



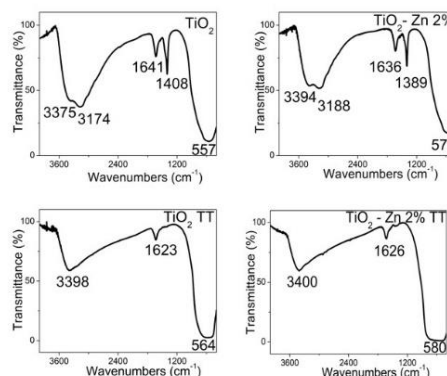
## FT-IR SPECTROSCOPY STUDY OF THE TiO<sub>2</sub> BASED POWDERS PREPARED BY THE SOL-GEL METHOD

Adriana RUSU,\* Luminița PREDOANĂ, Silviu PREDA, Daniela Cristina CULIȚĂ and Maria ZAHARESCU

“Ilie Murgulescu” Institute of Physical Chemistry of the Roumanian Academy, 202 Spl. Independentei, 060021 Bucharest, Roumania

Received August 14, 2024

In the present paper the results regarding the preparation by sol-gel method of the pristine and TiO<sub>2</sub> nanoparticles doped with Ce, Sn, Cu or Zn is presented. The as-prepared samples and the crystallized powders were investigated by Fourier transmission infrared spectroscopy (FT-IR). The FT-IR investigations are of great interest, especially for the amorphous as-prepared samples. In the cases of the studied samples, the FT-IR results obtained in both cases (amorphous and crystallized powders) have confirmed the interaction between TiO<sub>2</sub> and the different dopants. In the case of the as-prepared samples, the incorporation of the dopants in the TiO<sub>2</sub> structure is put in evidence by displacement of the νTi-O vibration to higher values of wavelength. The FT-IR results of the crystallized samples were confirmed by the XRD diffraction. The presence of the dopant in the TiO<sub>2</sub> structure was also confirmed by their influence on the photocatalytic investigations.



### INTRODUCTION

Among the chemical methods for pure or doped metal oxide films or powders preparation in liquid phase, the sol-gel technique is a versatile and efficient method.<sup>1–4</sup> The metal oxide preparation by the sol-gel method involves, two distinct steps, namely: (1) transformation of the solution into gels or amorphous nanopowders and (2) transformation of obtained amorphous samples (1), into vitreous or crystalline solids by adequate thermal treatment.<sup>5</sup>

As compared to other preparation methods, the sol-gel method shows some advantages, as: a good mixture of the reagents at the molecular level, leading to a homogeneous end product, the possibility to introduce dopants in large amount,

low processing temperature and control over the stoichiometry. It also presents the ability to obtain pre-established structures and shapes (gels, films, fibers, powders, etc.) by varying the experimental conditions.<sup>6</sup>

FT-IR spectroscopy represents an important method for the investigation of the sol-gel resulting materials in both steps of the sol-gel preparation. It has to be mentioned that FT-IR spectroscopy is one of the best methods for amorphous materials characterization.<sup>6,7</sup>

In the present paper the results regarding the preparation by sol-gel method of the pristine and TiO<sub>2</sub> nanoparticles doped with Ce, Sn, Cu, or Zn are presented, as well as their structural characterization by FT-IR investigations.

\* Corresponding author: adyrusu2001@yahoo.com

The influence of the mentioned dopants on the photocatalytic activity of the doped-TiO<sub>2</sub> samples was also underlined by comparing their structural properties with their photocatalytic properties, previously established.<sup>8-10</sup>

## RESULTS AND DISCUSSION

The as-prepared samples under the conditions described above consist of amorphous white powders for TiO<sub>2</sub> and the doped variants (TiO<sub>2</sub>-Sn 2.0%) and (TiO<sub>2</sub>-Zn 2.0%).

Conversely, other dopants produced colored powders: a greenish-white powder for TiO<sub>2</sub>-Cu 2.0% and a white-yellowish powder for TiO<sub>2</sub>-Ce 2.0%. The different colors of the samples are assigned to the presence of the different types of dopants in their compositions.

