

Sol – Gel Synthesis, Characterization and Optical Properties of TiO₂/TeO₂ powders

A. D. Bachvarova-Nedelcheva^{1*}, R. S. Iordanova¹, R. D. Gegova¹, P. V. Markov¹,
D. D. Nihtianova^{1,2} and Y. B. Dimitriev³

¹*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
“Acad. G. Bonchev” str., bld. 11, 1113 Sofia, Bulgaria. E-mail: albenadb@svr.igic.bas.bg*

²*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, “Acad. G. Bonchev” str., bld. 107,
1113 Sofia, Bulgaria*

³*University of Chemical Technology and Metallurgy - Sofia, “Kl. Ohridski” blvd, 8,
1756 Sofia, Bulgaria*

Received October 10, 2016; Revised November 20, 2016

The present investigation deals with the sol-gel synthesis and optical characterization of gels in the binary TiO₂ – TeO₂ system. Titanium butoxide and telluric (VI) acid (H₆TeO₆) were used as main precursors for preparation of the rich in TiO₂ (above 35 mol %) compositions. The heat treated up to 300°C gels are predominantly amorphous and contain small amount of metallic tellurium. Several crystalline phases TiTe₃O₈, TeO₂, TiO₂ (anatase) and TiO₂ (rutile) simultaneously exist above this temperature. Two maxima about 230 – 250 nm and 290 – 330 nm related to the isolated TiO₄ units and condensed TiO₆ groups, respectively were observed in the UV – Vis spectra. The heating of all samples above 500°C led to an increase of the UV absorption peak at 330 nm (instead of that at 230 nm) which is related to the greater condensation processes. In comparison to the pure Ti butoxide gel, a red shifting of the absorption edge for samples containing up to 50 mol % TeO₂ was observed, while composition containing higher TeO₂ amount (above 50 mol %) exhibited blue shifting.

Keywords: sol-gel, telluric (VI) acid, crystallization

INTRODUCTION

In the past decade much attention has been paid on the binary TiO₂ - TeO₂ system. From one side, TiO₂-based materials have always been of primary research interest for the materials chemists driven by the unique properties of TiO₂ and its ability to create high surface area structures for photocatalysis and sensing [1]. On the other side, the binary TiO₂-TeO₂ system is of special interest, as it has been shown that TiO₂ inhibits structural changes of the Te polyhedra and maintains a continuous amorphous network [2, 3]. It was found that the addition of TiO₂ increases the thermal stability of TeO₂-based glasses by replacing Te-O-Te linkages by more rigid Te-O-Ti ones [4]. However, it was established that the Ti⁴⁺ as an additive is the most influential ion for improving the optical properties of TeO₂ among all transition metal ions due to effect of its d orbital [5]. The pioneer's investigations with reference to sol-gel obtaining of TiO₂/TeO₂ thin films started by Weng and Hodgson [6]. In their earlier research the sol –

gel technique was applied as an alternative of the melt quenching method for synthesis of TeO₂ based thin films but the uncontrolled hydrolysis of tellurium isopropoxide was found as a problem. That question was widely discussed in several papers [4, 7 - 13]. Most of the authors reported that during the heat treatment of TeO₂ thin films highly dispersed metallic tellurium is present up to 340°C [7 - 9, 14]. The α-TeO₂ occurred when the heat treatment temperature was further increased. Addition of TiO₂ retard the crystallization of α-TeO₂ but promote the formation of other TiO₂ or TiTe₃O₈ phases [9, 15]. Recently, similar results in that system have been described in several papers [13, 16, 17]. Up to now, dense and transparent thin films were obtained by these methods in the TiO₂-TeO₂ system containing 10 mol % TiO₂ and in a more complex TiO₂ – TeO₂ – PbO system [18, 19].

