

PAPER • OPEN ACCESS

## Laser ablation of silicon monoxide and titanium monoxide in liquid: formation of mixed colloidal dispersion with photocatalytic activity

To cite this article: Lukáš Vála *et al* 2020 *J. Phys.: Conf. Ser.* **1527** 012046

View the [article online](#) for updates and enhancements.



**IOP | ebooks™**

Bringing together innovative digital publishing with leading authors from the global scientific community.

Start exploring the collection—download the first chapter of every title for free.

# Laser ablation of silicon monoxide and titanium monoxide in liquid: formation of mixed colloidal dispersion with photocatalytic activity

Lukáš Vála<sup>1</sup>, Veronika Vavruňková<sup>1</sup>, Věra Jandová<sup>1,2</sup>, Tomáš Křenek<sup>1\*</sup>

<sup>1</sup> University of West Bohemia, Research Centre New Technologies 30614 Pilsen, Czech Republic

<sup>2</sup> Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Rozvojova 135, 160 00 Prague 6, Czech Republic

E-mail: [tkrenek@ntc.zcu.cz](mailto:tkrenek@ntc.zcu.cz)

## Abstract

Silica–titania mixed oxides and composites have been extensively studied, whereas to the titanium monoxide (TiO) –silicon monoxide (SiO) counterparts has been devoted very little attention. Laser ablation of SiO and TiO in liquids is in according with literature completely unexplored. Here we report on Nd:YAG pulse laser ablation of SiO and TiO in ethanol which allows generation of SiO- and TiO-based nanoparticles and their agglomerates.

Mixed SiO-TiO colloid has been prepared by simple mixing of ablatively prepared individual colloids in 1:1 volume ratio. Measurement of size distribution by Dynamic Light Scattering (DLS) determines sizes of 24.85 nm and 262.3 nm for SiO colloid, 494.8 nm for TiO colloid and 35.2 nm and 397.5 nm for mixed colloid. Zeta potential values suggest incipient instability for all measured systems. Morphology of the particles captured on Ta substrate by evaporation of ethanol was studied using Scanning Electron Microscopy (SEM). Round-shaped, oval, and sheet-like particles and their agglomerates have been observed. Raman spectroscopy of the mixed SiO-TiO colloid revealed multiphase structure consisting of anatase and/or rutile, crystalline and amorphous silicon and silica and crystalline and amorphous titanium silicide TiSi<sub>2</sub>. Formation of TiSi<sub>2</sub> demonstrates unexpected low temperature disproportionation of SiO and TiO-based species and mutual reducing interactions. Catalytic activity of individual SiO and TiO colloids and of their mixture has been tested in terms of methylene blue (MB) degradation under the daylight. TiO-SiO mixture exhibits higher solar-light catalytic activity compared to individual colloids which could be explain by the presence of highly photocatalytic TiSi<sub>2</sub>. These results represent potential of SiO and TiO reducing interactions which are favorable for generation of photocatalytic materials for water remediation.

## 1. Introduction

TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides have been intensively studied as a sol-gel titanosilicates, glasses, various composites, nano-objects and thin films where inert TiO<sub>2</sub> and SiO<sub>2</sub> represent promising constituents thanks their electrical, optical and photocatalytic properties <sup>[1,2]</sup>. Contrary to TiO<sub>2</sub>-SiO<sub>2</sub> mixture its TiO-SiO counterparts have attracted very little attention though TiO finds use in semiconducting microelectronic layered structures and photocatalyst <sup>[eg. 3, 4]</sup> and SiO is useful as optical coatings, heat shielding and insulating layers in electronics and semiconductor technologies <sup>[eg. 5]</sup>.



Titanium monoxide is a non-stoichiometric solid consist of several polymorphs and possess a wide ( $\text{TiO}_{0.70}$  to  $\text{TiO}_{1.25}$ ) homogeneity range and up to 15% of structural vacancies on both titanium and oxygen sublattices [6–9]. Cubic, monoclinic and tetragonal lattices of non-stoichiometric polymorphs have been described [eg. 10]. The structure of the solid silicon monoxide is considered [11–13] to be composed of separated amorphous nanophases of silicon and silicon dioxide and boundary layers of mixed silicon co-ordinations between Si and  $\text{SiO}_2$ . The crystal and electronic structures of solid SiO are still under controversy [12]. It has been concluded that SiO is not a simple mixture of Si and  $\text{SiO}_2$  but has several tetrahedral configurations [14].

