

# NANOPULBERI DE $\text{SiO}_2\text{-TiO}_2$ sau $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ DOPATE CU ERBIU PREPARATE PRIN METODA SOL-GEL

## ERBIUM DOPED $\text{SiO}_2\text{-TiO}_2$ OR $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ NANOPOWDERS PREPARED BY SOL-GEL METHOD

ADRIANA RUSU, LUMINIȚA PREDOANĂ \*, SILVIU PEDA, JEANINA PANDELE CUSU,  
SIMONA PETRESCU, MARIA ZAHARESCU

Institute of Physical Chemistry "Ilie Murgulescu" – Romanian Academy of Sciences, 060021-Bucharest, ROMANIA

The  $\text{Er}^{3+}$  doped silica–titania or silica-titania-alumina nanopowders were prepared by sol-gel method that represents one of the most flexible and convenient way to prepare oxide films and nanopowders. The selected molar compositions were un-doped and 0.5% $\text{Er}_2\text{O}_3$  doped 90% $\text{SiO}_2\text{-10}\%$  $\text{TiO}_2$  and 85% $\text{SiO}_2\text{-10}\%$  $\text{TiO}_2\text{-5}\%$  $\text{Al}_2\text{O}_3$  systems. Similar compositions were previously used for obtaining films for waveguides applications but the mechanism of the phase formation by thermal treatment of the corresponding gels was not previously approached. The gels obtained by gelation of the solutions were analyzed by thermogravimetric and thermodifferential analysis (DTA/TGA) in order to determine their thermal behavior and by IR spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) to evaluate their structure and morphology. Based on the results obtained, the gels were thermally treated at 500°C and 900°C. The thermally treated powders were characterized by SEM, FT-IR, X-ray diffraction (XRD) and photoluminescence (PL). The significant influence of the  $\text{Er}^{3+}$  on the phase formation was established in both studied systems.

Nanopulberile de silice-dioxid de titan sau silice-dioxid de titan-alumină dopate cu  $\text{Er}^{3+}$  au fost preparate prin metoda sol-gel care reprezintă una dintre cele mai flexibile și convenabile metode de preparare ale filmelor și nanopulberilor oxidice. Compozițiile moleculare selectate au fost cele din sistemele 90% $\text{SiO}_2\text{-10}\%$  $\text{TiO}_2$  și 85% $\text{SiO}_2\text{-10}\%$  $\text{TiO}_2\text{-5}\%$  $\text{Al}_2\text{O}_3$  nedopate și dopate cu 0,5%  $\text{Er}_2\text{O}_3$ . Compoziții similare au fost utilizate anterior pentru obținerea filmelor pentru aplicații ca ghiduri de undă, dar mecanismul de formare al fazelor prin tratamentul termic al gelurilor corespunzătoare nu a fost abordat anterior. Gelurile obținute prin gelifierea soluțiilor au fost analizate prin analiză termogravimetrică și termodiferențială (DTA / TGA) pentru a determina comportamentul lor termic și prin spectroscopie IR (FT-IR) și Microscopie Electronică de Baleaj (SEM) pentru a evalua structura și morfologia lor. Pe baza rezultatelor obținute, gelurile au fost tratate termic la 500°C și 900°C. Pulberile tratate termic au fost caracterizate prin SEM, FT-IR, difracție de raze X (XRD) și fotoluminescență (PL). Influența semnificativă a  $\text{Er}^{3+}$  asupra formării fazelor a fost stabilită în ambele sisteme studiate.

**Keywords:** sol-gel method, erbium, nanopowders, phase formation

### 1. Introduction

The  $\text{Er}^{3+}$  doped silica–titania or silica-titania-alumina nanopowders were prepared by sol-gel method that represents one of the most flexible and convenient way to prepare oxide films and nanopowders. Lanthanide luminescent ion ( $\text{Ln}^{3+}$ )-doped inorganic materials have become an important topic of research in nanoscience and nanotechnology [1]. The optical properties of lanthanide ion-doped silicate systems are of great interest for fundamental studies and technological applications in optical devices, such as lasers, fiber amplifiers, and waveguides. Therefore, a detailed understanding of the local structure and bonding of dopant cations is important for optical device engineering [2]. The  $\text{SiO}_2\text{-TiO}_2$  binary system is commonly studied and can be obtained using different oxide combinations, synthesis processes,

and thermal treatments, and can be doped with transition metal ions to obtain luminescent materials [3, 4].

In a previous study the  $\text{Er}^{3+}$  doped silica–titania or silica-titania-alumina films with the molar compositions of 90% $\text{SiO}_2\text{-10}\%$  $\text{TiO}_2$  or 85% $\text{SiO}_2\text{-10}\%$  $\text{TiO}_2\text{-5}\%$  $\text{Al}_2\text{O}_3$  and 0.5% $\text{Er}_2\text{O}_3$  were prepared by sol-gel method for waveguide applications [5]. It was established that the presence of  $\text{Al}^{3+}$  in the composition enhanced the homogeneous distribution of  $\text{Er}^{3+}$  in the samples' composition, but decreased the resulted films' chemical stability. In order to explain the mentioned behaviour a comparative phase formation study on the gels resulted from the solutions used for films deposition could be of interest.

Among the different technologies which are employed to develop materials suitable for photonics, sol-gel processing exhibits several

\* Autor corespondent/Corresponding author,  
E-mail: lpredoana@icf.ro, lpredoana@yahoo.com

Table 1

Composition of the starting solutions and the experimental conditions for gels preparation  
 Compoziția soluțiilor inițiale și condițiile experimentale pentru prepararea gelurilor

Sample Probe	Reagents Precursori	Molar ratio / Raport molar				pH	Experimental conditions Condițiile experimentale	
		$\frac{ROH}{\sum precursor}$	$\frac{H_2O}{\sum precursor}$	$\frac{catalyst}{\sum precursor}$	$\frac{Er_2O_3}{\sum precursor}$		T (°C)	t (h)
ST	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> + Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	9.1	1.85	0.0174	-	3	50	3
ST-Er	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> + Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> +ErCl <sub>3</sub>	9.1	1.85	0.0174	0.5	3	50	3
STA	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> + Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> + Al(NO <sub>3</sub> ) <sub>3</sub>	19.3	1.85	0.0174	-	3.5	50	3
STA-Er	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> + Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> + Al(NO <sub>3</sub> ) <sub>3</sub> +ErCl <sub>3</sub>	19.3	1.85	0.0174	0.5	3.5	50	3

R= - C<sub>2</sub>H<sub>5</sub>; 0.5 mol% Er<sub>2</sub>O<sub>3</sub>

advantages in terms of composition, rare-earth solubility, design, tailoring of optical properties as well as fabrication of films, waveguides, photonic crystals, and bulk glasses. The binary silica-based systems, such as silica–titania [6, 7], silica–hafnia [8], silica–alumina [9], silica–zirconia [10] and phosphosilicate [11] are of particular interest allowing the tailoring of the optical and spectroscopic properties [12].

