesis of  $\text{TiO}_2/\text{TeO}_2/\text{ZnO}$  compositions is presented in Figure 1. A combination of Te(VI) acid (Aldrich) along with Ti butoxide (Fluka AG), Zn acetate (Merck) precursors dissolved in ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) (99% Aldrich)

### Samples characterization

Powder XRD patterns were registered at room temperature with a Bruker D8 Advance diffractometer using  $\text{Cu-K}_\alpha$  radiation. The morphology of the samples was examined by scanning electron microscopy (SEM) using a JEOL JSM 6390 elec-

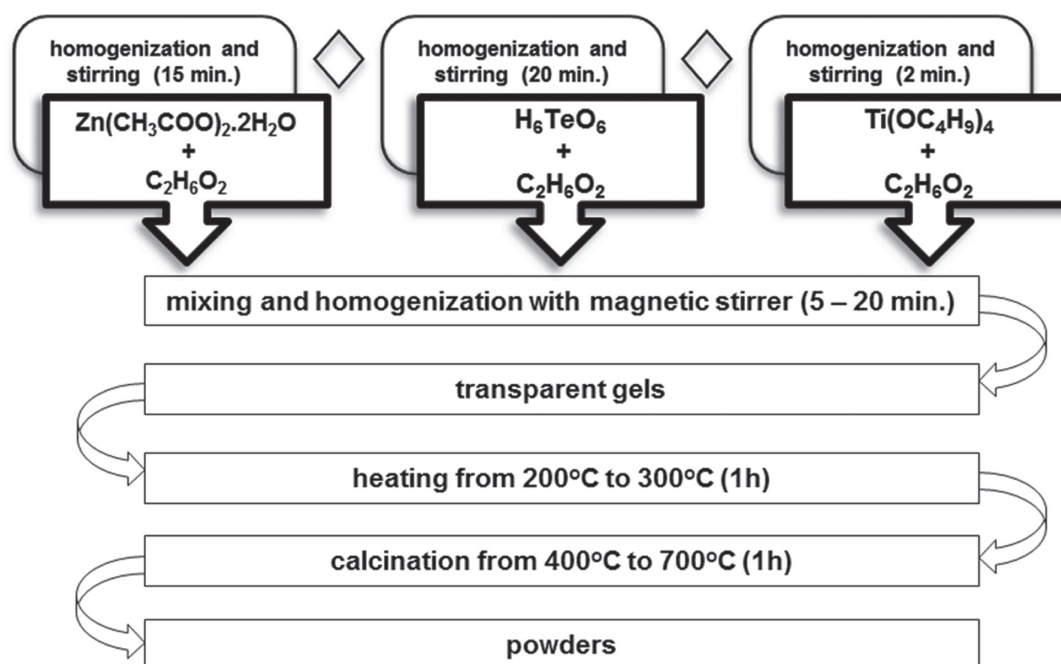


Fig. 1. Scheme for the sol-gel synthesis of  $\text{TiO}_2/\text{TeO}_2/\text{ZnO}$  gels

tron microscope (Japan), equipped with ultrahigh resolution scanning system (ASID-3D). The optical absorption spectra of the powdered samples in the wavelength range 200–1000 nm were recorded by a UV–VIS diffused reflectance Spectrophotometer “Evolution 300” using a magnesium oxide reflectance standard as the baseline. The absorption edge and the optical band gap were determined following Dharma et al. instructions [29]. The band gap energies ( $E_g$ ) of the samples were calculated by the Planck’s equation:

$$E_g = \frac{h.c}{\lambda} = \frac{1240}{\lambda} \quad (\text{eq. 1}),$$

where  $E_g$  is the band gap energy (eV),  $h$  is the Planck’s constant,  $c$  is the light velocity (m/s), and  $\lambda$  is the wavelength (nm). The infrared spectra were

registered in the range 1600–400  $\text{cm}^{-1}$  using the KBr pellet technique on a Nicolet-320 FTIR spectrometer with 64 scans and a resolution of  $\pm 1 \text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

