

PAPER • OPEN ACCESS

The influence of pulsed laser ablation in liquids parameters on the synthesis of ZnO nanoparticles

To cite this article: Carlos Andres Perez-Lopez *et al* 2020 *J. Phys.: Conf. Ser.* **1541** 012019

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

You may also like

- [Double-pulse laser ablation in liquids: nanoparticle bimodality reduction by sub-nanosecond interpulse delay optimization](#)
C Doñate-Buendia, M Spellauge, R Streubel *et al.*
- [A simple strategy for enhanced production of nanoparticles by laser ablation in liquids](#)
Yaakov Monsa, Gyora Gal, Nadav Lerner *et al.*
- [Fabrication of gold nanoparticles in Therminol VP-1 by laser ablation and fragmentation with fs pulses](#)
R Torres-Mendieta, R Mondragón, E Juliá *et al.*



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

The influence of pulsed laser ablation in liquids parameters on the synthesis of ZnO nanoparticles

Carlos Andres Perez-Lopez¹, Jaime Andres Perez-Taborda¹, Henry Riascos², Alba Avila¹

¹ Centro de Microelectronica, Departamento de Ingenieria Electrica y Electronica, Universidad de los Andes, Bogota, 111711, Colombia.

² Grupo Plasma Laser y Aplicaciones, Universidad Tecnologica de Pereira, Pereira, 660003, Colombia.

E-mail: a-avila@uniandes.edu.co

Abstract. Pulsed laser ablation in liquids (PLAL) synthesis of Nanoparticles (NPs) is a bottom-up process with the advantage of the absence of chemical reagents in the solutions. In this process, NPs shape and diameter distributions on PLAL experimental parameters. We research the hydrodynamic diameter of the ZnO Nps correlation to media, wavelength, fluence, and irradiation time. Nine solutions, five in methanol and four in ultra-pure water were processed with fluences ranged from 4 to 15 J cm⁻², target irradiation times from 8 to 15 min, and for wavelength of 532 nm and 1064 nm. We characterized the morphology and diameter distribution using Scanning Electron Microscopy (SEM) and Dynamic Light Scattering (DLS). Results showed that prolonging the irradiation time, reduces the diameter of the ZnO NPs by 41.4% in methanol and increases it by 19.8% in ultra-pure water. Change of medium from ultra-pure water to methanol revealed a maximum decrease of 84.2% in NPs diameter while lowering the fluence resulted in a 62.6% diameter reduction. The experimental results indicate that the medium and fluence were the most relevant parameters to obtain small NPs in methanol media with 80 nm diameter at 5 J cm⁻², a wavelength of 1064 nm, and 20 min irradiation time and the diameter was less dependent on wavelength. Understanding the synthesis parameters and their effect on Nps diameter dispersion is critical for the scaling-up production to meet the PLAL's promise of several grams per hour.

1. Introduction

Pulsed laser ablation in liquids (PLAL) synthesis of NPs is a bottom-up process with the advantage of the absence of chemical reagents and application under ambient pressure and temperature conditions [1, 2, 3]. The versatility of PLAL has been demonstrated by its capacity to produce NPs from noble metals, metal oxides, organic materials, and semiconductors with size-dependent optical, magnetic, and catalytic properties [4]. Aiming to produce nanoparticles for energy harvesting applications, we applied PLAL for the production of ZnO NPs. ZnO can be obtained from either a metallic or an oxide target [5, 3]. Additionally, ZnO is also attractive for its high piezoelectric constant d_{33} of 360×10^{-12} C N⁻¹ and relative permittivity of 3800, which makes it an excellent material for piezoelectric generators, sensors and actuators [6, 7, 8, 9, 10]. Controllable synthesis of NPs to engineer critical physical characteristics such as the particle shape, size in order to achieve the desired properties for energy applications requires