In the present paper the sol-gel preparation of the nanostructured Er<sup>3+</sup>-silica-titania and Er<sup>3+</sup>-silica-titania-alumina powders was approached and the mechanism of phase formation was investigated. The compositions were similar to those used previously for waveguide preparation.

## 2. Experimental

### 2.1. Gels and powders preparation

The experimental conditions used for obtaining the nanostructured oxide powders by sol-gel method were studied and are presented in Table 1. The selected compositions in the SiO<sub>2</sub>-TiO<sub>2</sub> binary and SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ternary system, undoped and doped with Er<sub>2</sub>O<sub>3</sub> were the following: 90%SiO<sub>2</sub>-10%TiO<sub>2</sub> or 85%SiO<sub>2</sub>-10%TiO<sub>2</sub>-5%Al<sub>2</sub>O<sub>3</sub> and 0.5 % Er<sub>2</sub>O<sub>3</sub>. The compositions were selected based on the literature data and our previous works [13, 14].

As precursors the corresponding alkoxides: tetraethyl-ortosilicate (TEOS) (p.a., Merck, Darmstadt, Germany) as SiO<sub>2</sub> and tetraethyle-ortotitanate, Ti(O-C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (p.a., Merck, Darmstadt, Germany) as TiO<sub>2</sub> sources and salts: Al(NO<sub>3</sub>)<sub>3</sub> (Aldrich) as Al<sub>2</sub>O<sub>3</sub> source and ErCl<sub>3</sub> (Aldrich) as erbium source were used. The ethanol, C<sub>2</sub>H<sub>5</sub>OH (absolute, Merck, Darmstadt, Germany) was used as solvent, the nitric acid, HNO<sub>3</sub> (65%, Merck, Darmstadt, Germany) as catalyst and the water for hydrolysis. The reaction was kept under stirring on water bath at 50°C for 3h. The solutions were kept at room temperature (40 days), to obtain gels. The

gels were thermally treated at 500 °C or 900 °C for 120 min, using a heating rate of 1 °C/min.

The resulting gels and powders, prepared from the solutions obtained were labeled as following: SiO<sub>2</sub>-TiO<sub>2</sub> (ST), SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (STA), Er<sup>3+</sup> doped SiO<sub>2</sub>-TiO<sub>2</sub> (ST-Er) and Er<sup>3+</sup> doped SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (STA-Er), respectively.

### 2.2. Samples characterization

The morphology of the samples was investigated by **scanning electron microscopy** (SEM) using a high-resolution microscope, FEI Quanta 3D FEG model, operating at 15 kV, equipped with an energy dispersive X-ray (EDX) spectrometer Apollo X. The analyses were done in high vacuum mode, with Everhart–Thornley secondary electron detector.

**Fourier-transform infrared** (FT-IR) spectra were obtained using a Nicolet Spectrometer 6700 between 400 and 4000 cm<sup>-1</sup>.

The **thermal behavior** of the synthesized gels was determined by differential thermal analysis and thermo-gravimetric analysis (TG/DTA) using Mettler-Toledo TGA/DTA 851<sup>e</sup> equipment in Al<sub>2</sub>O<sub>3</sub> crucibles and in flowing air atmosphere. The maximum temperature was set at 900 °C and the heating rate was of 10 °C/min.

The structure of the powders was determined by **X-ray diffraction** (XRD) method. The asymmetrical reflection measurements were performed with an Ultima IV diffractometer (Rigaku Corp., Japan), using Cu K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ), operated at 30 mA and 40 kV.

The visible **photoluminescence** (PL) spectra were recorded with a Jasco FP-6500 Spectrofluorometer, with the Epifluorescence attachment - Jasco EFA-383, using 5 nm band passes for the excitation and the emission monochromators, the detector response of 1 sec, the scan rate of 100 nm/min and data pitch of 0.5 nm. The excitation wavelength was 355 nm.