### Phase transformations

Transparent and monolithic gels were obtained applying the scheme shown in Fig. 1 and their images are given on Fig. 2. The gel formation region determined at room temperature is situated between 10–100 mol%  $\text{TiO}_2$ , up to 65 mol%  $\text{TeO}_2$  and 90 mol%  $\text{ZnO}$  (Fig. 3). In the binary  $\text{ZnO-TeO}_2$  system, gels are not obtained at given experimental conditions using  $\text{H}_6\text{TeO}_6$  and Zinc acetate as precursors.

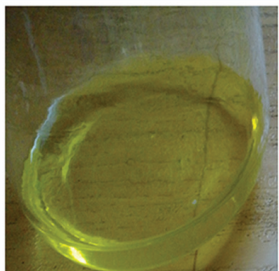

Samples	C	E
Composition, mol%	40TiO <sub>2</sub> .30TeO <sub>2</sub> .30ZnO	40TiO <sub>2</sub> .60ZnO
Images		

Fig. 2. Gel formation region in the investigated  $\text{TiO}_2\text{-TeO}_2\text{-ZnO}$  system

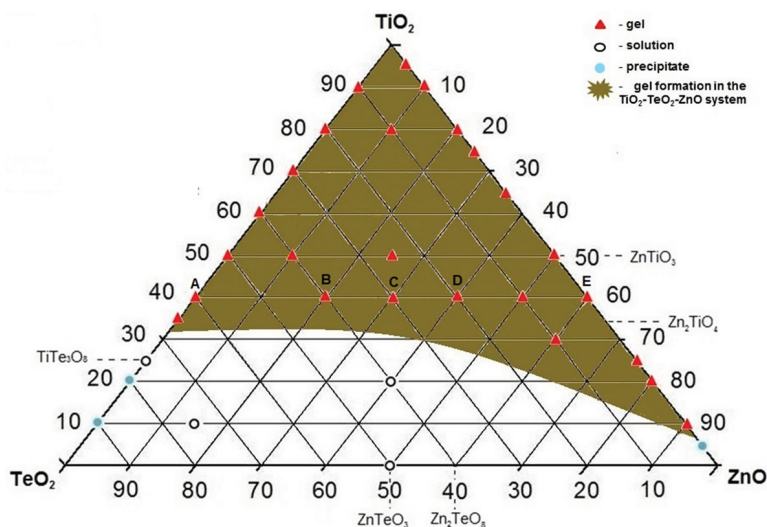
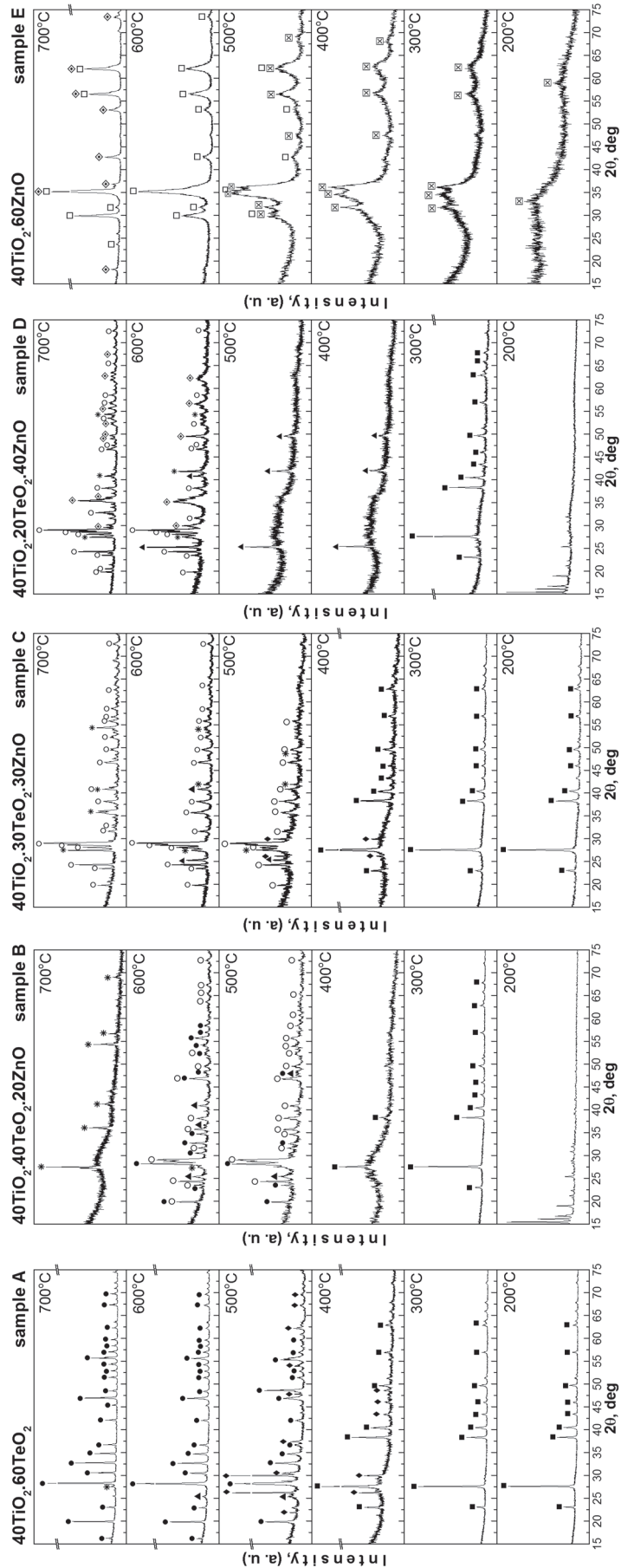