### As-prepared gels

The FT-IR spectrum of the TiO<sub>2</sub> as-prepared sample is shown in Fig. 1

In Fig. 1 the broad absorption bands between 3500 cm<sup>-1</sup> and 3100 cm<sup>-1</sup> indicate the presence of the hydroxyl groups and water. The band at 1641 cm<sup>-1</sup> is related to the bending vibration of the molecular water, while the vibration band at about 1400 cm<sup>-1</sup> is the typical vibration band of the coordinative bound water.

The broad vibration band with a maximum of 557 cm<sup>-1</sup> was assigned to Ti-O stretching vibrations of TiO<sub>6</sub>.

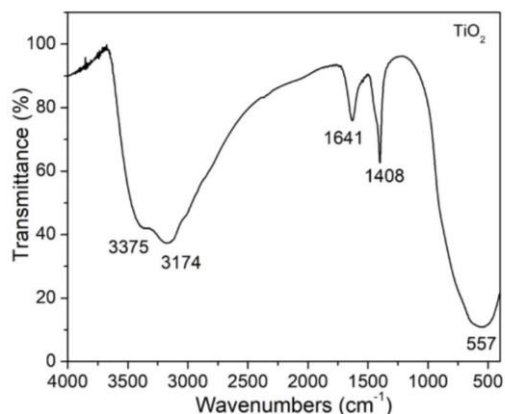


Fig. 1 – The FT-IR spectrum of the synthesized TiO<sub>2</sub> powder.

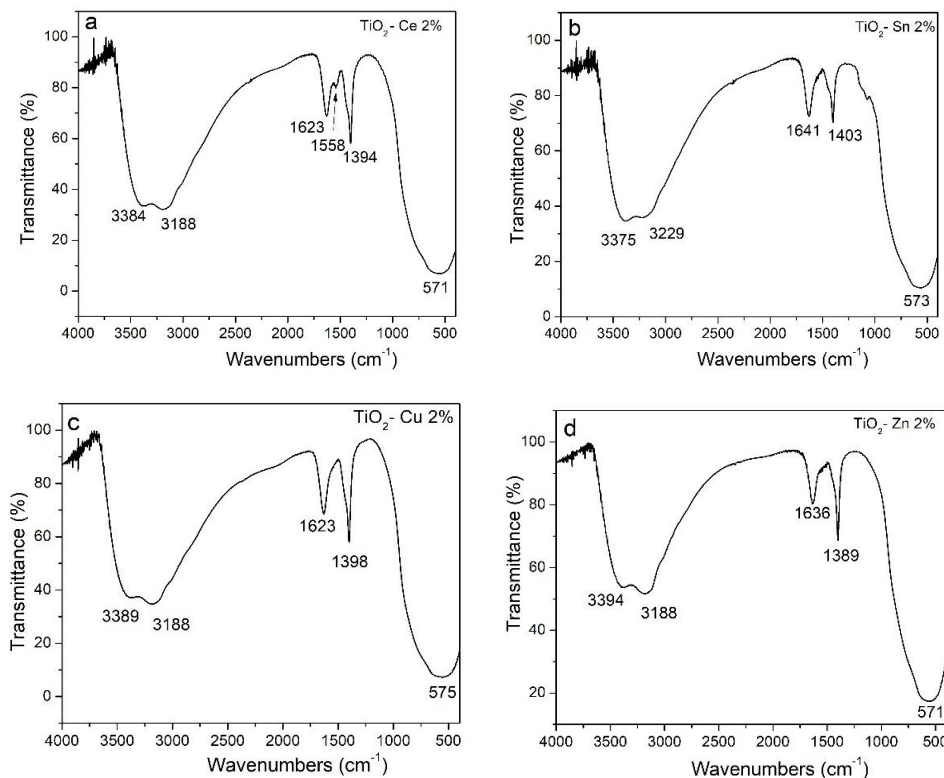


Fig. 2 – FT-IR spectra of the as-prepared powders: a) Ce-TiO<sub>2</sub>; b) Sn-TiO<sub>2</sub>; c) Cu-TiO<sub>2</sub>; d) Zn-TiO<sub>2</sub>.