Until recently, thermal reactions in the solid TiO–SiO mixture have remained unknown. Here we continue our recent research on mutual interactions in solid micro-sized SiO-TiO mixture which we explored under the conventional heating [15], cw-laser irradiation [16] and pulsed laser irradiation [17]. Various reducing reactions based on disproportionation of mutually interacting TiO and SiO has been observed whereas promising photocatalytic materials with visible light absorption have been obtained.

Here we report on laser ablation of TiO and SiO pellets in ethanol and on behaviour of mixed TiO-SiO colloid prepared by simple mixing of ablatively prepared individual colloids in order to clarify possible TiO-SiO interactions in the state of colloidal particles and to explore its potential photocatalytic effect.

## 2. Experimental

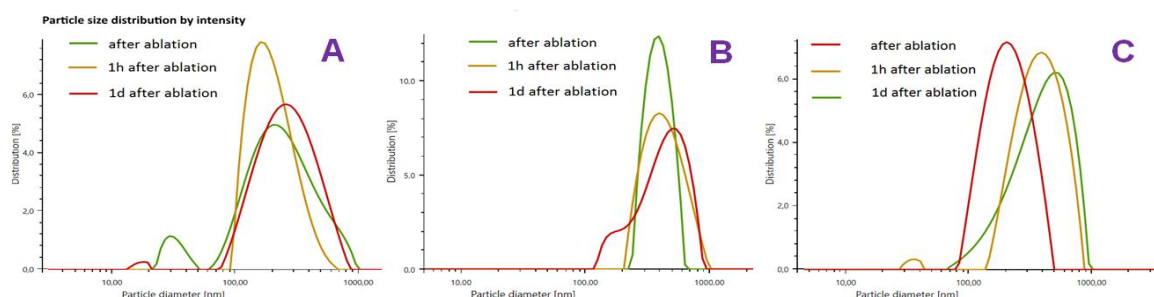
A 3rd harmonic of pulsed Nd:YAG laser with base wavelength 1064 nm (model Q SMART 850, wavelength: 355 nm, energy:  $180 \pm 5$  mJ per pulse, pulse duration: 10 ns, repetition rate: 10 Hz, pulse full width at half maximum: 23 ns) was focused by lens ( $f=15$  cm) on the spot area of  $0.02\text{cm}^2$  on SiO and TiO target. Simple tubular Pyrex reactor (70 mL in volume) reactor was furnished with a borosilicate glass windows and filled with ethanol. The duration of irradiation was 2 hours.

The irradiated target of SiO (compact irregular-shaped piece, Aldrich) and TiO (pellet with diameter 8.5 mm and height 5 mm, Aldrich) were positioned vertically in the center of the reactor. After the irradiation the colloids were divided in half for preparation of their mixture by simple stirring. Colloids and their mixture were characterized by Dynamic Light Scattering (DLS) – Litesizer™ 500 (Anton Paar) for the measurement of the size of particles and Zeta potential of the colloids. SEM (Scanning Electron Microscope, Tescan Indusem) with mounted EDS was used for the composition evaluation of the particles obtained by evaporation of the colloids. Particles were caught on Ta substrate and analyzed by SEM and EDS at acceleration voltage 15 kV. Raman spectra were measured using a DXR Raman microscope with Diode-pumped solid state laser emitting at 532 nm using high resolution gratings working in the range of  $50 - 1800\text{ cm}^{-1}$  and spectral resolution  $2\text{ cm}^{-1}$  FWHM. The photocatalytic oxidation of MB by SiO, TiO and SiO-TiO mixture dispersion in DEI water was performed as follows: 4ml of 0.05mM solution of methylene blue and 10 ml of colloid prepared by mixing nanoparticles in DEI water. This mixture was exposed to daylight (without external light source) for 180 min. Intensity of the light was  $\Phi \sim 800\text{ lm}$ . The depletion of MB was measured each 20 minutes by UV-Vis spectrometer (DU® Series 730 Beckman-Coulter).