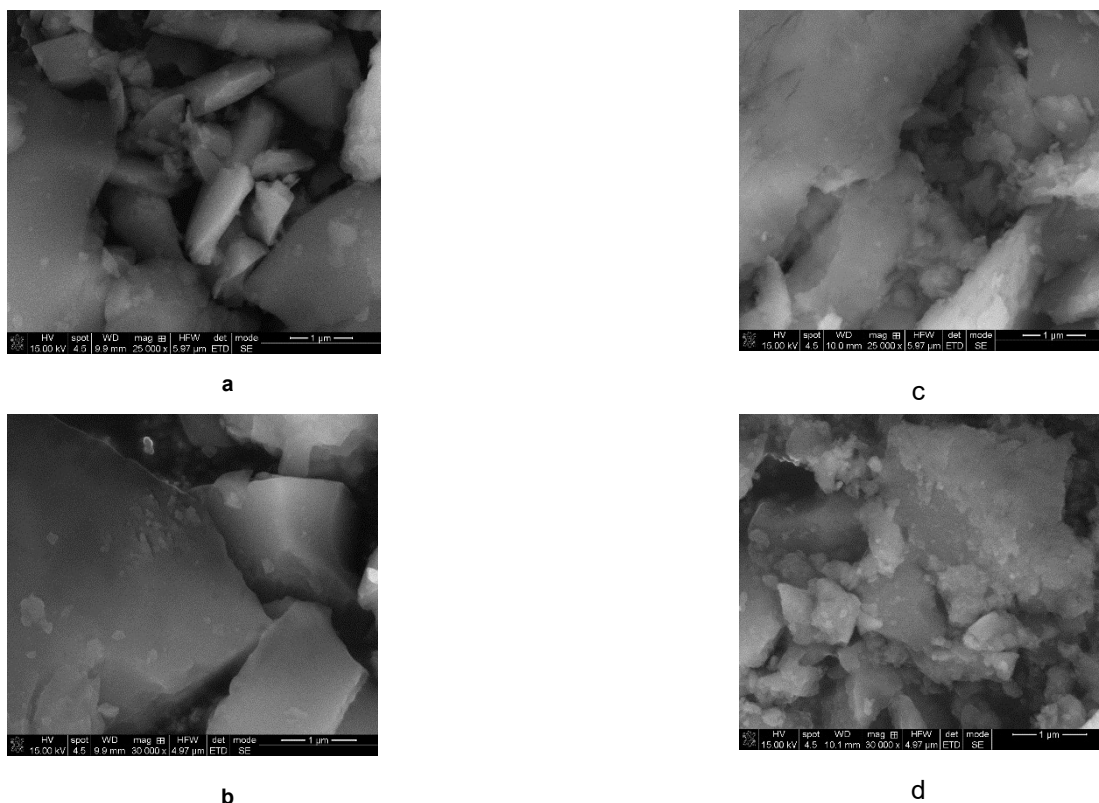


Fig. 1 - SEM images of the powders / *Imaginile SEM ale pulberilor* a)  $\text{SiO}_2\text{-TiO}_2$ , b)  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ , c)  $\text{SiO}_2\text{-TiO}_2\text{-Er}_2\text{O}_3$  and d)  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-Er}_2\text{O}_3$ .

### 3. Results and discussion

#### 3.1. Characterization of the as-prepared gels

As mentioned above (see Introduction) the studied gels were obtained from solutions used for preparation of films with optical properties. The resulted gels were amorphous as determined by XRD measurements (not presented here).

##### 3.1.1. Scanning Electron Microscopy

The morphology of the as-prepared gels is presented in Figure 1 (a, b, c, d).

In all cases formation of homogeneous gel aggregates is observed. The  $\text{Er}^{3+}$  and  $\text{Al}^{3+}$  doped gels lead to more fragmented pieces due probably, to the formation of additional phases as the results of the reaction between the dopants and the base components.

##### 3.1.2. Thermal behaviour

The thermal behavior of the as-prepared gels was investigated by TGA/DTA methods. The curves corresponding to the decomposition of obtained gels are presented in Figures 2a and b. It could be noticed that the thermal decomposition of the gels take place in two steps.

In the first step, the elimination of water takes place in the 20-150 °C temperature range accompanied by an endothermic effect.

In the second step (between 150-400 °C for all samples), the structural hydroxyls are eliminated and the organic residues are burnt out, without

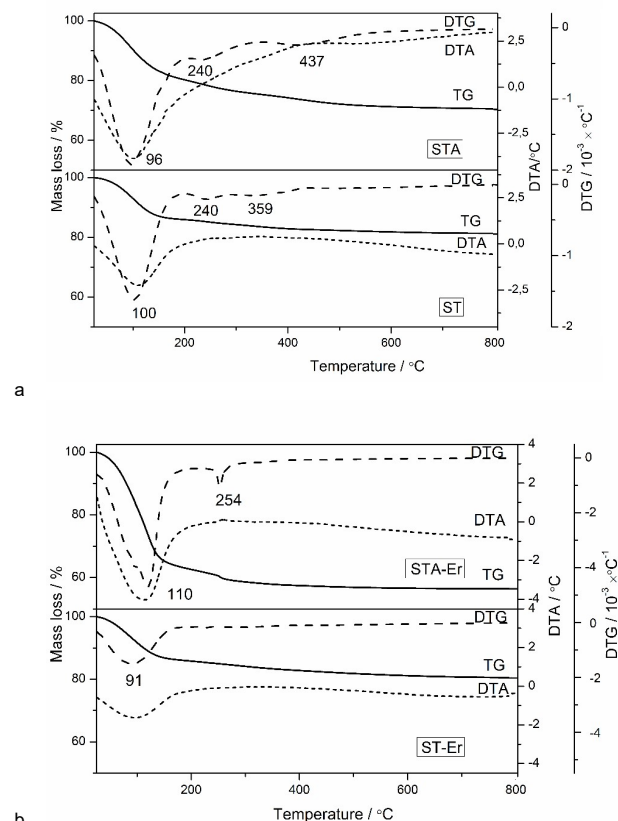


Fig. 2 - TG/DTG/DTA curves of the / *Curbele TG/DTG/DTA ale probelor* a)  $\text{SiO}_2\text{-TiO}_2$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ , b)  $\text{SiO}_2\text{-TiO}_2\text{-Er}_2\text{O}_3$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-Er}_2\text{O}_3$  samples (heating rate 10 °C/min) / *(viteza de încălzire 10°C/min)*.

**Table 2**

The assignment of the vibration bands in FT-IR spectra of the as-prepared gels in the undoped and Er-doped  $\text{SiO}_2\text{-TiO}_2$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  systems / Atribuirea benzilor de vibrație în spectrele FT-IR ale gelurilor preparate în sistemele  $\text{SiO}_2\text{-TiO}_2$  și  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  nedopate și dopate cu Er