In Fig. 2 the FT-IR spectra of doped TiO<sub>2</sub> as-prepared samples are shown. In the range of 3500–3100 cm<sup>-1</sup> the large band is noticed as in the case of

pristine TiO<sub>2</sub> sample. This band corresponds to the structural OH groups and water vibrations. The band around 1640–1623 cm<sup>-1</sup> is associated with the stretching

vibration of physically adsorbed molecular water, while the band around 1400–1380 cm<sup>-1</sup> corresponds to the vibration of coordinative bound water. The band around the 570 cm<sup>-1</sup> is due to  $\nu$ Ti-O of condensed octahedral (TiO<sub>6</sub>) with a small displacement.

In the case of Ce doped TiO<sub>2</sub> sample a supplementary band at 1558 cm<sup>-1</sup> appears assigned to -NH<sub>4</sub><sup>+</sup> group.<sup>11</sup>

In the case of the doped samples, the band assigned to the vibration of  $\nu$ Ti-O is shifted to higher values of wavelength due to the interaction between TiO<sub>2</sub> and the dopants.

The obtained results are important and provide evidence of the reactions that take place between TiO<sub>2</sub> and the different dopants.

### Thermally treated samples (powders)

The **FT-IR spectra** of TiO<sub>2</sub> treated powders are shown in Fig.3, and for doped TiO<sub>2</sub> powders in the Fig. 4. As compared to the as-prepared samples in the case of the thermally treated samples, the intensity of the characteristic bands assigned to Ti-O and Ti-O-Ti vibrations is significantly increased, showing a network ordering.<sup>7</sup>

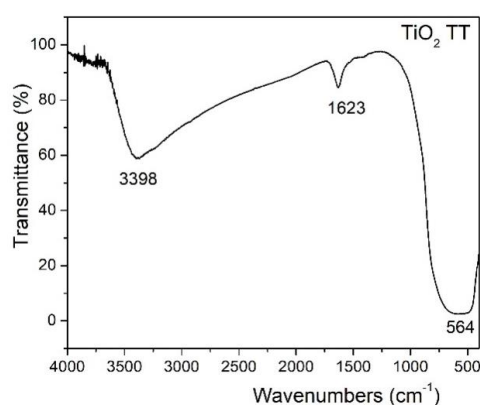


Fig. 3 – FT-IR spectrum of the thermally treated TiO<sub>2</sub> powder.