## 3. Results and discussion

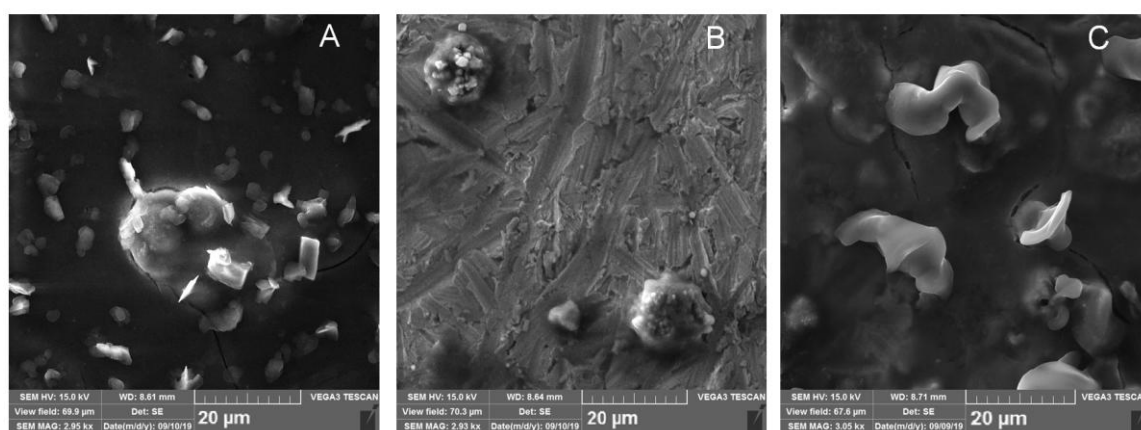
Highly focused pulsed irradiation of SiO and TiO target in ethanol results in generation of colloids based on SiO and TiO nanoparticles/agglomerates. The color of the solvent changed into bright grey for both SiO as well as TiO irradiation. The process of agglomeration and distribution of nanoparticles were measured by DLS. SiO colloid measured immediately after laser ablation exhibits size distribution of particles: 24.85 nm and 262.3 nm (Fig. 1 A). Measurement after 1 hour and 1 day suggest quite slow agglomeration during the time. DLS analysis of ablatively prepared TiO colloid shows constant size of particles with value of 494.8 nm (Fig. 1 B). Subsequent measurements after an hour and one day confirmed a constant particle size of agglomerates which corresponds with the formation of larger clusters already during the laser ablation in ethanol. SiO-

TiO mixture was prepared by simple mixing in volume ratio 1:1. The agglomeration tendency of mixed colloid was similar to that of SiO. Smaller particles of 35.2 nm and larger 397.5 nm were detected immediately after laser irradiation (Fig. 1 C). After one day, intensity of smaller particles decreased which suggest continuing of agglomeration process. The SiO particles generated via laser ablation in ethanol exhibit higher stability compared to TiO and SiO-TiO. Zeta potential of colloids measured immediately after irradiation represents values: SiO: -12.5 mV, TiO: -14.6 mV and SiO-TiO mixture: -11.7 mV which suggests incipient instability of the colloids.