Samples / Probe				Assignment and vibration mode Atribuirea benzilor de vibrație
ST	ST-Er	STA	STA -Er	
471	459	435	459	Si-O-Si
585	587	561	561	Ti-O, Al-O, Ti-O-Al
787	767	794	800	Si-O-Si symmetrical stretching in amorphous $\text{SiO}_2$ <i>Si-O-Si vibrație de întindere simetrică în <math>\text{SiO}_2</math> amorf</i>
946	946	946	946	Si-OH, stretching vibration <i>Si-OH, vibrații de întindere</i>
1074	1074	1074	1074	Si-O-Si asymmetric stretching in $\text{SiO}_2$ amorphous Al-O-Al <i>Si-O-Si vibrație de întindere asimetrică în <math>\text{SiO}_2</math> amorf, Al-O-Al</i>
1190	1190	1190	1190	Si-O-Si, LO mode asymmetrical stretching in $\text{SiO}_2$ amorf <i>Si-O-Si, LO mod de vibrație de întindere asimetrică în <math>\text{SiO}_2</math> amorf</i>
1389	1389	1389	1389	$\nu \text{NO}_3$
1638	1640	1641	1638	$\nu_s(\text{OH})$ in $\text{H}_2\text{O}$ in water / $\nu_s(\text{OH})$ în $\text{H}_2\text{O}$
2358	2358	2358	2358	$\text{CO}_3^{2-}$
2865	2854	2842	2847	$\nu_{\text{as}}(\text{CH})$
2928	2928	2914	2913	$\nu_{\text{as}}(\text{CH}_3)$
3448	3441	3436	3430	$\nu_{\text{as}}(\text{OH})$ adsorbed water / $\nu_{\text{as}}(\text{OH})$ apa adsorbită

specific effect on the DTA curves. This behavior indicating that the endothermic effects of the gels decomposition and the exothermal effects of burning out organic residues overlap and compensate each other. Over 400 °C a small weight loss around 1% can be observed for all gels.

There is no evidence of specific thermal effects corresponding to reactions between components.

### 3.1.3. FT-IR spectroscopy

The FT-IR spectra of the as-prepared gels are presented in Figure 3 and the assignment of the vibration bands are summarized in Table 2.

It can be noticed that the spectra are very similar with the spectra of the pure  $\text{SiO}_2$  gels [15, 16], due to high amount of the  $\text{SiO}_2$  in the samples.

Broad absorption bands in all gels between 3500  $\text{cm}^{-1}$  and 3200  $\text{cm}^{-1}$  were observed that indicate the presence of the hydroxyl groups and adsorbed water. The bands around 2850-2920  $\text{cm}^{-1}$  shows the presence of the organic residues.

The band at about 1389  $\text{cm}^{-1}$  is assigned to the  $\text{NO}_3^-$  vibration, due to the presence in the reaction mixture of  $\text{HNO}_3$  catalyst and of the  $\text{Al}(\text{NO}_3)_3$  used as Al precursor. The band at about 1638  $\text{cm}^{-1}$  is assigned to the bending vibration of the molecular water.

The band around 1074  $\text{cm}^{-1}$  is attributed to Si-O-Si asymmetrical stretching in amorphous  $\text{SiO}_2$ . The 946  $\text{cm}^{-1}$  band indicates the presence of Si-OH, stretching vibration while the band about 459  $\text{cm}^{-1}$  is attributed to Si-O-Si bonds.

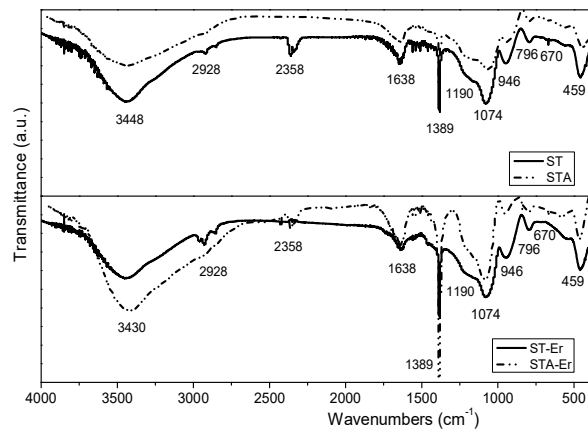


Fig. 3 - FT-IR spectra of the as-prepared gels  
Spectrele FT-IR ale gelurilor.

### 3.1.4. Photoluminescence (PL) measurements

The visible photoluminescence (PL) spectrum of  $\text{SiO}_2\text{-TiO}_2\text{-Er}$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-Er}$  gels are presented in Figure 4. In both cases at an excitation wavelength of 355 nm, four emission bands centered at 389, 401, 468 and 533 nm were observed. These emission bands which correspond to  $\text{Er}^{3+}$  luminescence, are weak in the gel form and consist of several very broad superimposed bands. Thus, the emission band at 401 nm may appear from the radiative transitions from the level  $^2\text{H}_{9/2}$  to the ground level  $^4\text{I}_{15/2}$ . The emission bands at 468 and 533 nm are attributed to the radiative transitions from the levels  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  and  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ ,

respectively. In the presence of Al<sup>3+</sup>, the intensity of the Er<sup>3+</sup> luminescence decreases and the emission bands at 401 and 422 nm (<sup>2</sup>H<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub>), remain well structured. Also, the emission band at 468 nm, attributed to <sup>4</sup>F<sub>5/2</sub> → <sup>4</sup>I<sub>15/2</sub> seems to be more intense and well structured as compared to that samples without Al<sup>3+</sup>.

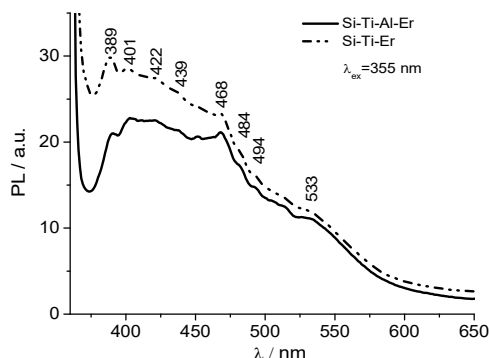


Fig. 4 - Visible photoluminescence spectra of the Er<sup>3+</sup>-doped SiO<sub>2</sub>-TiO<sub>2</sub> and SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> gels / Spectrele de fotoluminescență în vizibil ale gelurilor SiO<sub>2</sub>-TiO<sub>2</sub> și SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> dopate cu Er<sup>3+</sup>.

Previously [5], in the case of Er<sup>3+</sup>-doped SiO<sub>2</sub>-TiO<sub>2</sub> films, it was observed that the e<sup>-</sup>-hole pairs are generated in two photons transition in the electron subsystem of SiO<sub>2</sub>-TiO<sub>2</sub>, leading to a slow energy transfer to Er<sup>3+</sup>. Thus, we may assume that in the case of gels, the energy transfer to Er<sup>3+</sup> is very weak and the behavior may be attributed to the Er<sup>3+</sup> photoluminescence in the SiO<sub>2</sub> based structures and/or to the presence of the impurities in the silica matrix (structural OH, adsorbed CO<sub>2</sub> or H<sub>2</sub>O) dopate with Er<sup>3+</sup>.

