Properties of zinc titanates synthesized by microwave assisted hydrothermal method

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ABSTRACT

Zinc titanates are compounds that have shown great application versatility, including in the field of semiconductors. Solid state reactions, the polymeric precursor method and the hydrothermal method are the most mentioned synthesis of these compounds in the literature. In the present work, we use microwave assisted hydrothermal method (MAH) to synthesize zinc titanate and evaluate its potential for solar cell applications through structural and optical characterization techniques. The synthesized samples were also subjected to a variable temperature heat treatment in the range of 500 °C–800 °C. The analysis showed that the crystallization of the material starts at 500 °C and that samples submitted to temperatures of 600 °C–800 °C showed the formation of two phases of zinc titanates, being a cubic phase of ZnTiO₃, considered rare in the literature, predominant up to a temperature of 800 °C. The optical characterization, based on the techniques of photoluminescence spectroscopy and UV-Visible spectroscopy, showed that the photoluminescent activity and the energy of the band gap increased with the increase of the temperature of the heat treatment, having the highest response in 700 °C, facts that can be linked to the predominant formation of the cubic phase of ZnTiO₃ and simultaneous of the cubic and rhombohedral phases of ZnTiO₃ at 700 and 800 °C. Finally, we highlight as the most important results, the fact that it was possible to obtain these titanates at a temperature lower than that reported in the literature, and that the heat-treated sample at 500 °C is the one with the lowest energy expenditure to be synthesized and the one with the greatest potential for application in dye-sensitized solar cells (DSSCs).

1. Introduction

The great versatility of Titanium and zinc-based oxide applications, many related to photocatalysis, has been reported in the literature [1]. However, recently these compounds have attracted special attention for electrical applications, for example, as dielectric materials for capacitors and microwaves. Among the synthesis methods used for the formation of these oxides, the solid-state reactions with ZnO and TiO₂ stand out in the literature. Another method cited in the literature is the hydrothermal, as reported by Arin et al. 2017 [2], in which the authors used an aqueous solution of ammonium hydroxide (NH₄OH) and obtained as a result the titanates Zn₂TiO₄ and Zn₂Ti₃O₈, and also combined the hydrothermal method with a heat treatment at temperature of 750 °C. Additionally, an interesting fact reported in the literature to the synthesis of zinc titanates is the need for heat treatment at temperatures between 600 °C and 900 °C, so that at least two phases of these titanates occur [3, 4].

Recently, Chakraborty et al. 2019 [3] successfully synthesized Zn₂TiO₄ spinel and a ZnTiO₃ perovskite from a solid-state reaction between ZnO and TiO₂, where the authors formed the crystalline structures based on the stoichiometric proportion of the precursors. However, heat treatment was required, with temperatures above 600 °C. It is also a common report in the literature about syntheses of zinc titanates, especially those using zinc oxide (ZnO) and titanium dioxide (TiO₂) as precursors of zinc and titanium, respectively, result in the titanates (Zn₂TiO₄), (Zn₂Ti₃O₈) and (ZnTiO₃), the latter being a rhombohedral structure, in most cases. However, a cubic phase of ZnTiO₃, considered...
by the literature as rare and metastable, can form as a spinel-like structure. First determined by Yamaguchi et al. 1987 [5], the presence of this structure has also been reported in other works involving zinc titanates, as part of the Zn$_2$TiO$_4$ matrix [6, 7, 8]. Studies have already reported that this phase remains stable until 945 °C, and above this temperature, it becomes the spinel Zn$_2$TiO$_4$ and the rutile phase of TiO$_2$ [9]. The rhombohedral zinc titanate ZnTiO$_3$, synthesized by the sol-gel method, has already been reported in use in solar cells by other studies, with emphasis on the low band gap energy obtained with this material [10].

More recent studies also report bandgap energy of the order of 3.0eV, with phases of Zn$_2$TiO$_4$ and rhombohedral ZnTiO$_3$ [11]. In addition, phase formation would be mainly linked to the temperature used in the heat treatment after synthesis [4].