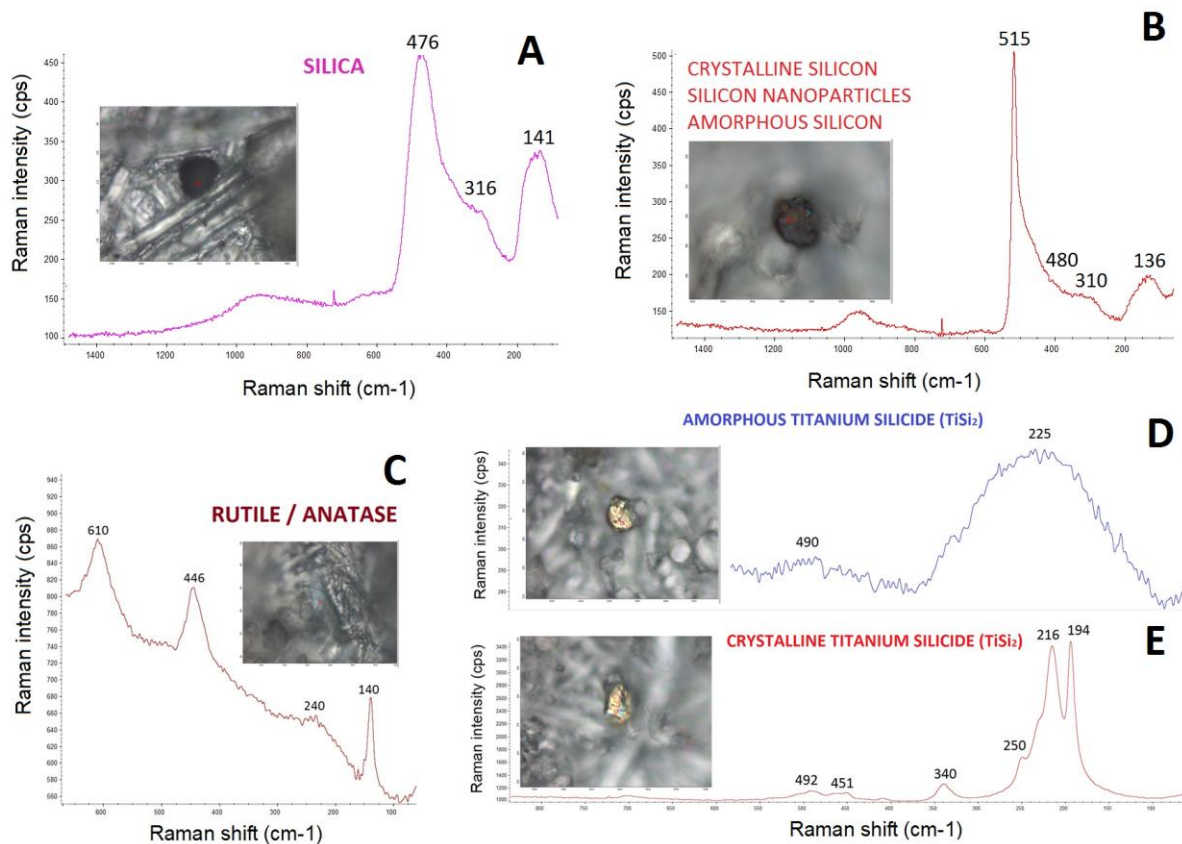
**Fig. 1** Size distribution of particles during one day of SiO (A), TiO (B), mixture SiO:TiO (C)

The SEM of particles obtained by evaporation of ethanol at 70°C on Ta substrate revealed sheet-like, roundshape and shapeless morphology (Fig. 2). In Fig. 2 A (SiO), a larger number of small sheet-like, sharp-edged and round-shaped particles including a larger ellipsoidal particle appeared. In the case of TiO (Fig. 2 B), spherical particles with smaller (spherical) protrusions were discovered. Apparently, the particles agglomerate during ethanol evaporation. In Figure 2 C (TiO-SiO mixture), random twisted and smaller round-shaped particles were observed. The size of particles/agglomerates varies from units of  $\mu\text{m}$  up to tens of nm.



**Fig. 2** SEM images of the SiO (A), TiO (B) and SiO:TiO (C) obtained after evaporation of ethanol

EDS analysis indicate wide range of Ti:Si ratio with suggest presence of areas with separated Si or Ti as well as particles with intermixed Si and Ti content indicating interdiffusion events.