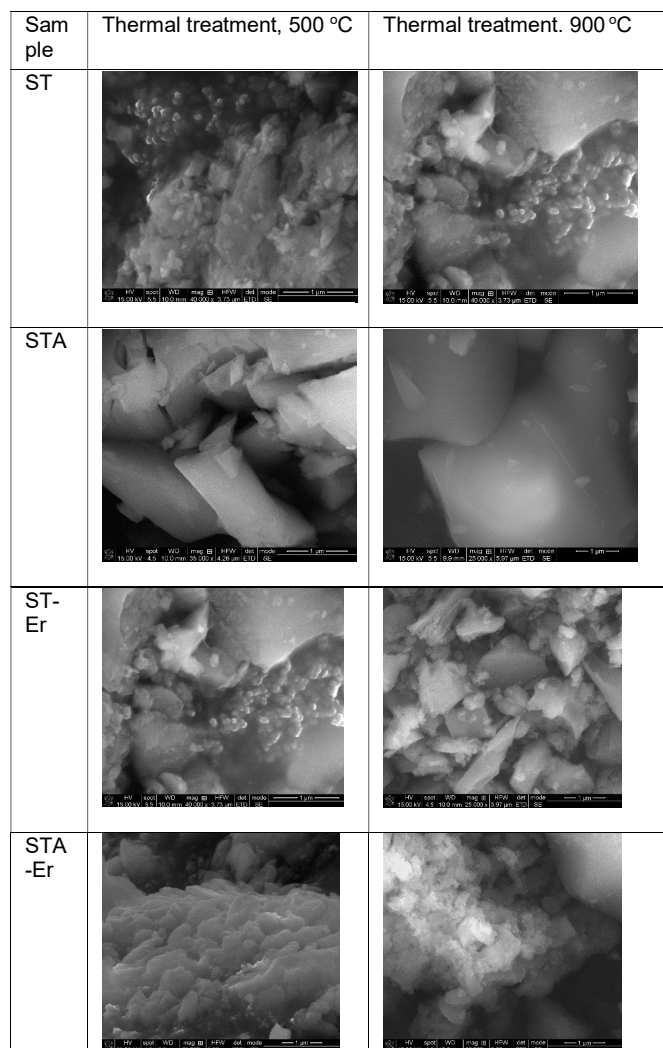


Fig. 5 - SEM images of the gels thermally treated at 500 and 900 °C / Imaginile SEM ale gelurilor tratate termic la 500 și 900 °C.

Table 3

The assignment of the vibration bands in FT-IR spectra of the thermally treated samples in the undoped and Er-doped SiO<sub>2</sub>-TiO<sub>2</sub> and SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> systems / Atribuirea benzilor de vibrație în spectrele FT-IR ale pulberilor tratate termic în sistemele SiO<sub>2</sub>-TiO<sub>2</sub> și SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nedopate și dopate cu Er

Samples								Assignment and vibration mode Atribuirea benzilor de vibrație
500°C				900°C				
ST	ST-Er	STA	STA-Er	ST	ST-Er	STA	STA-Er	
453	453	453	453	465	465	465	465	Si-O-Si
562	558	562	558	-	-	-	-	Ti-O, Al-O, Ti-O-Al
789	789	789	789	803	803	803	803	Si-O-Si symmetrical stretching in amorphous SiO <sub>2</sub> Si-O-Si vibrație de întindere simetrică în SiO <sub>2</sub> amorf
939	939	939	939	935	-	935	-	v <sub>as</sub> Si-O(H)
1071	1071	1071	1071	1095	1095	1095	1095	Si-O-Si asymmetric stretch in amorphous SiO <sub>2</sub> Si-O-Si vibrație de întindere asimetrică în SiO <sub>2</sub> amorf
1232	1232	1232	1232	1218	1218	1218	1218	Si-O-Si, LO mode of asymmetrical stretching in amorphous SiO <sub>2</sub> Si-O-Si, LO mod de vibrație de întindere asimetrică în SiO <sub>2</sub> amorf
1375	1380	1375	1380	1385	1380	1385	1380	vNO <sub>3</sub>
1636	1636	1636	1636	1638	1638	1638	1638	v <sub>s</sub> (OH) in water / în apă
2410	2410	2410	2410	2360	2365	2360	2365	CO <sub>3</sub> <sup>2-</sup>
2850	2850	2850	2850	2848	2850	2848	2850	v(CH)
2914	2914	2914	2914	2928	2928	2928	2928	v <sub>as</sub> (CH <sub>3</sub> )
3444	3447	3444	3447	3444	3442	3456	3444	v <sub>as</sub> (OH) adsorbed water / apa adsorbită

### 3.2. Thermally treated samples

Based on the results of thermal analysis the synthesized gels were thermally treated at 500 and 900 °C for 2 h.

#### 3.2.1. Scanning Electron Microscopy

The SEM images of the thermally treated samples are presented in the Figure 5.

In all cases the formation of homogeneous gel aggregates is observed. No significant modification of the morphology of the gels thermally treated at 500 and 900 °C is observed.

#### 3.2.2. FT-IR spectroscopy

The FT-IR spectra of the thermally treated powders are presented in Figure 6 and the assignment of the vibration bands is summarized in Table 3.

As compared with the as-prepared gels, the intensities of the vibration bands assigned to the hydroxyl groups, adsorbed water,  $\text{NO}_3^-$ , decreased for all thermally treated samples.

The vibration band of metal oxygen bonds at about  $450\text{ cm}^{-1}$  increases, indicating their better structuring. In the same time the vibration band at about  $935\text{ cm}^{-1}$  decreases. The decreasing of the mentioned band is explained by the polycondensation reactions that occur between the  $-\text{Si-OH}$  structural units or between the  $\text{Si-OH}$  and  $\text{Al-OH}$  ones, leading to the formation of  $\text{Si-O-Si}$  or  $\text{Si-O-Al}$  bonds.