In the present work, the objective is to use the "Microwave Assisted Hydrothermal" (MAH) method, in a solution of titanium isopropoxide and zinc acetate in absolute ethyl alcohol, for the synthesis of zinc titanates and subsequently evaluate the potential of its application as semiconductors in photovoltaic cells using optical and structural characterization techniques. The microwave-assisted hydrothermal method allows the formation of structures differently from other synthesis methods, even if further heat treatment is necessary, allowing the formation of structures more quickly and at lower temperatures [12]. The adoption of this synthesis method allows simplicity, speed and low cost in obtaining zinc titanates. The same method has already been used in other works involving the synthesis of titanium oxides [13] and other metals [14, 15] as well as the manufacture of components for DSSCs [16] with excellent results related to electrical properties.

2. Experimental procedures

First, 50ml of the ethyl alcohol (Synth® 99.9%) were heated to a temperature of 50 °C and kept at this temperature under constant stirring and with N$_2$ flow. Then, 0.01mol of zinc acetate (Sigma-Aldrich®) was added and after 0.01mol of titanium isopropoxide (Aldrich®). After dissolution of the precursors, an additional of 25 ml of ethyl alcohol was added to the solution and the stirring was continued until the temperature of the solution was stabilized at 50 °C. Then, the heating and N$_2$ flow were removed, and the solution was submitted to Microwave Assisted Hydrothermal synthesis method. A domestic microwave oven is used with a closed reactor chamber attached. The reactor made of Polytetrafluoroethylene has temperature and pressure control. The solution was kept under pressure in the range of 7–10 kgf/cm$^2$ at 100 °C during 80 min. After the reactor was naturally cooled for about 60 min, when it was already opened. Figure 1 illustrates details of this synthesis method. The obtained solution was washed and centrifuged with distilled water and isopropyl alcohol (Synth®) in alternate cycles of five minutes, totaling four washes (two with isopropyl alcohol and two with distilled water), always discarding the supernatant solution. At the end of the process, the measured pH was 7.0 and the powder obtained in the synthesis was sent to an oven and drying at 95 °C for 21h.

The obtained powder was separated into a set of five samples, one of which was not heat-treated and the remaining four samples were heat-treated at temperatures ranging from 500 °C to 800 °C for fixed time of 2h. The structural characterization of the samples was performed using X-ray diffraction (XRD) and Raman spectroscopy techniques. Diffraction patterns were obtained on Shimadzu Scientific Instruments equipment model XRD 6000, with copper tube and under the following analysis conditions: 30kV and 30 mA, scan speed of 2° /min, scan range (20) from 10° to 80°, scan step of 0.02° with time of 0.6s per step. In addition, a chemical analysis by Energy dispersive X-ray analysis (EDAX) was performed on a Shimadzu spectrometer model EDX-720. The morphology was evaluated using the Scanning electron microscopy (SEM) technique, which was performed on a Jeol high-low-mode scanning electron microscope with an EDS probe, model JSM-6610LV.

The optical characterization was made using some techniques. The Raman spectra were obtained from a Voyage Raman Confocal system model BWS435-785H-Y, which allows the detection of Raman spectra in the 100 - 2500cm$^{-1}$ spectral range, with 785nm excitation wavelength, operating at room temperature. The photoluminescence spectroscopy techniques on a PHOTON spectrometer, model Mini PL110, with excitation length of 248.6nm. The band gap determination was made by diffuse reflectance measurements using an Agilent Technologies Cary 5000 spectrophotometer with integrating sphere accessory, wavelength range of 200nm–800nm. The band gap energy of the samples, as a function of the temperature of the heat treatment, was obtained by the Kubelka-Munk equation [17], assuming that the light scattering coefficient is constant in the 200–800 nm wavelength range. and therefore, it does not change the shape of the absorption coefficient curve [18]. So, the remission function represents the behavior of the material absorption in this wavelength range. This is a very efficient method for calculating band gap energy, when it is not sure what the type of transitions involved (direct or indirect) [19, 20].

3. Results and discussion

The diffraction patterns in Figure 2 show the evolution of the crystallization of the material according to the heat treatment temperature. In the first diffraction pattern, it is clearly seen that the sample without heat treatment results in an amorphous material. On the other hand, in the sample treated at 500 °C, the material begins a crystallization process, as can be seen by the diffraction peak profile, which is mainly similar to the result of the sample treated at 600 °C.