**Fig.3** Raman spectroscopy of obtained particles with their optical images: A: Silica ( $\text{SiO}_2$ ), B: Crystalline and amorphous silicon, C: Rutile/Anatase ( $\text{TiO}_2$ ), D: Amorphous titanium silicide ( $\text{TiSi}_2$ ), E: Crystalline titanium silicide ( $\text{TiSi}_2$ )

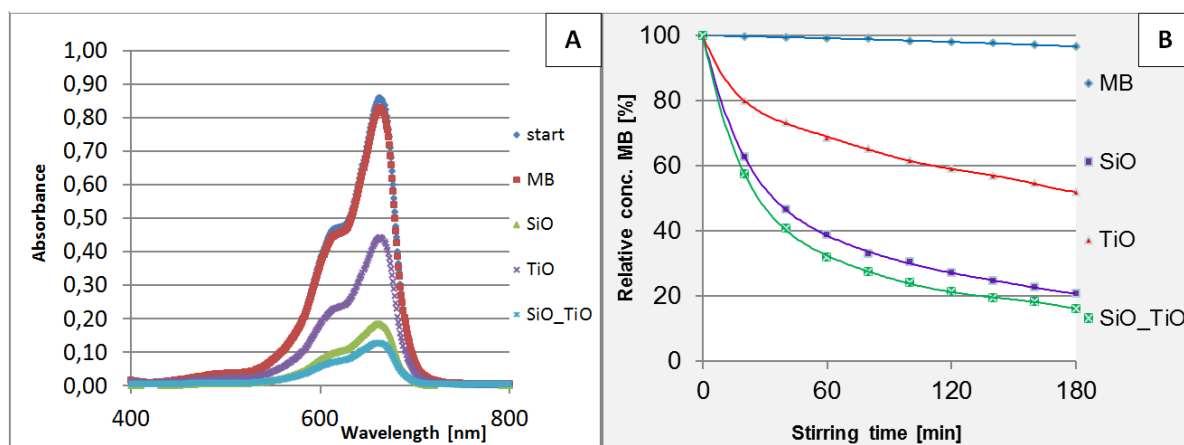
Raman spectroscopy (Fig.3) for the particles of SiO-TiO mixture reveals heterogeneous distribution of occurring phases. Broad peaks centered around 476, 316 and 141  $\text{cm}^{-1}$  (Fig. 3 A) are assignable to amorphous or partly crystallized silicon and/or silica [18]

Fig. 3 B shows sharp peak at 515  $\text{cm}^{-1}$  with the shoulder at 519  $\text{cm}^{-1}$  and broad peaks positioned at 136 and less intensive at 950  $\text{cm}^{-1}$  which agree with crystalline and nanocrystalline silicon [eg.19] and amorphous silicon and/or silica respectively [eg. 18]. Characteristic peaks for anatase and rutile (140, 240, 446 and 610  $\text{cm}^{-1}$ ) were identified in Fig. 3 C [eg. 20].

Fig. 3 D captures two broad peaks centered at 225  $\text{cm}^{-1}$  and less intense 490  $\text{cm}^{-1}$ . These peaks are attributable to the amorphous titanium silicide phase [21]. Next spectrum (Fig. 3 E) depicts two intense peaks at 194 and 216  $\text{cm}^{-1}$  followed by a less intense peak at 250  $\text{cm}^{-1}$  and three orders of magnitude equal to 340, 451, 492  $\text{cm}^{-1}$  corresponding to crystalline titanium silicide  $\text{TiSi}_2$  [21].

In summary, Raman spectroscopy revealed formation of multiphase structure composed of anatase, rutile, crystalline and amorphous silicon and silica, nanocrystalline silicon, and, interestingly, amorphous and crystalline titanium silicide  $\text{TiSi}_2$ . Formation of  $\text{TiSi}_2$  suggest disproportionation of both SiO as well as TiO phases and unexpected intensive reduction effect of mutually reacting SiO and TiO species under low temperature (70 °C). Such low temperature disproportionation defies thermodynamically equilibrium processes and encourages our effort to analyze and clarify mechanism of  $\text{TiSi}_2$  formation in more detail.