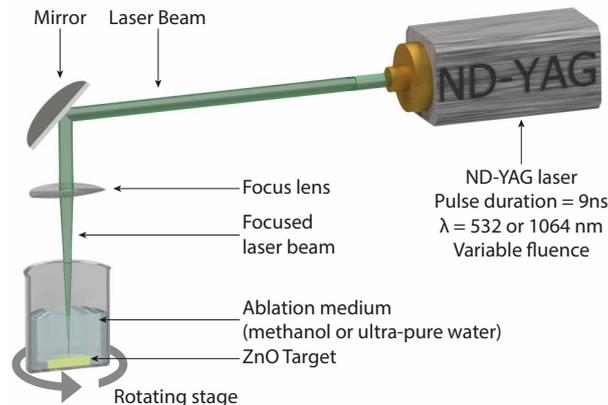


Figure 1: Schematic of the PLAL synthesis: an ND:YAG laser operating at the fundamental wavelength (1064 nm) and its harmonic (532 nm) laser is directed to a mirror, the reflection is focused the ZnO target that is submerged in liquid medium (methanol or ultra-pure water).

the understanding of the impact of the PLAL parameters: liquid medium, fluence, wavelength, and irradiation time [11].

In existing literature, multiple authors have studied the ZnO NPs synthesis by PLAL and the variation of its parameters from a metallic zinc target [3, 5, 12, 13, 14, 15, 16]. The use of nanosecond pulsed laser produced a decrease of NP diameter from 16 to 10 nm when using water compared to methanol as liquid medium [12]. In contrast, using a millisecond pulsed laser generated ZnO nanorods in water and spherical ZnO NPs in ethanol [13]. Reducing the fluence from 39.6 to 8.7 J cm⁻² exhibited a decrease from 88 to 39 nm in diameter, while increase from 30 to 40 nm diameter was detected when using 532 nm compared to 1064 nm [5]. A wavelength of 355 nm produced a diameter reduction from 20 to 4 nm when compared to 532 nm and 1064 nm [14]. We research the production of NPs from a zinc oxide target by varying multiple parameters to understand its effects on the nucleation, growth, coalescence of nuclei, and aggregation NPs.

In this study, we fabricated NPs from a ZnO target using the PLAL technique. We studied variations of the experimental parameters. We used Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM) techniques to analyze the samples produced. Then a discussion is given on the preliminary results that suggest a strong correlation between liquid medium, fluence, and irradiation time parameters and the ZnO NPs diameter.

2. Materials and methods

Experimental setup is shown in Figure 1: a ND-YAG laser (Spectra Physics) operating at 1064 nm fundamental wavelength and 532 nm second harmonic with pulse duration of 9 ns. The laser was pointed to a mirror, which reflected and focused the beam, passing through the lens on a 100 mL beaker filled with methanol (99.8%, Merck) and Type 1 water (also called ultra-pure water, obtained via Barnstead E-Pure D4641 water purification system, ThermoFisher Scientific). A 5N ZnO sputtering target (EJTZNOX501A2, Kurt J. Lesker Company) was placed at the bottom of the beaker resting on a motorised rotating platform..

The PLAL synthesis of the ZnO NPs depended on the pulsed laser ZnO target interactions in methanol and water media. It involves the process of energy absorption, plume formation and expansion, nucleation of ZnO NPs, the coalescence of liquid nuclei, and aggregation of NPs [17, 16]. This process can be divided into three stages, as described in the literature [17].

2.1. Early stage:

Once the laser pulse is emitted and directed to the ZnO target submerged in methanol or ultra-pure water, at their interaction, induced energy absorption is determined by the laser fluence, wavelength, and pulse duration (9 ns). In previous works this experimental system for the study of plasma or in the growth of thin films of different semiconductors has been used [18, 19]. Then, the ZnO target produced shock waves inside the target and media producing the release of vaporized ZnO and media species, forming what is known as cavitation bubble or plume.

2.2. Intermediate stage:

After the formation of the plume, the shortwave expands, followed by an adiabatic expansion of the plume. Then, the plume expansion, the released energy and vapors cause supersaturation conditions, which start the nucleation process and the coalescence between liquid nuclei and aggregation between NPs.

2.3. Later stage:

At this stage, the plume collapses, releasing the ZnO vapors and NPs into the medium in a colloidal solution. If the medium reaches ZnO supersaturation, it causes the additional NPs formation by new nucleation points. Furthermore, the released energy from the collapse can cause the second iteration of coalescence and aggregation by the collisions between the ZnO liquid nuclei and NPs formed during the intermediate and later stages. These collisions rates depend on the media temperature, which is proportional to fluence, pulse duration, and irradiation time.

During any of the above described stages, other two events can affect the final NPs diameter distribution. Firstly, the liquid medium can react chemically with the ZnO target, vaporized species, liquid nuclei, and NPs resulting in changes in growth and aggregation processes [12]. Secondly, suspended NPs in the liquid medium can intersect the laser path, causing a secondary ablation and therefore reducing the diameter distribution [16].