An interesting result is observed in the case of the  $\text{Er}^{3+}$  doped samples for which the mentioned vibration band practically vanished starting with the thermal treatment at 500 °C. It could be concluded that the presence of  $\text{Er}^{3+}$  enhanced the mentioned polycondensation reactions.

#### 3.2.3. X-ray diffraction measurements

Based on the TGA/DTA results, the samples were thermally treated at 500 °C and 900 °C for 2 h.

The X-ray diffraction patterns of the powders are presented in the Figure 7.

According to the results presented in the Figure 7, the powders without  $\text{Er}^{3+}$  are amorphous at those temperature, but the presence of the  $\text{Er}^{3+}$  in the samples determines a very low crystallization of anatase phase as identified with ICDD file no. 00-021-1272.

The influence of  $\text{SiO}_2$  matrix on the crystallization behavior of titanium dioxide is well-documented [17]. According to Best et al. [18],  $\text{TiO}_2$  and  $\text{SiO}_2$  are immiscible and any crystallization in the mixed system implies segregation or diffusion of Ti. Sankur et al. [19] reported that the segregation phenomenon of Ti is driven by the initial composition of the mixture, as well as crystallization temperature and the crystal

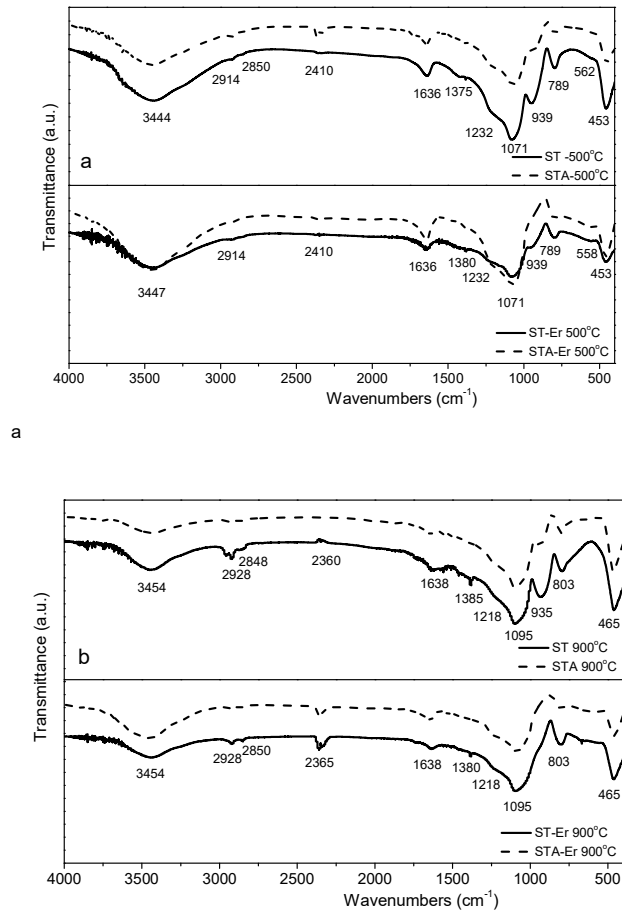


Fig. 6 - FT-IR spectra of the powders resulted by gels thermal treatment at a) 500 °C and b) 900 °C / Spectrele FT-IR ale pulberilor rezultate din tratamentul termic al gelurilor la a) 500 °C și b) 900 °C.

size. Chao et al. [20] reported that the addition of  $\text{SiO}_2$  into  $\text{TiO}_2$  matrix retards crystallization of the  $\text{TiO}_2$ . It was also noted that an increasing of the  $\text{SiO}_2$  content resulted in a decreasing particle size, confirmed by the XRD analysis taken after annealing the samples at 500 °C and 900 °C. Machida et al. [21] reported the presence of amorphous  $\text{SiO}_2$  around  $\text{TiO}_2$ , which would prevent the growth of  $\text{TiO}_2$  particles. Klein et al. [22] reported that the Si-excess in  $\text{SiO}_2\text{-TiO}_2$  systems remained in amorphous state up to 900 °C.

In crystallization, the most important parameter is the critical nucleus size. Around this value, there is a competition between the formation of new crystalline phase and the clusters dissolution. In the investigated systems, the  $\text{SiO}_2$  matrix may prevent the clustering of oxide particles ( $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ ) to form nuclei and reach the critical size, and, hence, crystal growth, which easily explain the amorphous state up to 900 °C of  $\text{SiO}_2\text{-TiO}_2$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  systems, for the given compositions. In the same time, at low loadings, the small size of crystals

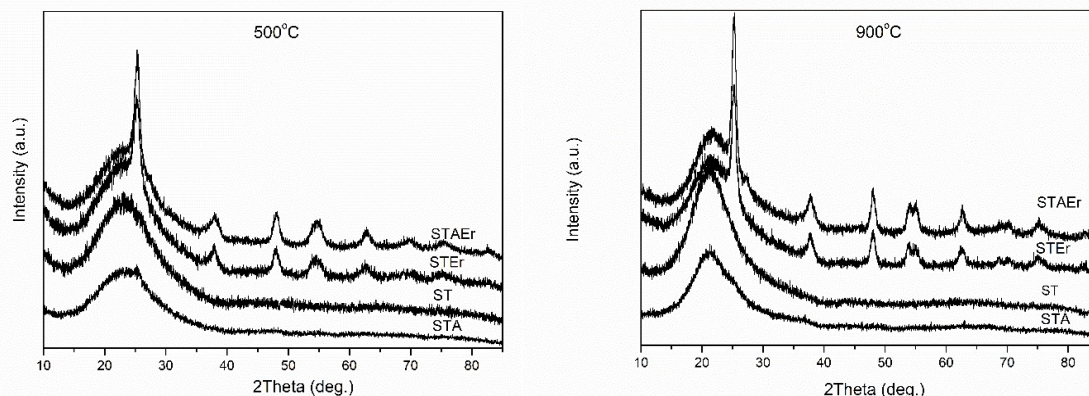


Fig. 7 - X-ray diffraction patterns of the thermally treated powders / Difractogramele pulberilor tratate termic.