The TiO₂/TeO₂ glasses, rich in TeO₂ (> 70 mol %) have been obtained by sol-gel techniques [10, 17] and the optical properties of the obtained materials were also verified. Melt quenched glasses in the TiO₂ - TeO₂ system were obtained in a narrow concentration range above 75 % TeO₂ [2, 20, 21]. Generally, it is difficult to be prepared

* To whom all correspondence should be sent:
E-mail: albenadb@svr.igic.bas.bg

glasses rich in TiO₂ by conventional melt – quenching route due to its high melting temperature (1843°C). We have chosen the sol – gel method as an alternative one for obtaining of rich in TiO₂ amorphous materials. Our earlier investigations in that binary system started with the phase transformations and photocatalytical properties of sol – gel derived TiO₂/TeO₂ powders containing from 70 to 90 mol % TiO₂ [13, 15]. Data on optical characterization of sol – gel derived TiO₂/TeO₂ powders containing higher TiO₂ content were not found in the literature that motivates our present study.

The purpose of this paper is to synthesize rich in titania TiO₂/TeO₂ powders applying a sol – gel technique and to characterize optically the prepared samples as well as to verify the morphology of the obtained products.

EXPERIMENTAL

Samples preparation

Various samples containing different TiO₂ content (above 40 mol %) were prepared and some of them were selected for detailed phase and optical investigations: 80TiO₂.20TeO₂ (*sample A*), 50TiO₂.50TeO₂ (*sample B*), 40TiO₂.60TeO₂ (*sample C*). In order to overcome the problem with high hydrolysis rate of tellurium (VI) alkoxides we used Te(VI) acid (Aldrich) [6, 22, 23] in combination with Ti butoxide (Fluka AG) and ethylene glycol (C₂H₆O₂) (99% Aldrich). Solutions (A and B) were prepared via dissolving of the precursors in ethylene glycol by means of vigorous magnetic stirring. Thus, transparent gels were obtained. For comparison, pure TiO₂ gel was obtained from Ti butoxide without addition of water or ethylene glycol (EG) and it is denoted as TBT. The as – prepared gels were subjected to heating at ~ 150°C and subsequently to calcination in the temperature range 200-700°C. The stepwise heating of the samples from 200 to 700°C for one hour exposure time in air was performed, until obtaining powders. The calcination temperature was selected on the basis of our previous investigations [13, 15]. The pH during the experiments was measured to be about 7.

Samples characterization

Powder XRD patterns were registered at room temperature with a Bruker D8 Advance diffractometer using Cu-K_α radiation. It has to be noted that the XRD patterns obtained below 200°C are complicated due to the presence of organic

complexes and they are not discussed. The morphology of the samples was examined by scanning electron microscopy (SEM) using a JEOL JSM 6390 electron microscope (Japan), equipped with ultrahigh resolution scanning system (ASID-3D). The accelerating voltage was 20kV, I~65 μA. Transmission Electron Microscopy (TEM) investigations were performed on a JEOL JEM 2100 instrument (Japan) at an accelerating voltage of 200 kV. The specimens were prepared by grinding and dispersing them in ethanol by ultrasonic treatment for 6 mins. The suspensions were dripped on standard carbon/Cu grids. The measurements of lattice fringe spacings recorded in HRTEM micrographs were made using digital image analysis of real space parameters. The analysis was carried out by the Digital Micrograph software. Additional support for the existence of all participated elements in the investigated samples was performed by X-ray energy dispersive spectrometry (XEDS) elemental mapping studies. The optical absorption spectra of the powdered samples in the wavelength range 200 – 800 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 [24]. The bandgap energies (E_g) of the samples were calculated by the Planck's equation:

$$E_g = \frac{h \cdot c}{\lambda} = \frac{1240}{\lambda}$$

where E_g is the bandgap energy (eV), h is the Planck's constant, c is the light velocity (m/s), and λ is the wavelength (nm).

RESULTS AND DISCUSSION

X – ray diffraction

Transparent and monolithic gels were obtained and the gel formation region determined at room temperature is situated between 35 - 100 mol % TiO₂ and up to 65 mol % TeO₂. According to the X-ray diffraction patterns heat treated gels up to 300°C consist of amorphous part and metallic tellurium only (JCPDS 78-2312) (Fig. 1, samples A, B, C). The residual organic component plays an important role in promoting the formation of tellurium [12]. According to Wei et al. [12] the samples heated at 300°C with preheated treatment at 200°C in O₂ showed great decrease in the metallic tellurium content and clearer amorphous phase in the XRD pattern. Looking at our results, at 400°C only tellurium was found in the XRD pattern