At 600 °C, the diffraction peaks corresponding to the zinc titanate phases begin to become more intense. An increase of 100 °C in the temperature of the heat treatment promotes a greater crystalline organization, as can be seen by the significant increase and tightening of the peaks, mainly around 35°. The diffraction pattern of the sample submitted to a temperature of 700 °C indicates a better crystalline organization of the structure. In addition to the peaks indicating the formation of the rhombohedral titanate ZnTiO$_3$ (JCPDS 26-1500), a cubic phase of ZnTiO$_3$ (JCPDS 39-190) was detected by XRD analysis, from a temperature of 500 °C and has been reported in other studies as part of the Zn$_2$TiO$_4$ spinel matrix [7]. This phase is considered metastable [6, 7, 8] but it is important to emphasize that, using the synthesis method used in this work, this phase of ZnTiO$_3$ (JCPDS 39-190) was obtained from 500 °C and remained stable as the main phase up to 800 °C. At this temperature, new peaks appear more frequently indicating the intensification of the rhombohedral ZnTiO$_3$ phase (JCPDS 26-1500). In addition, a secondary peak around 35° and the presence of peaks at 42, 56 and 60°, indicate the beginning of the formation of the Zn$_2$TiO$_4$ spinel (JCPDS 73-578) that would probably form if the temperature and/or treatment time thermal power were high. However, as the interest of the present work is to obtain a zinc titanate with the lowest temperature of heat treatment possible, higher temperatures were not analyzed.

Similar to other results obtained in the literature [4], the formation of the zinc titanate phases seems to be directly linked to the temperature used for the thermal treatment of these samples, which is also true for the synthesis method adopted in this work. However, when compared to other results obtained, in which the authors opted for other methods of synthesis of zinc titanates [3, 4, 11, 21], the method adopted by the present work allowed crystallization at a temperature of 500 °C, lower temperature than that obtained by the referred authors. In addition, the cubic phase of ZnTiO$_3$ has a spinel-like structure, considered rare in the literature and, until now, it has not been possible to obtain it with heat treatment at 500 °C and for 2 h [22] and its formation appears to be linked to the synthesis method used. The lack of information on atomic positions of this structure does not make it possible to calculate the percentage of phases by means of Rietveld analysis.

The X-ray dispersive energy analysis (EDAX) is an important tool to obtain the chemical composition of the samples. The results are shown in Table 1.
Corroborating to the results of the XRD technique, the Raman spectra in Figure 3 show that the sample without heat treatment does not have active modes, a result that was already expected, since this sample is amorphous. The heat-treated sample at 500 °C, however, does not have many active modes, indicating a low degree of crystallinity. The active modes are present with the increase of the heat treatment temperature. In samples submitted to temperatures of 600 °C, 700 °C and 800 °C, the spectra are very similar and the active modes for the wave numbers around 125cm⁻¹, 250cm⁻¹, 300cm⁻¹, 400cm⁻¹, 525cm⁻¹ and 725cm⁻¹, indicating the presence of traces of the Zn₂TiO₄ spinel [23, 24, 25] and other peaks present around 341cm⁻¹, 530cm⁻¹, 616cm⁻¹ and 703cm⁻¹ (the latter has an enlargement) indicate the presence of rhombohedral

![Figure 1. Home microwave oven adapted for Microwave Assisted Hydrothermal Synthesis.](image1)

![Figure 2. Evolution of crystallization of the material according to the heat treatment temperature.](image2)

| Table 1. EDAX results. |
|------------------------|
| As prepared | 500 °C | 600 °C | 700 °C | 800 °C |
| Zn | 59,51% | Zn | 60,43% | Zn | 59,62% | Zn | 59,92% | Zn | 60,28% |
| Ti | 39,56% | Ti | 39,42% | Ti | 40,38% | Ti | 40,04% | Ti | 39,72% |

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ZnTiO$_3$ [23, 26, 27] complement the discussion of the XRD analysis, in which some peaks are already indicating the presence of this phase in the diffraction patterns.

The Raman spectra obtained in the present work were compared with other spectra available in the literature for these materials and, although they have the same active modes, they do not have the same peak profile [23, 24, 25, 26]. Even though in some of the works cited [23, 25], the authors used a method of synthesis and heat treatment temperatures different from those used in the present work, in those that the heat treatment had similar temperatures [24, 26] it is found spectra with a different profile that obtained in the present work. This fact may be linked to the particularity in the formation phases of zinc titanates, such as the presence of the cubic spinel ZnTiO$_3$, which may be related to the use of the MAH method for the synthesis of these compounds, which is able to confer very specific properties to the materials and also cause small distortions in the crystalline structures, as already concluded in some works such as that of Fassbender et. al. (2015) [14].