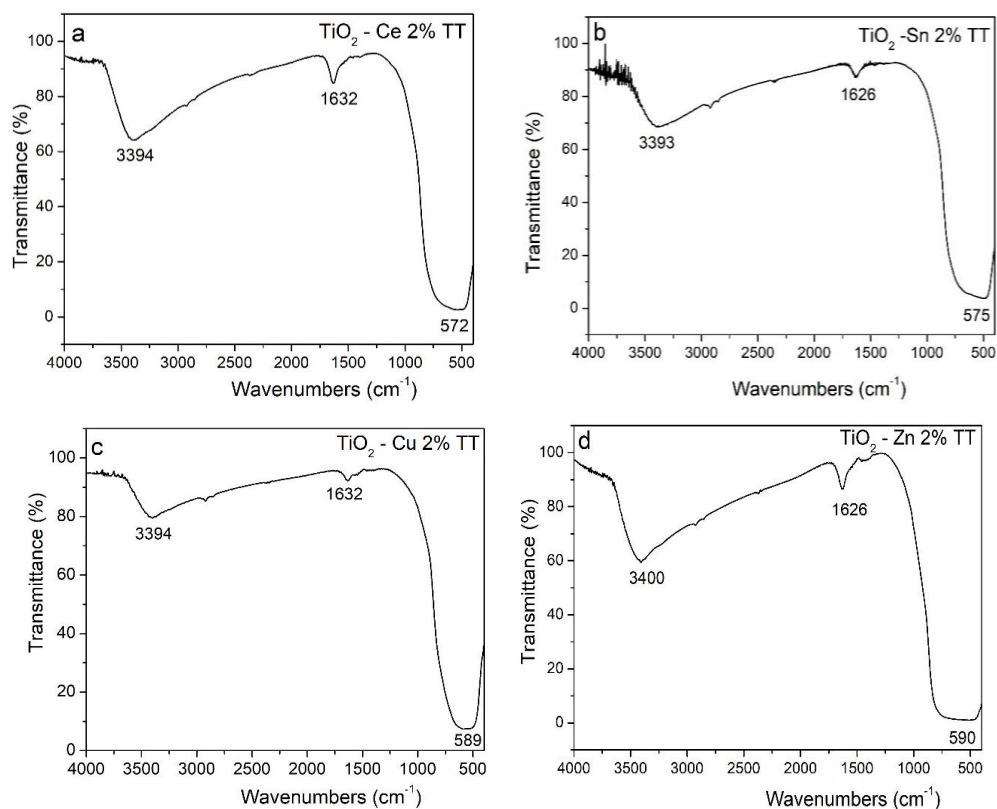


Fig. 4 – FT-IR spectra of the thermally treated powders: a) Ce -TiO<sub>2</sub>; b) Sn -TiO<sub>2</sub>; c) Cu-TiO<sub>2</sub> and d) Zn-TiO<sub>2</sub>

In the Figs. 3 and 4 the bands assigned to the hydroxyl groups (around  $3400\text{ cm}^{-1}$ ) and the water (around  $1630\text{ cm}^{-1}$ ) have much lower intensity due to the thermal treatment of the investigated samples.

By deconvolution of the large band between  $850\text{--}450\text{ cm}^{-1}$  one can see which bands are included in it. A summary of these bands is shown in Table 1.

Table 1

The assignment of the deconvoluted vibration bands in IR spectra of the samples

Wavenumber/ $\text{cm}^{-1}$					Assignments and vibration mode
TiO <sub>2</sub> TT	TiO <sub>2</sub> -Ce 2.0% TT	TiO <sub>2</sub> -Sn 2.0% TT	TiO <sub>2</sub> -Cu 2.0% TT	TiO <sub>2</sub> -Zn 2.0% TT	
805			812	789	Ti-O stretching vibration of TiO <sub>6</sub>
564	753	758	589	590	
483	475	473	488	461	Ti-O-Ti

The vibration bands of the dopants overlap the vibration bands of TiO<sub>2</sub>, which confirms the presence of dopants in the composition of the investigated samples.

### X-ray Diffraction (XRD)

The crystallinity and structure of the thermally treated samples were assessed by X-ray diffraction (XRD). Figure 5 shows the patterns of thermally treated Ce-, Sn-, Cu-, or Zn-doped TiO<sub>2</sub> samples at  $500\text{ }^{\circ}\text{C}$  for 1 h. Moreover, the undoped TiO<sub>2</sub> sample was measured as a reference. Single-phase anatase TiO<sub>2</sub> was identified in all the samples, according to ICDD file no. 21-1272.

No diffraction peaks of the dopants' crystalline phases were observed. The intensity of the (101) diffraction peaks of the doped powders decreased compared to the intensity of pure TiO<sub>2</sub> thus it can be concluded that dopant ions are incorporated within the TiO<sub>2</sub> lattice.

The diffraction results confirm the incorporation of the dopant in the TiO<sub>2</sub> structure, which was evidenced by FT-IR measurements.