for sample A (80TiO₂.20TeO₂), while for samples B and C containing higher TeO₂ content (50, 60 mol %) partial oxidation of tellurium to paratellurite (α -TeO₂, JCPDS 42-1365) was registered. Further increasing of the temperature (500°C) led to full oxidation of tellurium to TeO₂ and at this temperature it exists simultaneously with TiO₂ (anatase) (JCPDS 78-2486) and crystalline TiTe₃O₈ phase (JCPDS 50-0250). At higher temperatures (600, 700°C) all these phases coexist in the prepared composite materials (Fig. 1a). The TiO₂ (anatase) to TiO₂ (rutile) (JCPDS 21-1276)

transformation is observed at 700°C for all samples. Irrespective of using different precursor (Te^{VI} acid) in our experiments, the observed phase transformations are in good accordance with those obtained by other teams [7, 9, 14, 17]. For comparison, the XRD patterns of Ti butoxide gel, showed that it is amorphous up to 300°C and the first TiO₂ (anatase) crystals appeared at 400°C (Fig. 1b). The addition of TeO₂ (samples A, B, C) to Ti butoxide preserved the amorphous titania up to 400°C and first TiO₂ (anatase) crystals appeared at 500°C.

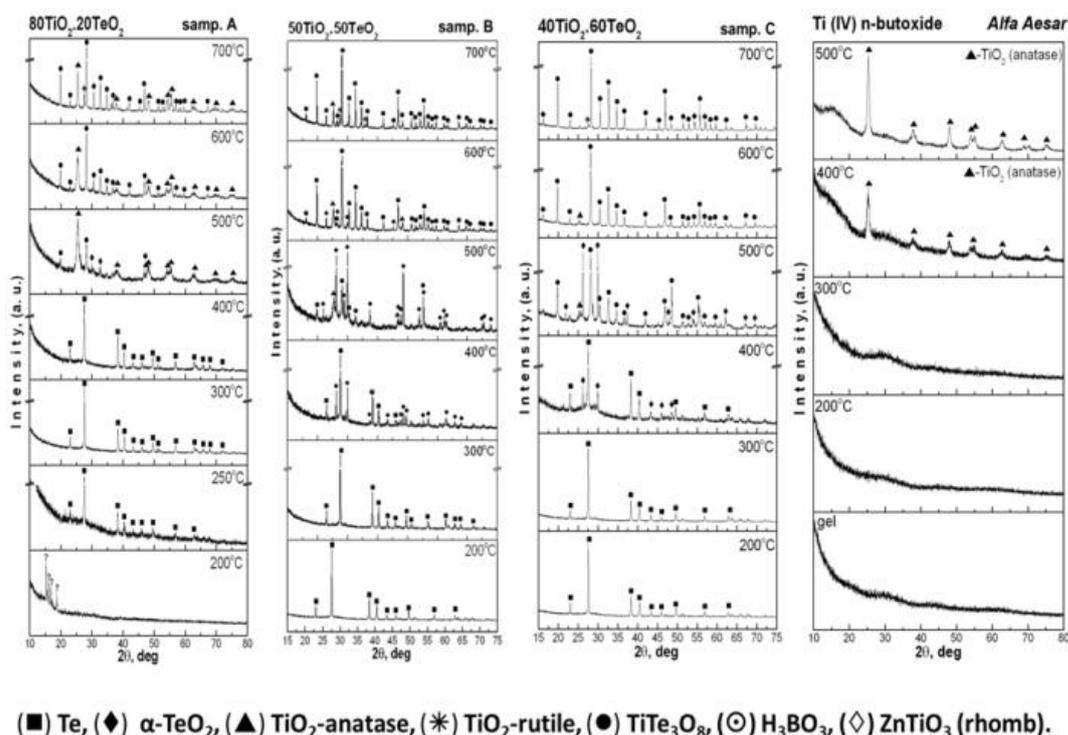


Fig. 1. XRD patterns of the: (a) investigated samples A (80TiO₂.20TeO₂), B (50TiO₂.50TeO₂) and C (40TiO₂.60TeO₂) and (b) pure Ti butoxide (TBT).