The results of scanning electron microscopy (SEM) are shown in Figure 4. The images aim to evaluate the evolution of morphology as a function of the temperature of the heat treatment. As with other works involving the synthesis of zinc titanates [28] such images reveal very similar structures, but with a common characteristic, presenting particle clusters, with a size of the order of 1μm, as shown in the images in Figure 3. This result shows that the synthesis method, adopted in the present work, makes it possible to obtain a material that, although it has many agglomerates, these have a smaller particle size than that reported by other methods of synthesis for recently used zinc titanates [4]. This feature provides a greater contact area for electronic transport and an advantage for application in dye-sensitized solar cells (DSSC) [29].

Additional optical characterization of the samples was made using the techniques of photoluminescence spectroscopy and UV-visible spectroscopy. Figure 5 shows the results of photoluminescence spectroscopy, in which the photoluminescent response was organized according to the heat treatment temperature given to each one of the samples.

Figure 3. Raman spectra of the samples, as a function of the heat treatment temperature.

Figure 4. Scanning electron microscopy images of the samples without heat treatment (a), heat treated at 500 °C (b), 600 °C (c), 700 °C (d) and 800 °C (e).
The sample without heat treatment, as well as the one that was subjected to a temperature of 500 °C, has practically no photoluminescent activity for the wavelengths in the visible region. The other samples show a photoluminescent response in this spectral region, more specifically around 475 nm. Such result may be related to the fact that the significant crystallization of the material begins at 600 °C for the temperature of the heat treatment, where the formation of the cubic phase of ZnTiO₃. Particularly, the sample heat treated at 700 °C has the most pronounced peak. It is believed that this may be related to the intensification of the crystallization of the material, mainly due to the intensification of the cubic phase of ZnTiO₃, which becomes predominant at the temperature of 700 °C, since at 800 °C the formation of rhombohedral ZnTiO₃ intensifies, reducing photoluminescence. In addition, for the purposes of the present work, the most interesting result is related to the sample heat treated at 500 °C, since this material does not show photoluminescent activity in the visible spectrum and can make it favorable for application in DSSCs since less electronic recombination is expected in this case.

Figure 6 shows a comparison of the UV-VIS spectrum between the sample subjected to heat treatment at 500 °C and the other samples. The results show that the lowest band gap value obtained is for the sample submitted to a heat treatment of 500 °C (gap ~3.71 eV). As the temperature increased, the band gap values increased to 3.85 eV (sample treated at 800 °C), a value close to that obtained for the sample without heat treatment (3.87 eV). The literature reports that the value of the band gap depends on the presence of oxygen vacancies, as well as intermediate energy levels in the material [30, 31]. These factors are dependent on the degree of organization of the structure and the formation of the intermediate phases of the material. The structure becomes more crystalline with the increase in the temperature of the heat treatment, and the intermediate phases disappear, causing an increase in the gap [32]. When the sample with heat treatment at 500 °C is compared with the sample

![Figure 5. Photoluminescent response from the heat treatment temperature.](image)

![Figure 6. Comparison of the calculated band gaps between the samples: without heat treatment and subjected to heat treatment of 500 °C (a); 500 °C and 600 °C (b); 500 °C and 700 °C (c); 500 °C and 800 °C (d).](image)
that was not subjected to heat treatment, as shown in Figure 6(a), it is noted that the energy of the band gap is greater in the untreated sample. This indicates that the lower temperature of heat treatment made it possible to obtain a material with electrical properties that motivate its application as a semiconductor, among the samples analyzed, the one with the greatest potential for application in DSSCs.