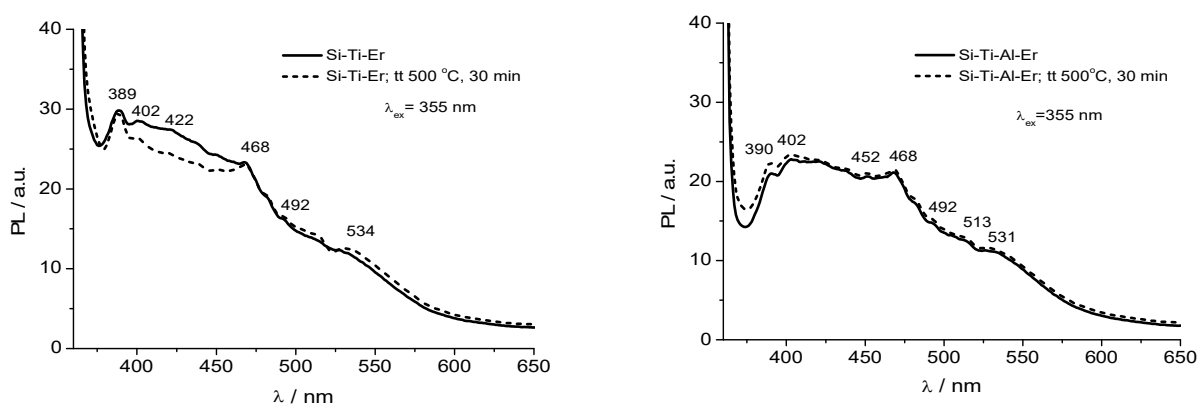


Fig. 8 - Visible photoluminescence spectra of the  $\text{Er}^{3+}$ -doped  $\text{SiO}_2\text{-TiO}_2$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  powders thermally treated at 500 °C / Spectrele de fotoluminescență în vizibil ale pulberilor  $\text{SiO}_2\text{-TiO}_2$  și  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  dopate cu  $\text{Er}^{3+}$  tratate termic la 500 °C.

and high dispersion in the amorphous  $\text{SiO}_2$  matrix causes significant line broadening in X-ray diffraction (XRD) powder patterns. Hence, the absence of lines from the crystalline phase in an XRD pattern does not necessarily rule out the presence of small particles of the crystalline oxide [23].

A different behavior it was noticed for  $\text{Er}^{3+}$  doped systems. Both systems ( $\text{SiO}_2\text{-TiO}_2$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ ) present a crystalline phase, which was identified as  $\text{TiO}_2$ , anatase. The competition between  $\text{Er}^{3+}$  ion clustering, which may act as crystal seeds for anatase crystal growth and  $\text{SiO}_2$  matrix constraints is favorable to the crystallization of anatase phase.

### 3.2.4. Photoluminescence (PL) measurements

The visible photoluminescence (PL) spectra of the as-prepared gels and thermally treated samples at 500 °C, are presented in the Figure 8. It could be noticed that for both  $\text{SiO}_2\text{-TiO}_2$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  systems, no significant changes between as-prepared gels and thermally treated samples was observed. As mentioned in the case of the gels, the very low energetic transfer

to  $\text{Er}^{3+}$  could be assigned to the photoluminescence of  $\text{Er}^{3+}$  in  $\text{SiO}_2$  based structures and/or to the presence of some impurities in the silica matrix (structural OH, adsorbed  $\text{CO}_2$  or  $\text{H}_2\text{O}$ ) dopate with  $\text{Er}^{3+}$ . The same aspects were observed also for the thermally treated samples leading to the conclusion that the residual impurities noticed stil in the case of thermally treated samples determine their low photoluminescence.

To bring more information on the matter the studies will be continued on samples thermally treated at 900°C and using a higher excitation wave, in the 950-1200 nm.

## 4. Conclusions

Gels and nanostructured powders were obtained by sol-gel method in the  $\text{Er}^{3+}$ -doped  $\text{SiO}_2\text{-TiO}_2$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  systems.

The as-prepared gels that contain mainly  $\text{SiO}_2$  in their composition present similar FT-IR spectra to that of pure  $\text{SiO}_2$ . The presence of the additives is put in evidence only by small displacements of the Si-O-Si and Si-OH characteristic vibration bands.

In the case of the thermally treated samples at 500 and 900 °C, FT-IR spectroscopy show the better structuring of M-O-M bonds, while significantly reducing the vibration bands of organic components, adsorbed water and structural hydroxyls.

An interesting behavior is observed in the case of  $\text{Er}^{3+}$  doped samples that shows its influence in enhancing the polycondensation of the Si-OH and Al-OH structural units.

The XRD measurements show an amorphous character of all un-doped samples after thermal treatment at both used temperatures (500 and 900 °C) while in the case of  $\text{Er}^{3+}$  doped samples the crystallization of  $\text{TiO}_2$  anatase phase crystallization was notice.

The  $\text{Er}^{3+}$  photoluminescence in gels and nanostructured powders is very weak due probably of the presence of the organic components, adsorbed water, and structural hydroxyls in their composition that could quench the fluorescence.

#### Acknowledgments

Support of the EU (ERDF) and Romanian Government, that allowed for acquisition of the research infrastructure under POS-CCE O2.2.1 project INFRANANO-CHEM – No. 19/ 01.03.2009, is gratefully acknowledged. The authors would like thank Dr. Mariana Voicescu from the "Ilie Murgulescu" Institute of Physical Chemistry, Bucharest, Romania, for photoluminescence measurements.