Sample	Medium	Wavelength (nm)	Fluence (J cm^{-2})	Irradiation Time (min)
ZnO-1	Methanol	532	10	8
ZnO-2		532	5	13
ZnO-3		1064	4	20
ZnO-4		1064	5	16
ZnO-5		532	5	10
ZnO-6	Type 1 Water	1064	5	25
ZnO-7		1064	10	10
ZnO-8		532	15	15
ZnO-9		532	5	10

Table 1: ZnO NPs samples synthesized by PLAL and experimental parameters varied during the synthesizing process: medium, laser wavelength, fluence, and irradiation time.

In our experiment we varied the wavelength, the media, the fluence, the irradiation time, nine samples were produced: five in methanol and four in ultra-pure water at a 532 nm and 1064 nm wavelengths, fluences ranged from 4 to 15 J cm^{-2} and irradiation times from 8 to 25 min, the NPs fabrication based on the tuning of the synthesis parameters is reported in Table 1. DLS

(ZetaSizer Nano ZS, Malvern Panalytical) was used to measure the hydrodynamic diameters after the PLAL process. We used EDAX- SEM (Lyra 3, Tescan) to analyze the NP's morphology and composition.. SEM samples were prepared by the drop-drying method: a 5 μL ZnO NPs suspension was deposited on a flat $3 \times 3 \text{ cm}^2$ intrinsic silicon wafer (Optim Wafer Services) that was left dry for 30 min. All the characterizations were performed at room temperature (25°C).

3. Results and discussion

Figures 2a and 2b show the hydrodynamic diameter distribution of the synthesized ZnO NPs in methanol and water, respectively. The analysis of the irradiation time variation was performed by comparing the mean hydrodynamic diameter \bar{D}_h and the relative standard deviation $\sigma_\%$ of two samples produced in the same medium, wavelength, and fluence. Samples are compared in two sets, the first produced in methanol and the second in ultra-pure water. The first set of samples ZnO-2 and ZnO-5 were produced at irradiation times of 13 min and 10 min, at 532 nm, and 5 J cm^{-2} . Here, the increase of 30% irradiation time produced a 41.3% decrease in \bar{D}_h and minimal change in $\sigma_\%$ ($< 3\%$). The second set of samples ZnO-7 and ZnO-8 were produced at irradiation times of 10 min and 15 min, at 1064 nm, where a 50% increment of irradiation time resulted in a 19.8% increment of \bar{D}_h and a reduction of 56% of $\sigma_\%$. The comparison of thermal conductivity (κ) of the two media ($0.2 \text{ W m}^{-1} \text{ K}^{-1}$ for methanol [20], and $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ for water [21]) show that water has greater ability to conduct heat in the solution inducing aggregation and coalescence. Thus, increasing the NPs \bar{D}_H in the late stage of ablation. In methanol, the lower κ resulted in decreased media absorption of the thermal energy, which limited the NPs movement in the medium, decreasing the ablation of NPs caused by the interception of the laser path. Hence, reducing its effect on $\sigma_\%$.

Additionally, SEM images of the samples displayed in Figure 2c for methanol and 2d for ultra-pure water show that the produced ZnO NPs were spherical with no noticeable surface imperfections or bumps regardless of the tuned parameters. The stable nanoparticle shape indicates that liquid ZnO nuclei coalescence dominated over solidified ZnO NPs aggregation in the late stage of ablation. Aggregations in ZnO-1 to ZnO-5 demand further study in the synthesis process and SEM sample preparation. EDAX results show methanol residues near to the aggregated NPS [22].