Electron microscopy

Sample C (40TiO₂.60TeO₂) heat treated at 400°C was subjected to SEM observations with microprobe analysis (Fig. 2). The sample morphology revealed shapeless agglomerates with a size around 50 - 100 μ m, that are probably a result of the crashing of the monolithic gels during the drying process. The microprobe analysis was performed in different points of the sample surface and the obtained data are summarized in Table 1. As it is seen there are aggregates with composition corresponding to TeO₂ (spectrum 1), other pieces with composition equivalent to the initial one

(spectrum 2) and regions with segregated Ti on the surface (spectrum 3).

The HRTEM images performed in different parts of sample C heat treated at 400°C confirmed the inhomogeneous nature of the sample at unit cell level (Fig. 3a). The SAED data exhibited presence of tetragonal TeO₂ (SG P4₁2₁2) with the lattice parameters $a = 4.810$ Å and $c = 7.612$ Å (Fig. 3b). This implies that the crystal is viewed along the [122] zone axis. The composition map via STEM-XEDS analysis was carried out to examine the distribution of elements in the composite sample. The results of mapping studies (Fig. 4) portray the coexistence of Ti, O, Te and C elements and their

homogeneous distribution. The TEM images of another part of the sample rich in carbon are shown in Fig. 5. Several pods fill up with smooth and spherical particles are observed with size between 20 nm to 2 μm. Elemental mapping studies in this part of the composite illustrate mainly existence of carbon and oxygen (Fig. 6).

Table 1. Electron probe microanalysis (EPMA) performed in different points on the surface of sample C (40TiO₂.60TeO₂).

Elements	Microprobe analysis (at %)			
	40TiO ₂ .60TeO ₂ (mol %)			
	initial composition, at %	400°C		
		sp. 1	sp. 2	sp. 3
Ti	13	-	11	23
Te	20	33	22	10
O	67	67	67	67

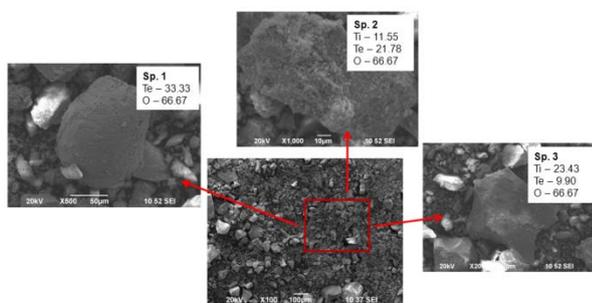


Fig. 2. SEM images of sample C (40TiO₂.60TeO₂) heat treated at 400°C.

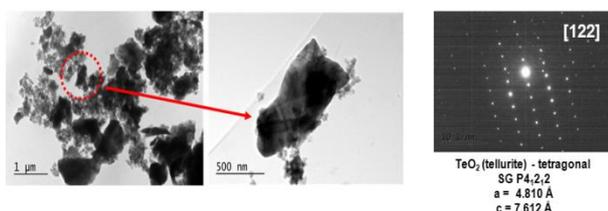


Fig. 3 (a, b). (a) Bright field TEM micrographs of sample C heat treated at 400°C and (b) SAED pattern of TeO₂ (paratellurite) particle from sample C, oriented along [122] direction.

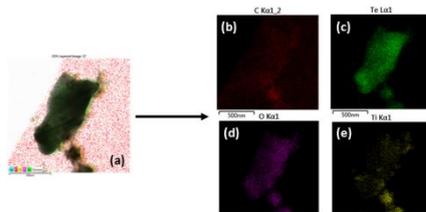


Fig. 4 (a,b,c,d,e). (a) Integral XEDS-STEM composition map of sample C heat treated at 400°C; (b) composition map of C; (c) composition map of Te; (d) composition map of O; (e) composition map of Ti.

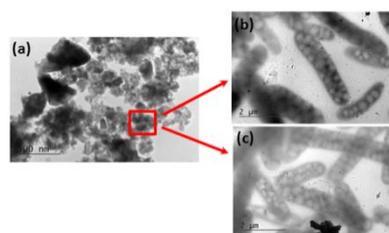


Fig. 5 (a,b,c). Bright field TEM micrographs from carbon rich areas of sample C heat treated at 400°C.

