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НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ
NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF ARMENIA

Հայաստանի քիմիական հանդես
Химический журнал Армении **76,** № **4, 2023** Chemical Journal of Armenia

DOI: 10.54503/0515-9628-2023.76.4-308

ОБЩАЯ, НЕОРГАНИЧЕСКАЯ И ФИЗИЧЕСКАЯ ХИМИЯ

MICROWAVE SYNTHESIS OF ZINC SILICATE FOR PHOTOCATALYSIS

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The aim of this work is to develop a new method -microwave synthesis of zinc orthosilicate for photocatalyst. A hydrothermal-microwave method for the synthesis of zinc orthosilicate for photocatalysis from water-soluble zinc salts and sodium silicate has been developed and its photocatalytic activity has been tested. The physicochemical properties of synthesized Zn_2SiO_4 have been studied and determined by various physicochemical analysis methods. Synthesized and heat-treated zinc orthosilicate-willemite has a band gap of about 3.75 *eV*. The photocatalytic activity of the obtained willemite was determined by the decomposition reaction of methylene blue under UV irradiation. The conversion of methylene blue was determined by the optical method. The obtaining zinc orthosilicate has a high photocatalytic activity and can successfully work as a photocatalyst under UV irradiation. The conducted studies have shown the efficiency of microwave synthesis of zinc orthosilicate compared to traditional methods.

Ref.36, fig. 9, tabl 1

Keywords: microwave synthesis, photocatalyst, zinc orthosilicate, willemite, methylene blue.

Introduction

Currently, research and practical application of the phenomenon of photocatalysis in various fields of science, technology and ecology are actively developing [1-7]. One of the most important tasks of ecology is wastewater cleaning in the production of leather, textile, paper, food, pharmaceutical industry, medicine, etc., where various dyes, pesticides and organic preparations are widely used. In particular, organic dyes (methylene blue (MB), methylene red, etc.) are very widely used in various fields, and wastewater cleaning containing these dyes is an urgent problem. One of the most important tasks of neutralizing organic dyes is their complete mineralization -the transformation of organic compounds into less harmful substances - carbon dioxide, inorganic salts - nitrates, phosphates, sulfates, etc. Various methods are used for this purpose, including UV ozonation, UV oxidation with hydrogen peroxide and heterogeneous catalytic decomposition. The cheapest method is considered to be photocatalytic oxidation. The photocatalytic activity depends on the type of catalyst, radiation source, reactor design, etc. Due to the growing demand for cheap effective photocatalysts, the creation of new composites with photocatalytic activity is becoming relevant. Research in recent years have shown that effective photocatalysts are semiconductors-oxides of iron, titanium, zinc, etc. [8-18]. The aim of this work is to develop a microwave (MW) method for the synthesis of a photocatalyst based on the ZnO-SiO_2 system - zinc orthosilicate. There are various methods for obtaining zinc silicate with a developed specific surface area - the calcination of zinc oxide and silicon dioxide, exchanging reactions between zinc salts and sodium silicate, sol-gel methods [19-23]. One of the foremost objectives in modern chemistry and materials science involves the development of novel synthesis techniques for substances to reduce energy consumption and accelerate the formation of final products. Among these promising methods is the microwave (MW) treatment of reaction mixture. MW synthesis proves to be an effective approach for obtaining inorganic materials due to its capacity for uniform and rapid heating, precise control over process duration and maintenance of high process purity conditions. Simultaneously, it enables achieving a high degree of structural motif unit packing in a short time frame while retaining grain sizes within the nanometer range.

We have developed a new microwave method for the synthesis of zinc silicate from solutions [24-25]. It was shown in [16-17, 24-31] that the MW method is one of the most effective ways to obtain nanomaterials. The MW synthesis of zinc orthosilicate from aqueous solutions of sodium silicate and water soluble zinc salts is highly promising, easy to implement, is more effective compared to solid phase or sol-gel methods and, most importantly, yields nanoscale catalyst particles.

This paper presents the results of studies on the preparation of zinc orthosilicate (Zn_2SiO_4) by the MW method and the study of its photocatalytic activity by the neutralization reaction of methylene blue. The choice of MB is due to two reasons - it is widely used in various fields, and based on its structure, MB can simulate the decomposition reaction of organic dyes.

Methods

The composition of the initial and final products was determined by physicochemical analysis methods (gravimetric, spectroscopic, photopolarimetric, flame photometric). X-ray phase analysis (XRD) of samples was carried on the URD 63 diffractometer, CuKa radiation. Differential thermal (DTA) and thermogravimetric (TG) analysis was carried on the "Derivatograph" Q 1500 device (Hungary). IR spectra of samples in the region of 400-4000 cm^{-1} were obtained using a FTIR spectrometer Cary 630 (USA). SEM analysis was carried out using a Philips XL 40 scanning electron microscope (Germany). The diffuse reflection spectra of Zn_2SiO_4 and the adsorbed MB dye on it were determined on the Cary 60 spectrometer (USA). The optical density of MB solutions was measured using a Cary 60 spectrometer. The UV lamp Navigator is used for photocatalytic reactions (maximum radiation of 253.7 *nm* and a power rating of 15 *W*).