**Fig.4** A) Final spectra of degradation of MB in presence SiO, TiO and mixture of nanoparticles (SiO-TiO) after 180 min in comparison with initial spectra; B) Degradation of MB in presence SiO, TiO and mixture of nanoparticles (SiO-TiO)

The photocatalytic effect of nanoparticles/agglomerates of SiO, TiO and their mixture in volume ratio 1:1 prepared via evaporation and subsequent dispersion in DEI water was tested in terms of MB degradation. The mixture of 4ml of 0.05mM solution of MB and 10 ml of as prepared colloids was exposed on daylight and the depletion of MB was measured by UV spectroscopy. Fig. 4 A shows comparison of initial and final spectra of individual colloids and SiO-TiO mixture. Fig. 4 B shows significant MB degradation proceeding under daylight irradiation (without any external light source).

Fig. 4 B depicts that SiO-TiO mixture exhibit higher photocatalytic activity compared to individual SiO and TiO colloids. After 180 minutes of irradiation ~16 % of original MB concentration remains. This effect could be explained by formation of  $\text{TiSi}_2$  which represent highly photocatalytic phase<sup>[eg. 22]</sup>.

#### 4. Conclusion

Laser ablation of SiO and TiO targets in the ethanol results in formation of nanoparticles and their clusters. The properties of the colloidal particles of individual SiO and TiO and SiO-TiO mixture formed by simple mixing of the prepared SiO and TiO colloids in a volume ratio of 1:1 were investigated by DLS, SEM and Raman spectroscopy. Moreover, photocatalytic effect of prepared colloids was tested. DLS measurement revealed size distribution of particles 24.85 nm and 262.3 nm for SiO colloid, 494.8 nm for TiO colloid and 35.2 nm and 397.5 nm for SiO-TiO mixture. Measurement of Zeta potential confirmed similar incipient instability by following values: -12.5 mV for SiO, -14.6 mV for TiO, and -11.7 mV for SiO-TiO mixture. The morphology of the obtained particles was measured after evaporation of the ethanol of colloids and the particles and their agglomerates were captured on Ta substrate. Shapeless, round shape and sheet-like microparticles and their agglomerates were shown by SEM. Raman spectroscopy of the mixed colloid shows the presence of anatase and/or rutile, crystalline and amorphous silicon and silica and detects interestingly also crystalline and amorphous titanium silicide  $\text{TiSi}_2$ . These complementary analyses revealed unexpected low temperature (70°C) interactions and disproportionation of SiO and TiO nanoparticles which results in formation of photocatalytic  $\text{TiSi}_2$ . Solar photocatalytic tests show that the effect of SiO-TiO mixture is higher compared to SiO and TiO individuals which could be caused by  $\text{TiSi}_2$  presence. These findings suggest that simple mixing of ablatively prepared SiO/TiO colloids leads to low temperature reducing interactions which yield promising materials for photocatalytic degradation of organic residues under the daylight.

### Acknowledgements

The result was developed within the CENTEM project, reg. no. CZ.1.05/2.1.00/03.0088, cofunded by the ERDF as part of the Ministry of Education, Youth and Sports OPRDI programme and, in the follow up sustainability stage, supported through CENTEM PLUS (LO1402) by financial means from the Ministry of Education, Youth and Sports under the National Sustainability Programme I. Computational resources were provided by MetaCentrum (LM2010005) and CERIT-SC (CZ.1.05/3.2.00/08.0144) infrastructures.

The result was developed within the SGS project, reg. no. SGS-2019-025, cofunded by the University of West Bohemia.