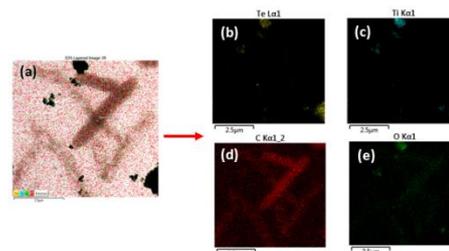


Fig. 6. (a,b,c,d,e). (a) Integral XEDS-STEM composition map from carbon rich area of sample C heat treated at 400°C; (b) composition map of Te; (c) composition map of Ti; (d) composition map of C; (e) composition map of O.

UV – Vis DRS characterization

The diffuse reflectance spectroscopy (DRS) studies were executed in order to determine the absorption edge (cut - off) as well as to calculate the band gap energy (E_g) of the binary and pure TBT gels (aged at room temperature) as well as of the heat treated at 600°C samples (Fig. 7a, b; Table 2). Generally, for the heated samples (200 - 400°C) these optical characteristics could not be determined because of the high absorption above 400 nm caused by the presence of carbon. Such absorption is illustrated by the UV – Vis spectra of pure TBT (Fig. 7c). The UV – Vis spectra of the investigated binary gels were compared to those of pure Ti butoxide gel (TBT). All spectra of the gels (samples A, B, C and TBT) are characterized with good transparency in the visible region. Useful structural information on the coordination number of Ti atoms was additionally obtained by UV–Vis spectroscopy. The appearance of two absorption bands below and above 300 nm, could be related to the charge transfer of electrons from O to Ti. The main building units in the unhydrolyzed Ti butoxide are isolated TiO₄ groups with absorption band in the region 240-260 nm. These groups change their coordination geometry to TiO₆ (300 – 330 nm) as a result of the polymerization processes (Ti–O–Ti links between TiO₆ units) [25, 26]. The UV – Vis spectra of as-prepared binary gels showed more intensive absorption peak about 300 - 310 nm that

could be associated with greater degree of hydrolysis and condensation processes (samples A, B) in comparison to pure TBT. It is also evident that TeO₂ increased the absorption in the UV region (samples A, B, C).

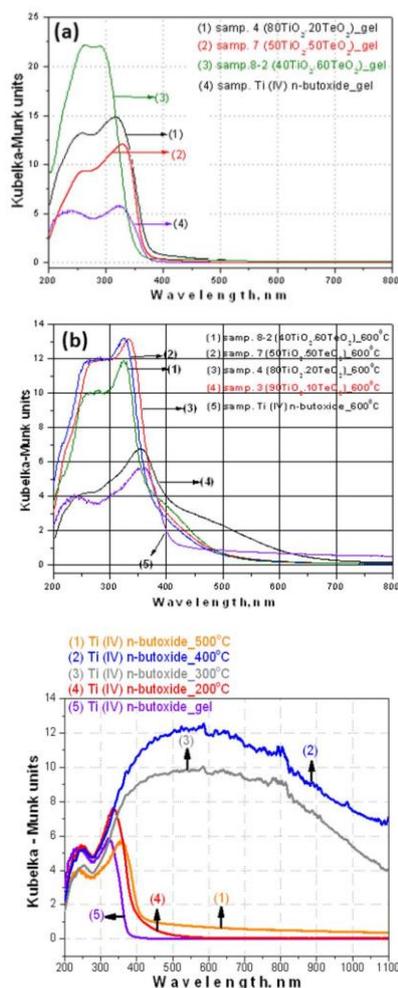


Fig. 7. UV-Vis DRS of samples: (a) gels, (b) heat treated at 600°C powders and (c) pure Ti butoxide.

It is clearly observed that the gel (sample A) containing lowest TeO₂ content (20 mol %) showed shifting of the absorption edge towards a longer wavelength (red shift) (~ 403 nm) compared to pure TBT gel (~ 390 nm). The highest TeO₂ content (60 mol %, sample C) led to shifting of the absorption edge towards a lower wavelength (blue shift) in respect to TBT gel (sample C, ~ 381 nm, Table 2). It is well known that E_g depends on many factors: generally, disordered systems cause blue shift; increasing the covalency of the bonds and the degree of polymerisation shift the absorption to the visible range [27]. Obviously, the binary gel 80TiO₂.20TeO₂ with more completed polymerization processes exhibited red shifting of the

absorption edge, while the gel 40TiO₂.60TeO₂ with uncompleted polymerization showed blue shifting.