Fig. 3. Images of selected gels



**Fig. 4.** XRD patterns of the investigated samples: (■) Te, (◆)  $\alpha\text{-TeO}_2$ , (▲)  $\text{TiO}_2$ -anatase, (\*)  $\text{TiO}_2$ -rutile, (⊠)  $\text{ZnO}$ , (●)  $\text{TiTe}_3\text{O}_8$ , (○)  $\text{ZnTeO}_3$ , (◇)  $\text{Zn}_2\text{TiO}_4$ , (□)  $\text{ZnTiO}_3$ -cubic



According to the X-ray diffraction patterns in the temperature range 200–500 °C composite materials containing an amorphous phase and different crystalline phases {metallic Te (JCPDS 78-2312),  $\alpha\text{-TeO}_2$  (JCPDS 42-1365), anatase (JCPDS 78-2486), rutile (JCPDS 21-1276),  $\text{ZnTeO}_3$  (JCPDS 44-0240),  $\text{ZnTiO}_3$  (cubic, JCPDS 39-0190) and  $\text{Zn}_2\text{TiO}_4$  (JCPDS 25-1164)} are prepared. As one can see at 200 and 300 °C the amorphous phase co-exists with metallic tellurium while at 400 °C simultaneous presence of amorphous phase and metallic tellurium,  $\alpha\text{-TeO}_2$ , anatase or ZnO (JCPDS 78-2486) is observed (Fig. 4, samples A, B, C, D and E). The oxidation of tellurium starts at 400 °C and it is fully oxidized to  $\text{TeO}_2$  about 500 °C. In the binary composition  $40\text{TiO}_2\cdot 60\text{ZnO}$  (sample E) (Fig. 4) ZnO appears even at 200 °C. In sample D ( $40\text{TiO}_2\cdot 20\text{TeO}_2\cdot 40\text{ZnO}$ ), ZnO remains in the amorphous phase in the temperature range 200–500 °C. The anatase appears at lower temperature (400 °C) in sample D ( $40\text{TiO}_2\cdot 20\text{TeO}_2\cdot 40\text{ZnO}$ ) and conversion to rutile is observed at 600 °C. In the binary sample A ( $40\text{TiO}_2\cdot 60\text{TeO}_2$ ), anatase appears at 500 °C and a small amount is converted to rutile at 700 °C, while in the sample E ( $40\text{TiO}_2\cdot 60\text{ZnO}$ ), anatase did