The presence of the dopant in the TiO<sub>2</sub> structure was also confirmed by their influence on the photocatalytic investigations. The photocatalytic degradation of methyl orange (MO) solution in the presence of undoped and doped TiO<sub>2</sub> was carried out under UV and visible light irradiation and the results are presented in our previous published papers.<sup>9-10</sup>

It was observed that the presence of a doping metal (Sn, Cu, respectively, Zn) led to an increase in the photocatalytic activity in the visible domain compared to undoped TiO<sub>2</sub>. In the UV domain, all TT samples, presented the highest activity in

photocatalytic degradation of MO, removing  $\sim 85\%$  of the dye in 300 min.

Under visible light irradiation, the highest efficiency was obtained for the TiO<sub>2</sub>-Zn 2.0% TT sample.

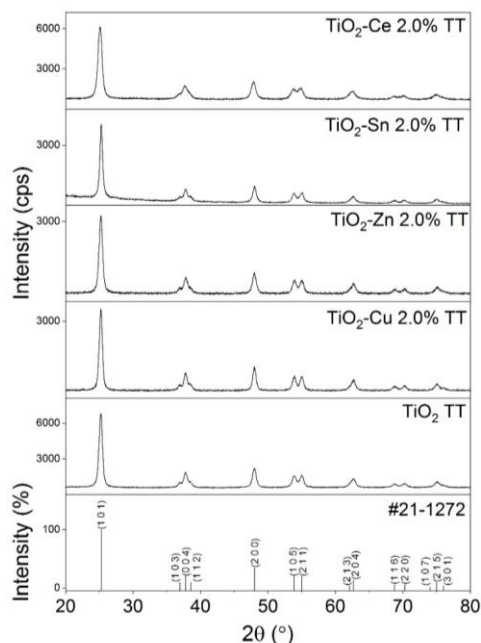


Fig. 5 – X-ray patterns for powders thermally treated at  $500\text{ }^{\circ}\text{C}$  1h.

## EXPERIMENTAL

### Gels and powders preparation

#### Gels preparation

Pristine or Ce-, Sn-, Cu- or Zn-doped TiO<sub>2</sub> powders were prepared by the sol-gel method. The initial calculated compositions for doped powders correspond to a TiO<sub>2</sub>: dopant oxide molar percentage of 98:2.0.

The precursor for TiO<sub>2</sub> preparation was titanium (IV) butoxide [TBOT = Ti(OC<sub>4</sub>H<sub>10</sub>)<sub>4</sub>] (Merck). The precursors for the dopants were the followings: cerium nitrate Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O as cerium precursor, tin(II) 2-ethylhexanoate [CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH(C<sub>2</sub>H<sub>5</sub>)CO<sub>2</sub>]<sub>2</sub>Sn (Sigma) as tin precursor, copper nitrate [Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O] (Merck) as copper precursor or zinc nitrate [Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] (Merck) as zinc precursor.

Butanol [C<sub>4</sub>H<sub>9</sub>-OH] (J.T. Baker) was used as solvent, H<sub>2</sub>O as hydrolysis agent, and ammonium hydroxide [NH<sub>4</sub>OH] (Riedel-de Haën) as catalyst.