Table 2. Investigated binary gels, observed cut-off and calculated optical band gap values (E_g).

Compositions, mol %	as prepared gels (25 °C)	
	E_g , eV	cut-off, nm
TiO ₂ (Ti (IV) n-butoxide)	3.18	389.71
80TiO ₂ .20TeO ₂	3.08	402.86
50TiO ₂ .50TeO ₂	3.39	365.55
40TiO ₂ .60TeO ₂	3.25	381.58

The UV-Vis spectra of the investigated samples (A, B and C) heat treated at 600°C possessing two – edge absorption (Fig. 7b) that could be related to the simultaneous existence of different crystalline phases [TiTe₃O₈, TeO₂ and TiO₂ (anatase)] (Fig. 1) and probably the absorption curves contain the contributions from each of the components. Similar explanations are made by other authors [28]. It was also stated [28] that in such cases the dominant is the influence of the compound with smaller E_g .

CONCLUSIONS

By the new combination of organic and inorganic precursors a simple route for obtaining of complex homogeneous gels in the TiO₂ – TeO₂ system is offered. The crystallization process started about 400°C and above this temperature sol – gel derived composite powders containing TiO₂ (anatase), α -TeO₂ (paratellurite) and TiTe₃O₈ were obtained depending on composition. By UV – Vis spectroscopy was established that the gels are characterized with good transparency in the visible region. It is also found that the low TeO₂ content (20 mol %) causes red shifting of the absorption edge while higher TeO₂ (60 mol %) amount leads to the blue shifting, both cases compared to pure Ti butoxide gel. It was found that the sol-gel method is suitable for obtaining of amorphous samples which are difficult to be prepared by conventional melt quenching route due to the high melting temperature of TiO₂.

REFERENCES

1. G. Arrachart, D. J. Cassidy, I. Karatchevtseva & G. Triani, *J. Am. Ceram. Soc.*, **92**, 2109 (2009).

2. M. Arnaudov, V. Dimitrov, Y. Dimitriev & L. Markova, *Mater. Res. Bull.*, **17**, 1121 (1982).
3. R. Iordanova, R. Gegova, A. Bachvarova-Nedelcheva, Y. Dimitriev, *Europ. J. Glass Sci. Techn., Part B: Phys. Chem. Glasses*, **56** (4), 128 (2015).
4. M. Udovic, P. Thomas, A. Mirgorodsky, O. Durand, M. Soulis, O. Masson, T. Merle-Méjean, J. C. Champarnaud-Mesjard, *J. Solid State Chem.*, **179**, 3252 (2006).
5. M. E. Lines, *J. Appl. Phys.*, **69**, 6876 (1991).
6. S. N. B. Hodgson, L. Weng, *J. Non-Cryst. Sol.*, **276**, 195 (2000).
7. L. Weng and S. N. B. Hodgson, *J. Mater. Sci.*, **36**, 4955 (2001).
8. L. Weng, S. N. B. Hodgson, X. Bao, K. Sagoe - Krentsil, *Mater. Sci. Engineer.*, **B107**, 89 (2004).
9. S. N. B. Hodgson and L. Weng, *J. Mater. Sci.*, **37**, 3059 (2002).
10. L. Weng, S. N. B. Hodgson, *Mater. Sci. Engineer. B*, **87**, 77 (2001).
11. S. Coste, A. Lecomte, P. Thomas, T. Merle-Mejean, J. C. Champarnaud-Mesjard, *J. Sol-Gel Sci. Techn.*, **41**, 79 (2007).
12. H-Y. Wei, W-H. Huang, Z-B. Feng, D-W. Li, *Mater. Sci. Engineer. B*, **164**, 51 (2009).
13. R. Iordanova, R. Gegova, A. Bachvarova-Nedelcheva, Y. Dimitriev, *Bulg. Chem. Commun.*, **45** (4), 485 (2013).
14. L. Weng, S. N. B. Hodgson, *Opt. Mater.*, **19**, 313 (2002).
15. A. Bachvarova-Nedelcheva, R. Gegova, R. Iordanova, A. Stoyanova, Y. Dimitriev, and N. Ivanova, *Nanoscience and Nanotechnology*, **13**, 56 (2013).
16. J.-N. Beaudry, S. Grenier, S. Amrate, M. Mazzer, A. Zappettini, *Mater. Chem. Phys.*, **133**, 804 (2012).
17. T. Hayakawa, H. Koyama, M. Nogami, Ph. Thomas, *J. Univ. Chem. Technol. Metall.*, **47** (4), 381 (2012).
18. S. Hodgson, L. Weng, *J. Non – Cryst. Sol.*, **297**, 18 (2006).
19. S. Hodgson, L. Weng, *J. Mater Sci: Mater Electron.*, **17**, 723 (2002).
20. W. Kingery, H. Bowen & D. Uhlmann, “*Introduction to Ceramics*”, 2-nd ed., John Wiley, NY, 1976, p. 669.
21. J.-C. Sabadel, P. Armand, P. E. Lippens, D. C. Herreilat & E. Philippot, *J. Non-Cryst. Sol.*, **244**, 143 (1999).
22. A. Lecomte, F. Bamiere, S. Coste et al., *J. Europ. Cer. Soc.*, **27**, 1151 (2007).
23. L. Weng, S. N. B. Hodgson, *J. Non-Cryst. Sol.*, **297**, 18 (2002).
24. J. Dharma, A. Pisal, Simple method of measuring the band gap energy value of TiO₂ in the powder form using a UV/Vis/NIR spectrometer. Application note. PerkinElmer, Shelton, CT, (2009).
25. V. Barlier, V. Bounor-Legare, G. Boiteux, J. Davenas, *Appl. Surf. Sci.*, **254**, 5408 (2008).
26. S. Klein, B. M. Weckhuysent, J. Martens, W. Maier, P. Jacobs, *J. Catal.*, **163**, 489 (1996).
27. R. Iordanova, R. Gegova, A. Bachvarova-Nedelcheva, Y. Dimitriev, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, **56** (4) 128 (2015).
28. El. Ross-Medgaarden and I. E. Wachs, *J. Phys. Chem. C*, **111**, 15089 (2007).