The influence of the medium, fluence, and wavelength parameters on the average hydrodynamic diameter \bar{D}_h and the error bars σ in the two media (represented in yellow for ultra-pure water and violet methanol), at two wavelengths (532 nm in green and 1064 nm in magenta) are shown in Figure 2e. Liquid medium variation can be studied by comparing the samples ZnO-5 (in methanol) and ZnO-9 (in ultra-pure water) synthesized at a wavelength of 532 nm, fluence of 5 J cm^{-2} , and irradiation time of 10 minutes where methanol produced a reduction of 73.2% on \bar{D}_H . For all the synthesized NPs in methanol medium, \bar{D}_H was reduced from 46.4 to 84.2% compared to ultra-pure water with identical wavelengths and similar fluence and irradiation time. The \bar{D}_H reduction could be a result of the limited heat transfer from the plume to methanol. The plume energy promotes its expansion and the increase of NPs nucleations in the intermediate stage of ablation; this also affects the nucleation in the next stage as it reduces the amount of vaporized ZnO available for the second nucleation that produces NPs with increased diameter [17]. Another explanation of the \bar{D}_H variation relies on methanol and ZnO chemical reactions. Previous studies indicate that the ZnO surfaces could absorb methanol, were oxygen species of the ZnO NPs interact with methanol yielding formaldehyde and formic acid in the plume at high temperatures ($> 1000^\circ\text{C}$ [11]); this creates a shell that limits the ZnO NPs growth. Residues of carbon, along with zinc and oxygen, were identified in the EDAX analysis in Figure 2f, which support this hypothesis.

ZnO \bar{D}_H effect from fluence variation was studied by comparing samples ZnO-1 and ZnO-2 produced in methanol, at 532 nm, and irradiation time of 8 min and 13 min, a decrease of 62.6%