not appeared in the XRD patterns. At 400 °C the average crystallite size (calculated using Sherrer's equation) of  $\text{TiO}_2$  (anatase) in the powdered sample D is about 58 nm (Fig. 4). At higher temperatures (600–700 °C) crystalline phases only (anatase, rutile,  $\alpha\text{-TeO}_2$ ,  $\text{TiTe}_3\text{O}_8$  (JCPDS 50-0250),  $\text{ZnTeO}_3$  and  $\text{Zn}_2\text{TiO}_4$ ) were found in the prepared composite materials (Fig. 4).

SEM observations of a representative sample with nominal composition  $50\text{TiO}_2\cdot 25\text{TeO}_2\cdot 25\text{ZnO}$ , heat treated at 400 °C were performed (Fig. 5). As one can see the morphology is a result from the crashing of the monolithic gels during the drying process. The microprobe analysis in different points of the sample showed that the obtained weight ratio of  $\text{TiO}_2\text{:TeO}_2\text{:ZnO}$  ( $49\text{:}22\text{:}29 \approx 2\text{:}1\text{:}1$ ) is similar as in the initial nominal composition.

#### Optical properties and structural transformations

The diffuse reflectance absorption spectra of selected binary and ternary  $\text{TiO}_2\text{/TeO}_2\text{/ZnO}$  gels (aged at room temperature) as well as of pure Ti butoxide gel are illustrated in Figure 6 a, b. The observed

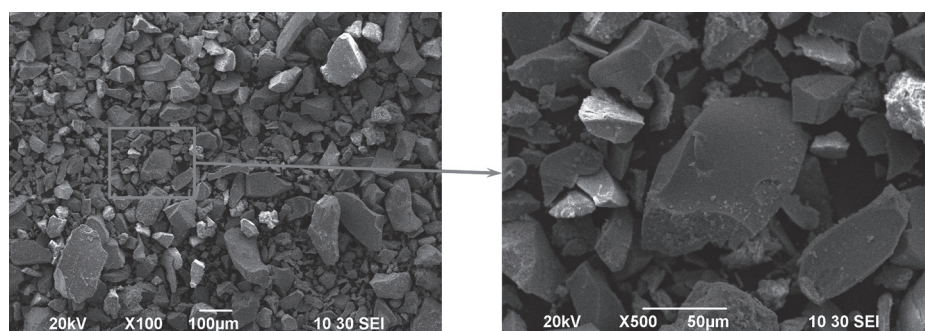


Fig. 5. SEM images of composition  $50\text{TiO}_2\cdot 25\text{TeO}_2\cdot 25\text{ZnO}$  heat treated at 400 °C