ЗОЛ- ГЕЛЕН СИНТЕЗ, ХАРАКТЕРИЗИРАНЕ И ОПТИЧНИ СВОЙСТВА НА TiO₂/TeO₂ ПРАХОВЕ

А. Д. Бъчварова-Неделчева¹, Р. С. Йорданова¹, Р. Д. Гегова¹, П. В. Марков¹,
Д. Д. Нихтянова^{1,2} и Я. Б. Димитриев³

¹ Институт по Обща и Неорганична Химия, БАН, ул. “Акад. Г. Бончев”, бл. 11, 1113 София, България

² Институт по Минералогия и Кристалография, БАН, ул. “Акад. Г. Бончев”, бл. 107, 1113 София, България

³ Химикотехнологичен и Металургичен Университет, бул. “Кл. Охридски”, 1756 София, България.

Постъпила на 10 октомври 2016 г.; коригирана на 20 ноември, 2016 г.

(Резюме)

В настоящото изследване са обсъдени зол – гелният синтез и оптичното характеризиране на гели от двукомпонентната TiO₂ – TeO₂ система. Телурова (VI) киселина и титанов бутоксид са използвани за синтеза на богати на TiO₂ (над 40 мол %) състави. Рентгенофазовият анализ на термично третираните до 300°C гели показва присъствие предимно на органична аморфна фаза и метален телур. Над тази температура, няколко кристални фази TiTe₃O₈, TeO₂, TiO₂ (анатаз) и TiO₂ (рутил) са регистрирани. УВ – Вис спектроскопията показва присъствие на две абсорбционни ивици при 230 – 250 nm и 290 – 330 nm, които могат да се отнесат съответно към изолираните TiO₄ и TiO₆ групи. Нагряването на всички образци над 500°C доведе до повишаването на абсорбционния пик при 330 nm, което може да се свърже с по-пълно протеклите кондензационни процеси. За състави съдържащи до 50 мол % TeO₂ бе наблюдавано едно отместване на абсорбционният ръб към по – високите стойности на дължината на вълната, докато при състави съдържащи над 60 мол % TeO₂ отместването на абсорбционният ръб е към по – ниските стойности на дължината на вълната.