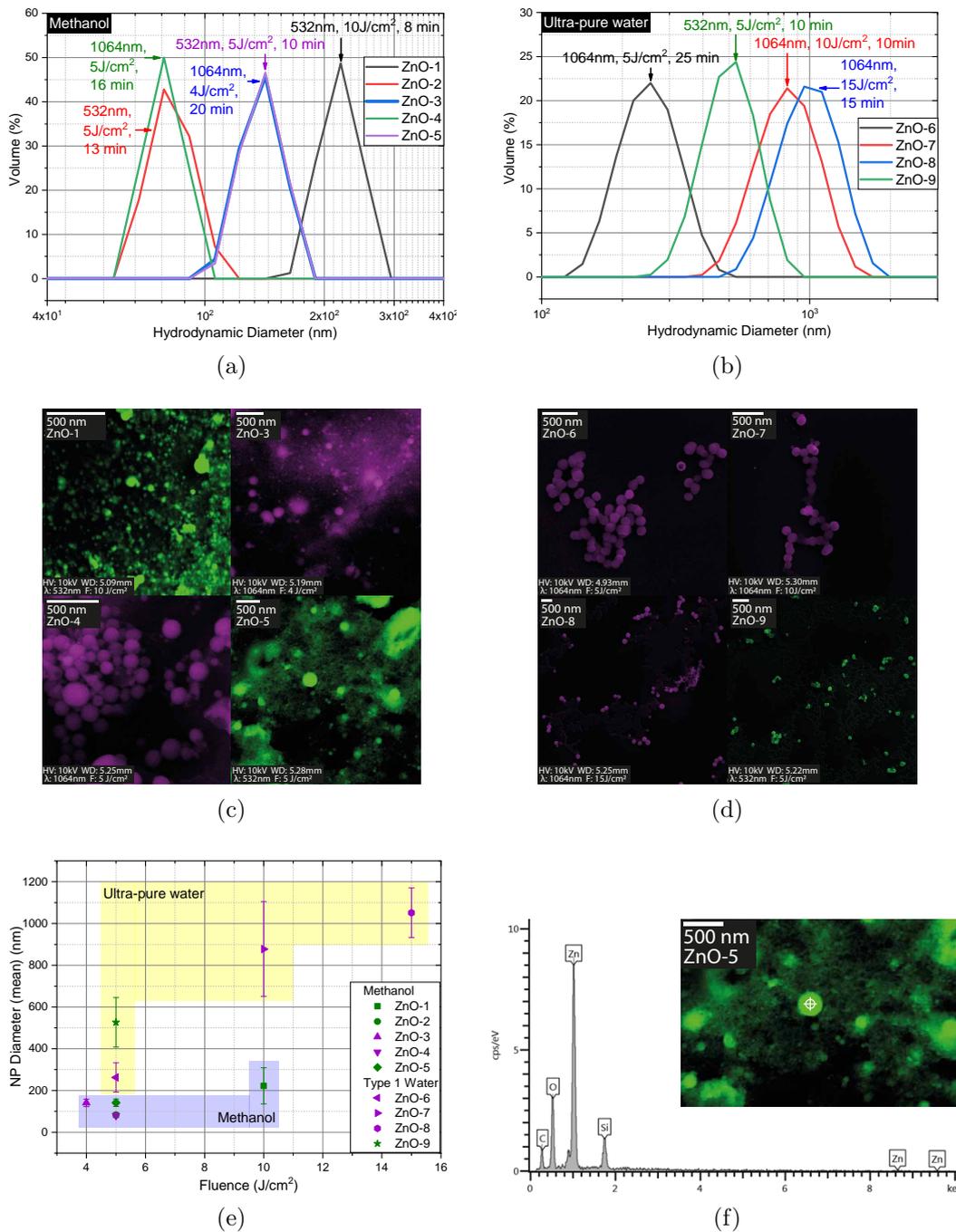


Figure 2: Normalized ZnO NP hydrodynamic diameter distributions are shown in (a) for methanol, and (b) for ultra-pure water, the peaks are labeled with the corresponding wavelengths, fluence, and irradiation time experimental parameters. SEM images of eight samples are shown in (c) for methanol, and (d) for ultra-pure water, images are colored in pseudo-color, green indicates zones with ZnO NPs produced at 532 nm and violet at 1064 nm. The effect of the different medium is presented in (e); in blue for methanol and yellow for ultra-pure water, symbols in green indicates samples produced at 532 nm and violet at 1064 nm. An EDX analysis of a single NP in ZnO-5 sample is shown in (f), inset indicates the analyzed region on the sample.

in \bar{D}_H was observed at a third of the laser fluence. Moreover, the samples produced in ultra-pure water, ZnO-7 and ZnO-8 at 1064 nm, and irradiation time of 10 min and 15 min exhibited a reduced reduction of 16.5% at half the fluence. The \bar{D}_H increment at higher fluence can be related to the increase of ZnO volume expelled from the target in the early stage of ablation caused by the additional energy absorbed by the ZnO target. The additional vaporized ZnO can increase \bar{D}_H under three scenarios. First, the growth of ZnO NPs was increased due to the increase of ZnO species available during the intermediate stage. Second, the distance between generated NPs was decreased as the ZnO nuclei increased in number in the intermediate stage and caused increased aggregation and coalescence during the plume collapse in the later stage of ablation. Third, the vaporized ZnO species not consumed in the intermediate stage were released in the liquid medium during the late stage and caused new nucleation points that resulted in bigger NPs compared to the ones produced in the intermediate stage.

The studied the effect of the wavelength by comparing samples ZnO-2 and ZnO-4, produced in methanol, at an equal fluence of 5 J cm^{-2} , and similar irradiation time of 13 min and 16 min. ZnO-2 was synthesized at 532 nm wavelength while ZnO-4 at 1064 nm. Despite the difference of wavelength, the difference in \bar{D}_H and $\sigma\%$ are under 3% and 10%, respectively. Therefore, the change wavelength produced no significative effect on the NPs diameter distribution.

4. Conclusions

In this research, we demonstrated that the irradiation time, medium, and fluence the significantly affect the diameter distribution of the ZnO NPs synthesized by PLAL. The change of medium from ultra-pure water to methanol exhibited the most substantial reduction of 84.2% on the ZnO NPs hydrodynamic diameter, followed by the decrease of 62.6% by the lessening of the fluence. At the same time, the increment of irradiation time resulted in the reduction of the hydrodynamic diameter by 41.3% for samples prepared in methanol and an increase of 19.8% in ultra-pure water. The change of wavelengths slightly affected the ZnO NPs diameter. The presented results provide key information for the understanding of the effect of PLAL synthesis parameters in the NPs diameter distribution, which is useful to meet the PLAL production scale-up promise of several grams per hour.

Acknowledgments

The authors acknowledge the financial support from Colombia's *Department of Science, Technology, and Innovation (Colciencias)* fellowship for the grant agreement No. 811, and agreement No. 808 under the project *design and fabrication of nanostructures*, 2018; and also from the joint research program *Convocatoria Interinstitucional de investigación en Ingeniería* between the Pontificia Universidad Javeriana, Cali and Universidad de los Andes under the project *Explorando rutas en transformación de energía mecano-eléctrica: Piezo y Triboelectricidad*, 2017.