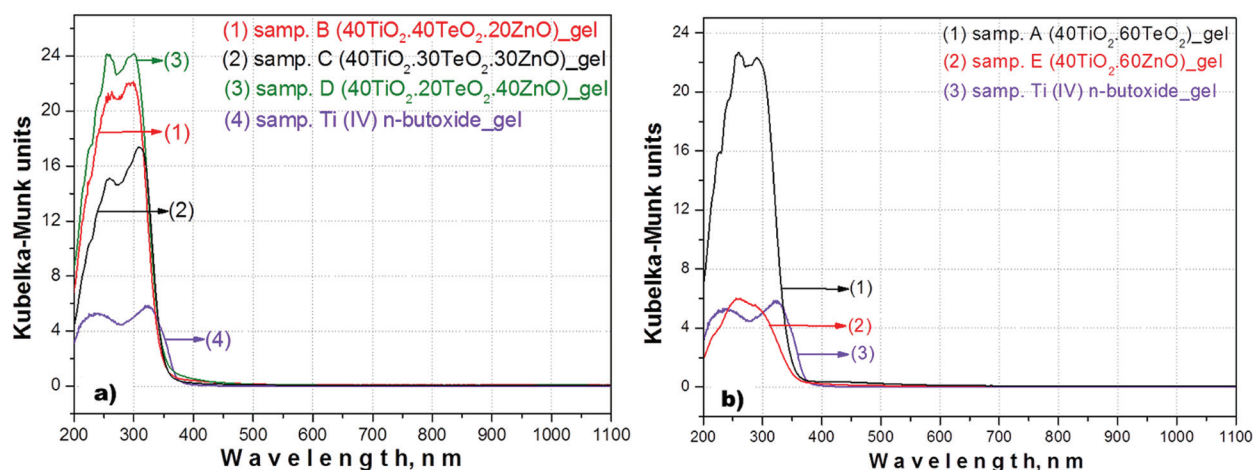


Fig. 6. UV-Vis spectra of: a) binary and b) ternary gels in the investigated ternary system

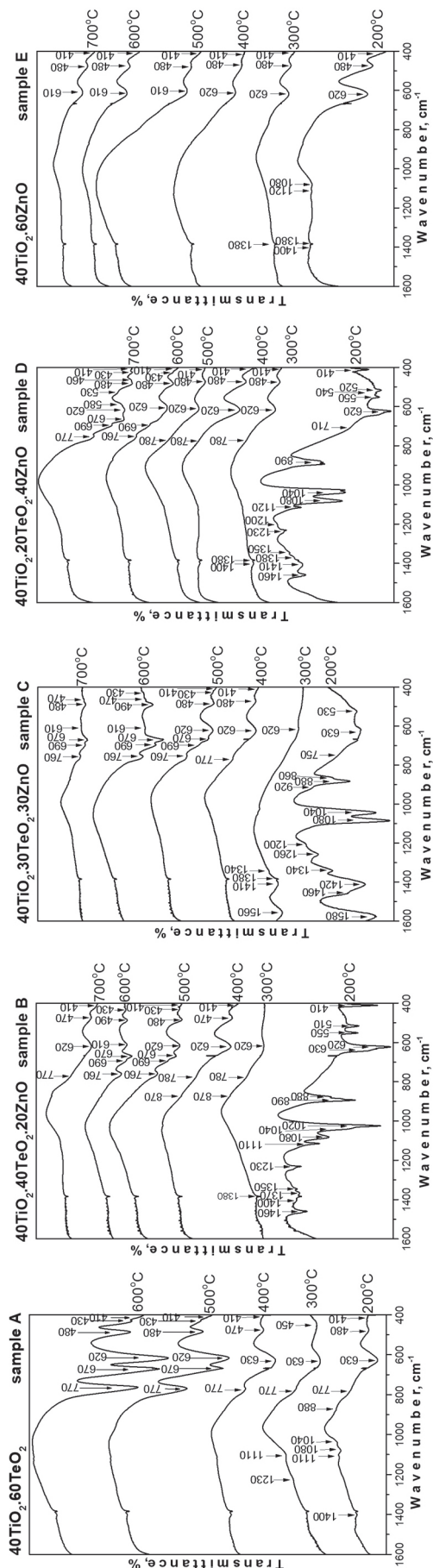
**Table 1.** Investigated binary and ternary gels, observed cut-off and calculated optical band gap values (Eg)