### References

- [1] Dutoit, D. 1995 *Journal of Catalysis* **153** (1) 165 <https://doi.org/10.1006/jcat.1995.1118>
- [2] Ingale, S. V., Sastry, P. U., Wagh, P. B., Tripathi, A. K., Rao, R., Tewari, R., Gupta, S. C. 2012 *Mat. Chemistry and Physics* **135** (2-3) 497 <https://doi.org/10.1016/j.matchemphys.2012.05.014>
- [3] Simon, P., Pignon, B., Miao, B., Coste-Leconte, S., Leconte, Y., Marguet, S., Herlin-Boime, N. 2010 *Chemistry of Materials* **22** (12) 3704 <https://doi.org/10.1021/cm100653q>
- [4] Banakh, O., Schmid, P. E., Sanjinés, R., & Lévy, F. 2002 *Surface and Coatings Technology* **151-152** 272 [https://doi.org/10.1016/S0257-8972\(01\)01605-X](https://doi.org/10.1016/S0257-8972(01)01605-X)
- [5] Baba, Y., Sekiguchi, T., Shimoyama, I., Hirao, N. 2013 *Surface Science* **612** 77
- [6] WAHLBECK, P. G., GILLES, P. W. 1966 *Journal of the American Ceramic Society* **49** (4) 180 <https://doi.org/10.1111/j.1151-2916.1966.tb13229.x>
- [7] H. Iwasaki, N.F.H. Bright 1970 *J. Less-Common Met.* **21** 353
- [8] Valeeva, A. A., Tang, G., Gusev, A. I., Rempel, A. A. 2003 *Physics of the Solid State* **45** (1) 87 <https://doi.org/10.1134/1.1537416>
- [9] Valeeva, A. A., Gusev, A. I. 2006 *Physics of the Solid State* **48** (9) 1689 <https://doi.org/10.1134/S1063783406090113>
- [10] Gusev, A. I. 2013 *J. of Solid State Chemistry* **199** 181 <https://doi.org/10.1016/j.jssc.2012.12.025>
- [11] Schulmeister, K., Mader, W. 2003 *Journal of Non-Crystalline Solids* **320** (1-3) 143 [https://doi.org/10.1016/S0022-3093\(03\)00029-2](https://doi.org/10.1016/S0022-3093(03)00029-2)
- [12] Hohl, A., Wieder, T., van Aken, P., Weirich, T., Denninger, G., Vidal, M., Fuess, H. 2003 *J. of Non-Crystalline Solids* **320** (1-3) 255 [https://doi.org/10.1016/S0022-3093\(03\)00031-0](https://doi.org/10.1016/S0022-3093(03)00031-0)
- [13] Hirata, A., Kohara, S., Asada, T., Arao, M., Yogi, C., Imai, H., Chen, M. 2016 *Nature Communications* **7** 11591 <https://doi.org/10.1038/ncomms11591>
- [14] Kim, P.-S., Tang, Y.-H., Sham, T. K., Lee, S. T. *J. of Chem.* **85** (10) 695 <https://doi.org/10.1021/ja015619v>
- [15] Jandová, V., Pokorná, D., Kupčik, J., Bezdička, P., Křenek, T., Netrvalová, M., Pola, J. 2017 *R. on Chem. Int.* **44** (1) 503 <http://doi-org-443.webvpn.fjmu.edu.cn/10.1007/s11164-017-3116-z>
- [16] Křenek, T., Tesař, J., Kupčik, J., Netrvalová, M., Pola, M., Jandová, V., Pola, J. 2017 *J. of Inorganic and Organometallic Polymers and Materials* **27** (6) 1640 ISSN: 1574-1443
- [17] Jandová, V., Pokorná, D., Kupčik, J., Dytrych, P., Cuřínová, P., Fajgar, R., Pola, J. 2017 *Journal of Photochemistry and Photobiology A: Chemistry* **332** 376 <http://dx.doi.org/10.1016%2Fj.jphotochem.2016.09.019>
- [18] Biswas, R. K., Khan, P., Mukherjee, S., Mukhopadhyay, A. K., Ghosh, J., Muraleedharan, K. 2018 *J. of Non-Crystalline Solids* **488** 1 <https://doi.org/10.1016/j.jnoncrysol.2018.02.037>
- [19] <http://rruff.info>
- [20] Jandova, V., Fajgar, R., Dytrych, P., Kostejn, M., Drinek, V., Kupcik, J. 2015 *Thin Solid Films* **590** 270 <http://dx.doi.org/10.1016/j.tsf.2015.07.052>

- [21] Lim, E., Karunasiri, G., Chua, S., Shen, Z., Wong, H., Pey, K., Chan, L. 1998 *Microelectronic Engineering* **43-44** 611 [https://doi.org/10.1016/S0167-9317\(98\)00234-2](https://doi.org/10.1016/S0167-9317(98)00234-2)
- [22] Chu, D., Zhang, C., Yang, P., Du, Y., Lu, C. 2016 *Catalysts* **6** (9) 136 <https://doi.org/10.3390/catal6090136>