4. Conclusions

The use of Microwave Assisted Hydrothermal enabled the formation of a cubic ZnTiO3 spinel, a phase considered rare and metastable in the literature, but which remained stable and predominant until the temperature of 700 °C. In relation to electrical properties, samples with heat treatment at 500 °C present the lower Photoluminescence, indicating that its electron after excitation is more stable and can take part of photocurrent if a DAP is applied, instead of recombination process and hance photoluminescence emission. This indication that sample heat treated at 500 °C is the better candidate to DSSC is also supported by the lower band gap obtained, allowing photoexcitation of less energetic electrons. Its important that band gap can not be interpreted as a direct transition of 3.7eV due to many localized states into de band gap denoted by slope present in UV-vis absorptions. Therefore, the results obtained suggest that the MAH method is a good synthesis route for zinc titanates, as it was possible to obtain a very homogeneous material, although with several particle aggregations. However, this method is simpler and uses less time and energy than reported in other studies published in the literature for the synthesis of zinc titanates. In addition, the sample that was subjected to heat treatment at a temperature of 500 °C, has the lowest photoluminescent response and thus a probability of occurring electronic recombination. It was also this sample that presented the lowest band gap energy, motivating its application in DSSCs, although the low degree of crystallinity can cause difficulties in this case. Thus, because it requires a heat treatment temperature lower than those mentioned in the literature for the synthesis of zinc titanates, the sample heat treated at 500 °C is the one with the lowest energy expenditure to be synthesized and the one with the greatest potential for application in dye-sensitized solar cells (DSSCs).

Declarations

Author contribution statement

Leandro Lemos Gonzales: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
Marlon da Silva Hartwig, Rafael Uarth Fassbender: Conceived and designed the experiments; Performed the experiments.
Eduardo Geretta Moreira, Marcelo Barbalho Pereira: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.
Pedro Lovato Gomes Jardim, Cristiane Wienke Raubach: Contributed reagents, materials, analysis tools or data.
Mário Lucio Moreira: Analyzed and interpreted the data.
Sérgio da Silva Cava: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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References