Samples	Compositions, mol. %	Cut-off, nm	Eg, eV
	Ti (IV) n-butoxide gel	389.71	3.18
A	40TiO <sub>2</sub> .60TeO <sub>2</sub>	348.07	3.56
B	40TiO <sub>2</sub> .40TeO <sub>2</sub> .20ZnO	347.36	3.57
C	40TiO <sub>2</sub> .30TeO <sub>2</sub> .30ZnO	348.90	3.55
D	40TiO <sub>2</sub> .20TeO <sub>2</sub> .40ZnO	366.89	3.38
E	40TiO <sub>2</sub> .60ZnO	386.82	3.21

absorption edges and calculated optical band gap values are pointed out in Table 1. It is evident that the ternary gels containing TiO<sub>2</sub>, TeO<sub>2</sub> and ZnO exhibit higher absorption in the UV region in comparison to pure Ti butoxide gel. Another peculiarity is the appearance of two absorption bands below and above 300 nm, the so called charge transfer bands. For the isolated TiO<sub>4</sub> units, the ligand to metal charge transfer band is in the region 200–260 nm, while in a titania network (anatase) the charge transfer in TiO<sub>6</sub> is above 300 nm [30–32]. The TiO<sub>4</sub> groups are the main building units in the unhydrolyzed Ti butoxide and the coordination geometry is changed to TiO<sub>6</sub> as a result of polymerized Ti species (Ti-O-Ti links between TiO<sub>6</sub> units) [32]. For the three component gels, the observed more intensive absorption peak about 300–340 nm is associated with an increase of the polymerization degree of Ti atoms in comparison to pure Ti butoxide gel. Similar data was obtained by Klein et al. [32] which investigated the UV-Vis spectra of TiO<sub>2</sub>/SiO<sub>2</sub> gels. The UV-Vis spectra of the binary 40TiO<sub>2</sub>.60ZnO gel (with high ZnO content) (Fig. 6a) is different from those of sample A (40TiO<sub>2</sub>.60TeO<sub>2</sub>) and pure Ti butoxide. The charge transfer of O → Ti is in the range 260–300 nm but it is known that the exciton absorption peak of bulk ZnO exists in the same region (300–360 nm, Eg ~3.24 eV) [33]. Due to the overlapping of these absorption bands it is difficult to obtain more precise information for the influence of ZnO on the polymerization ability of Ti. The absorption edge of our gels varies between 348.07 to 386.82 nm (± 0.01 precision). According to several authors [24, 25] TiO<sub>2</sub>/TeO<sub>2</sub>/ZnO glasses (containing up to 35 mol% ZnO) exhibit optical band gap value about 2.94–3.00 eV. Our values obtained for gels are higher (3.2–3.28 eV) than those pointed out in the literature but lower than the value of melted bulk tellurite glass (~3.79 eV).

The phase transformations during the heat treatment (in the temperature range 200–700 °C) were monitored also by IR spectroscopy (Fig. 7). The as-

signments of the vibrational bands of the separate structural units are made on the basis of well-known spectral data of the precursors (Ti (IV) n-butoxide, H<sub>6</sub>TeO<sub>6</sub> and zinc acetate) and crystalline phases existing in the system [8, 34–35]. In the obtained by us IR spectra of samples heat treated up to 200 °C the absorption bands in the 1120–1040 cm<sup>-1</sup> region (Ti-O-C stretching vibrations) are very weak in the binary 40TiO<sub>2</sub>.60TeO<sub>2</sub> and 40TiO<sub>2</sub>.60ZnO compositions (Fig. 7, samples A, E) while in the ternary ones these bands are very intensive (Fig. 7, samples B, C, D). This observation could be explained by the greater degree of hydrolysis and condensation processes in the binary samples. The bands above 1000 cm<sup>-1</sup>, characteristic for the organic groups are not visible above 300 °C and the spectra in the temperature range 300–500 °C are characterized mainly with bands below 900 cm<sup>-1</sup> typical for the inorganic units. At 300 and 400 °C these bands are broadened, with low intensity that is a peculiarity of the disordered systems. According to the XRD data at these temperatures (300 and 400 °C) the obtained composite materials contain mainly an amorphous phase along with elementary tellurium. An exception is the sample E (40TiO<sub>2</sub>.60ZnO), where the composite contains an amorphous phase and ZnO. Basis on the IR and XRD results the observed absorption bands in the IR spectra of samples heated at 300 and 400 °C could be related to the vibrations of structural units building up the amorphous network: TeO<sub>4</sub> (780–770 cm<sup>-1</sup>; 630–620 cm<sup>-1</sup>; TiO<sub>6</sub> and ZnO<sub>4</sub> (630–620 cm<sup>-1</sup>, 480 and 410 cm<sup>-1</sup>) [36–44]. It is well known that the elementary tellurium does not exhibit absorption bands in the IR spectral region. At higher temperatures (above 500 °C) the content of the amorphous phase decreases (it is negligible at 500 °C). In this case the observed absorption bands in the IR spectra are assigned to the vibrations of inorganic structural units building up the crystalline phases (TiTe<sub>3</sub>O<sub>8</sub>, ZnTeO<sub>3</sub>, Zn<sub>2</sub>TiO<sub>4</sub> and ZnTiO<sub>3</sub>). It is difficult to distinguish the vibrations of TiO<sub>6</sub> and ZnO<sub>4</sub> structural units due to their strong over-