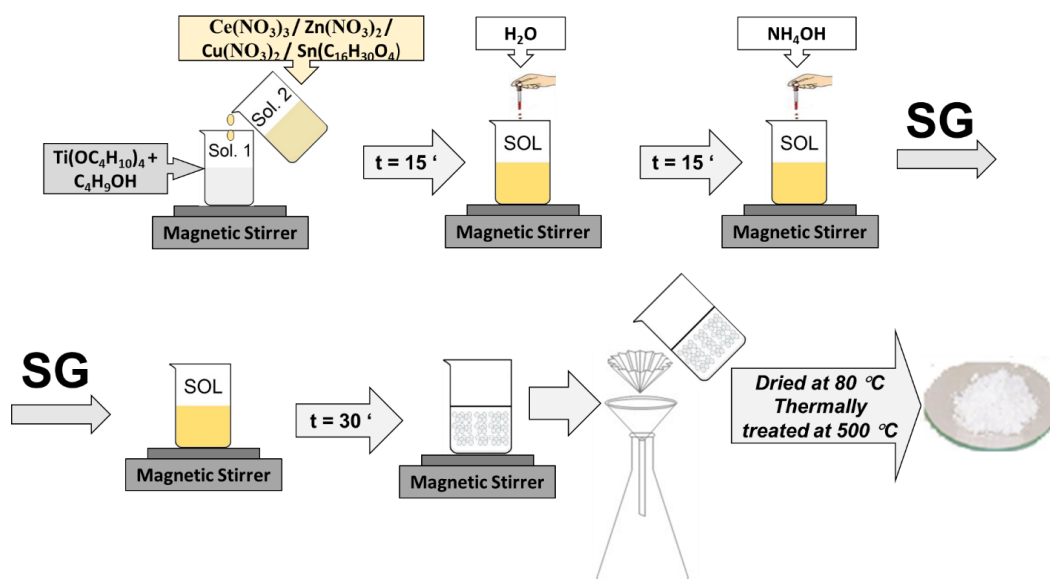
The details about the preparation method were presented in previously published papers.<sup>8–10</sup> A flowchart of the methodology used for the sample preparation is given in Fig. 6.

The composition of the solutions and the experimental conditions used are shown in Table 2.

Table 2

Composition of the initial solution and the experimental conditions of sol preparation

Sample	Reagents	Molar ratio			Sol pH	Experimental conditions	
		$\frac{ROH}{\sum \text{precursor}}$	$\frac{H_2O}{\sum \text{precursor}}$	$\frac{\text{catalyst}}{\sum \text{precursor}}$		T (°C)	t (min)
TiO <sub>2</sub>	Ti(OC <sub>4</sub> H <sub>10</sub> ) <sub>4</sub>	36.5	3	0.003	10	25	60
TiO <sub>2</sub> -Ce 2.0%	Ti(OC <sub>4</sub> H <sub>10</sub> ) <sub>4</sub> + Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	36.5	3	0.003	10	25	60
TiO <sub>2</sub> -Sn 2.0%	Ti(OC <sub>4</sub> H <sub>10</sub> ) <sub>4</sub> + [CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(C <sub>2</sub> H <sub>5</sub> )CO <sub>2</sub> ] <sub>2</sub> Sn	36.5	3	0.003	10	25	60
TiO <sub>2</sub> -Cu 2.0%	Ti(OC <sub>4</sub> H <sub>10</sub> ) <sub>4</sub> + Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	36.5	3	0.003	10	25	60
TiO <sub>2</sub> -Zn 2.0%	Ti(OC <sub>4</sub> H <sub>10</sub> ) <sub>4</sub> + Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	36.5	3	0.003	10	25	60

ROH = C<sub>4</sub>H<sub>9</sub>-OH.Fig. 6 – The flowchart of preparation of undoped and doped TiO<sub>2</sub> amorphous powders.

### Powder preparation

In order to obtain the powders intended for different applications, the as-prepared powders were thermally treated. The thermal treatment was established based on the TG/DTG/DTA results at 500 °C for 1 h with a heating rate of 1 °C/min.

The samples were denoted (TiO<sub>2</sub>), (TiO<sub>2</sub>-Ce 2.0%), (TiO<sub>2</sub>-Sn 2.0%), (TiO<sub>2</sub>-Cu 2.0%) and (TiO<sub>2</sub>-Zn 2.0%), and the thermally treated samples (TiO<sub>2</sub> TT), (TiO<sub>2</sub>-Ce 2.0%TT), (TiO<sub>2</sub>-Sn 2.0%TT), (TiO<sub>2</sub>-Cu 2.0% TT) and (TiO<sub>2</sub>-Zn 2.0% TT), respectively

### Methods of gels and powders characterization

**FT-IR spectra** of the as-prepared samples and powders resulting after thermal treatment were recorded over the range of

4000–400 cm<sup>-1</sup> on a Jasco FT-IR-4700 spectrophotometer using the KBr disc method.