[1] Rodrigo B. Pinto, Patrício Peralta-Zamora, Fernando Wypych, Fabrication of ZnO- Zn2TiO4 nanocomposite from zinc hydroxide nitrate and its photocatalytic efficiency, J. Photochem. Photobiol. Chem. 353 (2018) 46–52.
[2] Jimpong Arin, et al., Template synthesis of Zn2TiO4 and Zn2TiO4 nanorods by hydrothermal-calcination combined processes, Mater. Lett. 193 (2017) 270–273.
[3] Mitesh Chakraborty, Vinnet Kumar Rai, Kuntal Mitra, Investigation on the electrical and optical properties of some zinc titanate ceramics, Pramana 92 (3) (2019) 46–52.
[4] K.R.M. Macedo, et al., Titanium dioxide (Degussa P25) photocatalyst precursor: influence of thermal treatment on structural, thermal, optical characteristics of zinc titanates, Mater. Chem. Phys. (2019) 121768.
[5] Osamu Yamaguchi, et al., Formation and transformation of Zn2TiO4, J. Am. Ceram. Soc. 70 (5) (1987) C97–C98.
[6] Z.K. Chen, et al., Dehydrogenation of isobutane over zinc titanate thin film catalysts, J. Catal. 161 (2) (1996) 730–741.
[7] Chunfui Li, et al., Precipitate within the spinel-type Zn2TiO4 matrix studied by high-resolution analytical transmission electron microscopy, Mater. Res. Bull. 35 (3) (2000) 351–358.
[8] S.K. Manik, S.K. Pradhan, Preparation of nanocrystalline microwave dielectric Zn2TiO4 and ZnTiO3 mixtures and X-ray microstructure characterization by Rietveld method, Phys. E Low-dimens. Syst. Nanostruct. 33 (1) (2006) 69–76.
[9] Xianglei Liu, et al., Effects of WO3 additions on the phase structure and transition of zinc titanate ceramics, J. Alloys Compd. 450 (1-2) (2008) 440–445.
[10] Jing Yu, et al., Application of ZnTiO3 in quantum-dot sensitized solar cells and numerical simulations using first-principles theory, J. Alloys Compd. 681 (2016) 88–95.
[11] Anurag Sahu, et al., Nanostructured zinc titanate wide band gap semiconductor as a photoelectrode material for quantum dot sensitized solar cells, Sol. Energy 163 (2018) 338–346.
[12] Mario L. Moreira, et al., A description of the formation and growth processes of CaTiO3 monocrystal: a joint experimental and theoretical approach, Mole. Syst. Design Eng. 5 (7) (2020) 1205–1266.
[13] Daniela C. Manfrío, et al., Titanate nanotubes produced from microwave-assisted hydrothermal synthesis ofphotocatalytic and structural properties, Ceram. Int. 40 (9) (2014) 14483–14491.
[14] Rafael Uarth Fassbender, et al., Fingerprints of short-range and long-range structure in Ba Zn1–xHxO3 solid solutions: an experimental and theoretical study, Phys. Chem. Chem. Phys. 17 (17) (2015) 11341–11349.
[15] Catia L. Ucker, et al., Investigation of the properties of niobium pentoxide for use in dye-sensitized solar cells, J. Am. Ceram. Soc. 102 (4) (2019) 1884–1892.
[16] Luciano T. Gualte, et al., In situ microwave-assisted deposition of CoS counter electrode for dye-sensitized solar cells, Sol. Energy 198 (2020) 658–664.
[17] Paul Kubelka, New contributions to the optics of intensely light-scattering materials, Part I. Josa 38 (5) (1948) 448–457.
[18] Ernesto Schulz Lang, et al., Synthesis, thermogravimetry, optical features and X-ray structural characterization of a new HzO–Te dinuclear cluster compound obtained using an ultrasonic bath, J. Organomet. Chem. 724 (2013) 135–138.
[19] Paulo Ricardo Nunes da Conceição, Karina Oliveira Comim, Carlos Otávio Petter, Determinação do espectro de reflectância de misturas de catalis de atmav da Função de Kubelka-Munk, Rev. Soc. Bras. Fis. 52 (3) (2001) 281–286.
[20] Rosendo López, Ricardo Gómez, Band-gap energy estimation from diffuse reflectance measurements on so l– gel and commercial TiO2: a comparative study, J. Sol. Gel Sci. Technol. 61 (1) (2012) 1–7.
[21] Ramesh Singampalli, Phase Formation and Electrical Properties of Zinc Titanate Ceramics, 2018.
[22] G.L. Bhagyalakshmi, AP Neethu Sha, Deepthi N. Rajendran, Luminescence kinetics of low temperature nano ZnTiO3: Eu 3+ red spinel under NUV excitation, J. Mater. Sci. Mater. Electron. 30 (11) (2019) 10673–10685.
[23] Lokesh Budigi, et al., Structural and optical properties of zinc titanates synthesized by precipitation method, J. Chem. Sci. 127 (3) (2015) 509–518.
[24] T. Santhaveesuk, et al., Zn2TiO4 nanostuctures prepared by thermal oxidation method, in: Advanced Materials Research, Trans Tech Publications Ltd, 2008, pp. 641–644.
[25] Zhongwu Wang, S.K. Saxena, C.S. Zha, In situ X-ray diffraction and Raman spectroscopy of pressure-induced phase transformation in spinel Zn₂TiO₄, Phys. Rev. B Condens. Matter 66 (2) (2002), 024103.

[26] Izabela Bobowska, et al., Synthesis and dielectric investigations of ZnTiO₃ obtained by a soft chemistry route, Mater. Chem. Phys. 134 (1) (2012) 87–92.

[27] Lei Hou, et al., Formation and transformation of ZnTiO₃ prepared by sol–gel process, Mater. Lett. 59 (2-3) (2005) 197–200.

[28] Hamed Eskandarloo, et al., Ultrasonic-assisted synthesis of Ce doped cubic–hexagonal ZnTiO₃ with highly efficient sonocatalytic activity, Ultrason. Sonochem. 29 (2016) 258–269.

[29] Maurya, Ishwar Chandra, et al., Effect of particle size on the performance of TiO₂ based dye-sensitized solar cells, ChemistrySelect 3 (34) (2018) 9872–9880.

[30] Linabarg, R. Matthew, et al., Cs₁₋ₓRbx PbCl₃ and Cs₁₋ₓRbxPbBr₃ solid solutions: understanding octahedral tilting in lead halide perovskites, Chem. Mater. 29 (8) (2017) 3507–3514.

[31] Zailan Zhang, et al., Superconductivity, pseudo-gap, and stripe correlations in high-Tc cuprates, Phys. B Condens. Matter 536 (2018) 747–751.

[32] Vukoman Jokanović, et al., Ultra-high and near-zero refractive indices of magnetron sputtered thin-film metamaterials based on TiO₂, Adv. Mater. Sci. Eng. 2016 (2016).