Bibliography

- [1] Link S, Burda C, Nikoobakht B and El-Sayed M A 2000 *The Journal of Physical Chemistry B* **104** 6152–6163 ISSN 1520-6106 URL <https://pubs.acs.org/doi/10.1021/jp000679t>
- [2] Simakin A, Voronov V, Kirichenko N and Shafeev G 2004 *Applied Physics A* **79** 1127–1132 ISSN 0947-8396 URL <http://link.springer.com/10.1007/s00339-004-2660-8>
- [3] Zhao C, Huang Y and Abiade J T 2012 *Materials Letters* **85** 164–167 ISSN 0167577X URL <http://dx.doi.org/10.1016/j.matlet.2012.06.088>
- [4] Zhang W, Guo L P, Deng Q W and Li M X 2019 *Optik* **196** ISSN 00304026
- [5] Ismail R A, Ali A K, Ismail M M and Hassoon K I 2011 *Applied Nanoscience (Switzerland)* **1** 45–49 ISSN 21905517
- [6] Denishev K 2016 *Journal of Physics: Conference Series* **764** ISSN 17426596
- [7] Janotti A and Van De Walle C G 2009 *Reports on Progress in Physics* **72** ISSN 00344885

- [8] Ponnamma D, Cabibihan J J, Rajan M, Pethaiah S S, Deshmukh K, Gogoi J P, Pasha S K, Ahamed M B, Krishnegowda J, Chandrashekar B N, Polu A R and Cheng C 2019 *Materials Science and Engineering C* **98** 1210–1240 ISSN 18730191 URL <https://doi.org/10.1016/j.msec.2019.01.081>
- [9] Liu T, Zhao Q, Xie Y, Jiang D, Chu Z and Jin W 2020 *Biosensors and Bioelectronics* **156** 112145 ISSN 18734235 URL <https://doi.org/10.1016/j.bios.2020.112145>
- [10] Dagdeviren C, Hwang S W, Su Y, Kim S, Cheng H, Gur O, Haney R, Omenetto F G, Huang Y and Rogers J A 2013 *Small* **9** 3398–3404 ISSN 16136810 URL <http://doi.wiley.com/10.1002/sml.201300146>
- [11] Yang G 2012 *Laser Ablation in Liquids* (Jenny Stanford Publishing) ISBN 9780429086106 URL <https://www.taylorfrancis.com/books/9789814241526>
- [12] Svetlichnyi V A and Lapin I N 2013 *Russian Physics Journal* **56** 581–587 ISSN 1064-8887 URL <http://link.springer.com/10.1007/s11182-013-0071-z>
- [13] Honda M, Goto T, Owashi T, Rozhin A G, Yamaguchi S, Ito T and Kulinich S A 2016 *Physical Chemistry Chemical Physics* **18** 23628–23637 ISSN 14639076 URL <http://dx.doi.org/10.1039/C6CP04556A>
- [14] Kim K K, Kim D, Kim S K, Park S M and Song J K 2011 *Chemical Physics Letters* **511** 116–120 ISSN 00092614 URL <http://dx.doi.org/10.1016/j.cplett.2011.06.017>
- [15] Chakravarty U, Ganeev R A, Naik P A, Chakera J A, Babu M and Gupta P D 2011 *Journal of Applied Physics* **109** 084347 ISSN 0021-8979 URL <http://aip.scitation.org/doi/10.1063/1.3580329>
- [16] Huang H, Lai J, Lu J and Li Z 2019 *AIP Advances* **9** ISSN 21583226 URL <http://dx.doi.org/10.1063/1.5082695>
- [17] Itina T E 2011 *Journal of Physical Chemistry C* **115** 5044–5048 ISSN 19327447
- [18] Duque Buitrago J S, Mesa Yandy A M and Riascos Landázuri H 2019 *Journal of Physics: Conference Series* **1247** ISSN 17426596
- [19] Taborda J A P, Landázuri H R and Londoño L P V 2016 *IEEE Sensors Journal* **16** 359–364 ISSN 1530437X
- [20] Methanol Thermal Conductivity: Datasheet from "Dortmund Data Bank (DDB) – Thermophysical Properties Edition 2014" in SpringerMaterials
- [21] Water Thermal Conductivity: Datasheet from "Dortmund Data Bank (DDB) – Thermophysical Properties Edition 2014" in SpringerMaterials
- [22] Alcohol M and Oh C H 2017 (Methyl Alcohol) *ACS Reagent Chemicals* ed Francis T and James T (American Chemical Society) ISBN 9780841230460