#### REFERENCES

- M.P.S. Almeida, L.M. Nunes, L.J.Q. Maia, R.R. Goncalves, S.J.L. Ribeiro, Structural properties and visible emission of  $\text{Eu}^{3+}$ -activated  $\text{SiO}_2\text{-ZnO-TiO}_2$  powders prepared by a soft chemical process, *Opt. Mater.*, 2016, **62**, 438.
- E. Cordoncillo, P. Escribano, J. Guaita, C. Philippe, B. Viana, C. Sanchez, Optical Properties of Lanthanide Doped Hybrid Organic-Inorganic Materials, *J. Sol-Gel Sci. Technol.*, 2002, **24(2)**, 155.
- J. Castaneda-Contreras, M.A. Meneses-Nava, O. Barbosa-Garcia, R. Chiu-Zarate, M.V. Felix, R. Rodriguez, Up-conversion luminescence saturation under pulsed excitation of erbium-doped,  $\text{SiO}_2\text{-TiO}_2$  sol-gel powders, *J. Lumin.*, 2010, **130(12)**, 2356.
- M. Langlet, in *Handbook of Sol-gel science and technology. Processing, Characterization and Applications vol I Sol-gel processing*, edited by Sumio Sakka. (Kluwer Academic Publishers, Boston/Dordrecht/London 2005)
- L. Predoana, S. Preda, M. Anastasescu, M. Stoica, M. Voicescu, C. Munteanu, R. Tomescu, D. Cristea, Nanostructured  $\text{Er}^{3+}$ -doped  $\text{SiO}_2\text{-TiO}_2$  and  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  sol-gel thin films for integrated optics, *Opt. Mater.* 2015, **46**, 481.
- A. Łukowiak, R. Dylewicz, S. Patela, W. Strek, K. Maruszewski, Optical properties of  $\text{SiO}_2\text{-TiO}_2$  thin film waveguides obtained by the sol gel method and their applications for sensing purposes, *Opt. Mater.*, 2005, **27**, 1501
- M. Zaharescu, M. Crișan, L. Predoană, M. Gartner, D. Cristea, Hybrid inorganic-organic sol-gel coatings in the  $\text{SiO}_2\text{-TiO}_2$  system, *J.Sol-Gel. Sci. Technol.* 2004, **32**, 173.
- A. Lukowiak, A. Chiappini, A. Chiasera, D. Ristic, I. Vasilchenko, C. Armellini, A. Carpentiero, S. Varas, G. Speranza, Sol-gel-derived photonic structures handling erbium ions luminescence, *Opt. Quant. Electron* 2015, **47**, 117.
- M. Hayer, V. Matejec, D. Berkova, I. Kasik, J. Kanka, P. Peterka, P. Honzatko, Effect of High-Temperature Treatment on Optical Properties of Silica Films Doped with  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$  and Rare-Earth Elements *J. Sol-Gel. Sci. Technol.* 2000, **19**, 293.
- M. Crisan, M. Gartner, L. Predoana, R. Scurtu, M.Zaharescu, R. Gavrilă, Sol-gel  $\text{SiO}_2\text{-ZrO}_2$  coatings for optical applications, *J. Sol-Gel. Sci. Technol.* 2004, **32**, 167
- J. Shen, A. Li, J. Zheng, L. Zhang, G. Liu, W. Zheng, Y. Zhang, Phosphosilicate glass film for optical waveguide by sol-gel method, *Optoelectron. Lett.* 2005, **1**, 0121.
- C.F. Song, M.C. Lu, P. Yang, D. Xu, D.R. Yuang, Structure and photoluminescence properties of sol-gel  $\text{TiO}_2\text{-SiO}_2$  films, *Thin Solid Films* 2002, **143**, 155.
- L. Zampedri, M. Ferrari, C. Armellini, F. Visintainer, C. Tosello, S. Ronchin, R. Rolli, M. Montagna, A. Chisera, S. Pelli, G.C. Righini, A. Monteil, C. Duverger, R.R. Goncalves, Erbium-Activated Silica-Titania Planar Waveguides, *J. Sol-Gel. Sci. Technol.* 2003, **26**, 1033.
- M. Zaharescu, L. Predoana, M. Gartner, M. Anastasescu, D. Cristea, P. Obreja,  $\text{SiO}_2\text{-TiO}_2$  Undoped or ( $\text{Er}^{3+}$ ) Doped Thin Layers for Integrate Optics Prepared by Sol-Gel Method, *Proc. of International Semiconductor Conference (CAS)* 2007, **1**, 215.
- A. Bertoluzza, C. Fagnano, M. A. Morelli, V. Gottard, M. Guglielmi, Raman and Infrared spectra on silica gel evolving toward glass, *J.Non-Cryst Solids*, 1982, **48**, 117.
- M. Sahini, M. Zaharescu, L. Constantinescu, E. Barbulescu and G. Jitianu, Uvegek felulete szerkezetének es kemiai stabilitasanak osszefuggese, *Epiloanyag*, 1982, **34**, 170.
- A. Hodroj, O. Chaix-Pluchery, M. Audier, U. Gottlieb, J.L. Deschanvres, Thermal annealing of amorphous Ti-Si-O thin films. *J. Mater. Res.*, 2008, **23** (3), 75.
- M.F. Best, R.A. Condrate, A Raman study of  $\text{TiO}_2\text{-SiO}_2$  glasses prepared by sol-gel processes, *J. Mater. Sci. Lett.* 1985, **4**, 994.
- H. Sankur, W. Gunning, Crystallisation and diffusion in composite  $\text{TiO}_2\text{-SiO}_2$  thin film, *J. Appl. Phys.* 1989, **66**, 4747.
- S. Chao and W.H. Wang: Characteristics of ion-beam-sputtered high refractive index  $\text{TiO}_2\text{-SiO}_2$  mixed films. *J. Opt. Soc. Am.* 1999, **A 16**, 1477.
- M. Machida, K. Norimoto, T. Watanabe, K. Hashimoto, A. Fujishima, The Effect of  $\text{SiO}_2$  Addition in Super-Hydrophilic Property of  $\text{TiO}_2$  Photocatalyst, *J. Mater. Sci.*, 1999, **34**, 2569.
- S. Klein, S. Thorimbert, W.F. Maier. Amorphous Microporous Titania-Silica Mixed Oxides: Preparation, Characterization, and Catalytic Redox Properties, *J. Catal.*, 1996, **163(2)**, 476.
- S. Srinivasan, A.K. Datye, M Hampden-Smith, I.E. Wachs, G. Deo, J.M. Jehng, A.M. Turek, C.H.F. Peden. The Formation of Titanium Oxide Monolayer Coatings on Silica Surfaces, *J. Catal.*, 1991, **131**, 260.

\*\*\*\*\*