←  
**Fig. 7.** IR spectra of the investigated samples

lapping. The obtained IR spectra proved the phase transition established by XRD (Fig. 4).

### CONCLUSIONS

The gel formation region in the ternary TiO<sub>2</sub>-TeO<sub>2</sub>-ZnO system was determined. New original gel derived composite materials consisting of amorphous and different crystalline phases: TiO<sub>2</sub> (anatase), ZnTiO<sub>3</sub>, TiTe<sub>3</sub>O<sub>8</sub> and ZnTeO<sub>3</sub> were obtained depending on composition. The decrease in the TeO<sub>2</sub> content (20 mol%, sample D) stimulates the crystallization of TiO<sub>2</sub> (anatase) at lower temperatures (400 °C). At constant TiO<sub>2</sub> content (40 mol%) and define TeO<sub>2</sub>/ZnO ratios 2:1 and 1:1 (samples B, C), the anatase → rutile transition occurred at 500 °C. By IR spectroscopy was established that organic and OH groups participate in the amorphous organic-inorganic structure below 300 °C. At higher temperatures (300–400 °C) the inorganic amorphous phases consist of TiO<sub>6</sub>, ZnO<sub>4</sub> and TeO<sub>4</sub> structural units.

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## СИНТЕЗ И КРИСТАЛИЗАЦИЯ НА ГЕЛИ В СИСТЕМАТА $\text{TeO}_2\text{-TiO}_2\text{-ZnO}$

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(Резюме)

Прозрачни и монолитни гели са получени в трикомпонентната система  $\text{TeO}_2\text{-TiO}_2\text{-ZnO}$  и е установено, че областта на гелообразуване е разположена между 10–100 mol%  $\text{TiO}_2$ , до 65 mol%  $\text{TeO}_2$  и 90 mol%  $\text{ZnO}$ . Телурова киселина ( $\text{H}_6\text{TeO}_6$ ), цинков ацетат и титанов бутоксид са използвани като прекурсори за синтеза. Фазовите промени на гелите са изследвани в температурния интервал 200–700 °С. Чрез РФА е установено, че получените композити съдържат аморфна фаза и различни кристални фази –  $\text{TiO}_2$  (анатаз),  $\alpha\text{-TeO}_2$ ,  $\text{TiTe}_3\text{O}_8$ ,  $\text{ZnTeO}_3$ ,  $\text{ZnTiO}_3$  и  $\text{Zn}_2\text{TiO}_4$ , в зависимост от състава и температурата на нагряване. С ИЧ спектроскопия е установено, че близкият порядък на аморфните фази, които са част от композитните материали, са изградени от  $\text{TiO}_6$ ,  $\text{ZnO}_4$  и  $\text{TeO}_4$  структурни единици.