**X-ray diffraction (XRD)** patterns were recorded using a Rigaku Ultima IV X-ray diffractometer. The equipment operated at 40 kV and 30 mA, using CuK $\alpha$  radiation (K $\alpha$  = 1.54056 Å). The data were collected over the 2 $\theta$  range 20–80° at a scanning rate of 2°/min.

## CONCLUSIONS

FT-IR spectroscopy has proven to be a valuable tool in the characterization of TiO<sub>2</sub> and TiO<sub>2</sub> doped powders, providing detailed information on structural changes induced by dopants and heat treatment. The sol-gel method, combined with a precise control of

synthesis parameters, enables the fabrication of nanomaterials with tailored properties for various industrial and environmental applications.

In the present paper, the FT-IR study of pristine and Ce<sup>-</sup>, Sn<sup>-</sup>, Cu<sup>-</sup> or Zn<sup>-</sup>-doped TiO<sub>2</sub> doped TiO<sub>2</sub> nanometric powders prepared by the sol-gel method was presented.

The interaction between TiO<sub>2</sub> and the mentioned dopants was put in evidence by shifting the wavelength band assigned to the vibration of  $\nu$ Ti-O to higher values.

For thermally treated samples, the FT-IR results were confirmed by XRD results.

The presence of the dopants in the TiO<sub>2</sub> lattice has also influenced the photocatalytic activity of the samples.

*Acknowledgments.* This work was performed within the frame of the research program "Oxide Compounds and Materials Science" of the "Ilie Murgulescu" Institute of Physical Chemistry, financed by the Roumanian Academy.

## REFERENCES

1. A. V. Vinogradov and V. V. Vinogradov, *RSC Adv.*, **2014**, *4*, 45903–45919.
2. S. Sakka, "Sol-Gel Process and Applications", in "Handbook of advanced ceramics", Amsterdam: Elsevier; 2013, pp. 883–910.
3. H. Schmidt, *J. Non-Cryst. Solids*, **1988**, *100*, 51–64.
4. C. J. Brinker, G. W. Scherer, "Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing", San Diego: Academic Press; 1990, pp. 11–14.
5. S. Sakka and K. Kamyra, *J. Non-Cryst. Solids*, **1982**, *48*, 31–46.
6. M. Zaharescu and O. C. Mocioiu, "Infrared Spectroscopy", in "Chemical Solution Deposition of Functional Oxide Thin Films", T. Schneller, R. Waser, M. Kosec and D. Payne (Eds.), Springer, Wien, 2013, pp. 213–230.
7. R. M. Almeida and A. C. Marques, "Characterization of Sol-Gel Materials by Infrared Spectroscopy", in L. Klein, M. Aparicio and A. Jitianu, (Eds.), "Handbook of Sol-Gel Science and Technology", Springer, 2016.
8. J. Pandele-Cusu, S. Petrescu, S. Preda, G. Petcu, M. Ciobanu and L. Predoana, *J. Therm. Anal. Calorim.*, **2022**, *147*, 13111–13124.
9. S. Preda, J. Pandele-Cuşu, S. V. Petrescu, E. M. Ciobanu, G. Petcu, D. C. Culiţă, N. G. Apostol, R. M. Costescu, I. Raut, M. Constantin and L. Predoană, *Gels*, **2022**, *8*, 673–679.
10. L. Predoană, E. M. Ciobanu, G. Petcu, S. Preda, J. Pandele-Cusu, E. M. Anghel, S. V. Petrescu, D. C. Culiţă, A. Băran, V.-A. Surdu, B. S. Vasile and A. C. Ianculescu, *Catalysts*, **2023**, *13*, 534–540.
11. B. Norman, L. Colthup, H. Dally and S. E. Wiberly, "Introduction to infrared and Raman Spectroscopy", in "Major Spectra Structure correlation by Spectral regions", Book Second Edition, Chapter 13, 1975, pp. 365–458.