The reactor was a silica glass with a volume of 300 *ml* and a diameter of 80 *mm*, the distance of the UV lamp from the surface of the test solution was 100 *mm*. The specific surface area and pore volume of the samples were measured by nitrogen adsorption by the BET method (on the device "AccuSorb 2300E" (Micromeritics, USA) and adsorption of benzene vapor by the weight method.

Experiment

The synthesis of zinc orthosilicate (Zn_2SiO_4) was carried out in a CE1073AR (Samsung) microwave oven, the microwave frequency was 2.45*GHz*, the output power was 600 *W*, in an open pyrex glass flask equipped with a reverse refrigerator and a stirrer. A flask with a volume of 1000 *ml* was loaded 2/3 by the initial solutions - 300 *ml* of zinc sulfate (1,0 *mol / l*) and 300 *ml* of sodium silicate (0.5 *mol /l*), reaction temperature 95-100°*C*, reaction time - 30 *minutes*. The obtaining zinc orthosilicate precipitate was filtered and repeatedly washed with distilled water (70-80°*C)* to remove Na+ and SO_4^{2-} ions and dried at 115-120°*C.* To obtain the crystalline phase of zinc orthosilicate – willemite, the samples were heat-treated in an electric furnace of the brand LHT 08/17 of the company “Nabertherm" (Germany) at a temperature of 1000°*C* for 2 *hours* on the air.

The photocatalytic activity of willemite was determined by the degradation reaction of methylene blue under UV irradiation under various conditions. The initial concentration of MB was 10 *mg/l*, the the volume of MB solution was 100 *ml*, the amount of catalyst was 100 *mg*, the UV irradiation time was 5-60 *min*. The decomposition reaction was carried out with free access of air. To obtain a homogeneous mass, the solution with the catalyst was mixed with a magnetic stirrer for 30 *min* in the dark and the resulting suspension was irradiated with a UV lamp. Samples (about 2 *ml*) were taken every 5-10 *min*, centrifuged and analyzed. The MB concentration before and after irradiation in the presence of a catalyst was determined by measuring the optical density of the solution at 664 *nm*.

Results and discussion

The results of the analyses show that zinc orthosilicate of the composition Zn_2SiO_4, which is a white, fine powder, has been synthesized. On the basis of XRD (fig.1), it was found that during heat treatment of synthesized zinc silicate, a crystalline phase is formed – willemite (JCPDS 70-12350).

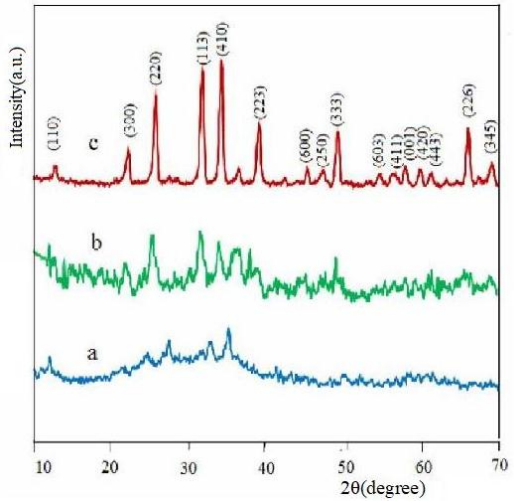

Fig.1. XRD patterns of zinc orthosilicate, a –MW synthesis (100^oC), b –heat-treated at 700^oC, c – heat treated at 1000^oC.

Heat treatment of the sample leads to the improvement of the triclinic crystal structure of willemite. This is also evidenced by the IR spectra (fig.2). Displacement and narrowing of IR absorption bands (fig.2 a, b) caused by deformation fluctuations of Zn-O-Si bonds with maxima at 922 cm^{-1} and 535 cm^{-1} at 890 cm^{-1} and 574 cm^{-1} respectively. Displacement and narrowing of IR absorption bands 890 cm^{-1} (fig.2 a, b) are caused by υ symmetric stretching SiO_4^{-2}, 932 and 974 cm^{-1} -υ asymmetric stretching

SiO_4^{-2}, 462 cm^{-1} -υ asymmetric deformation SiO_4^{-2}, 574 cm^{-1} -υ symmetric stretching ZnO_4 and 605 cm^{-1} -υ asymmetric stretching ZnO_4. The appearance of the vibrations of SiO_4 and ZnO_4 groups clearly suggest the formation of the Zn_2SiO_4 phase [32, 33].

At the same time, the absorption bands of valence vibrations of OH groups (3000-3500 cm^{-1}) and deformation vibrations of H_2O at 1632 cm^{-1} disappear.

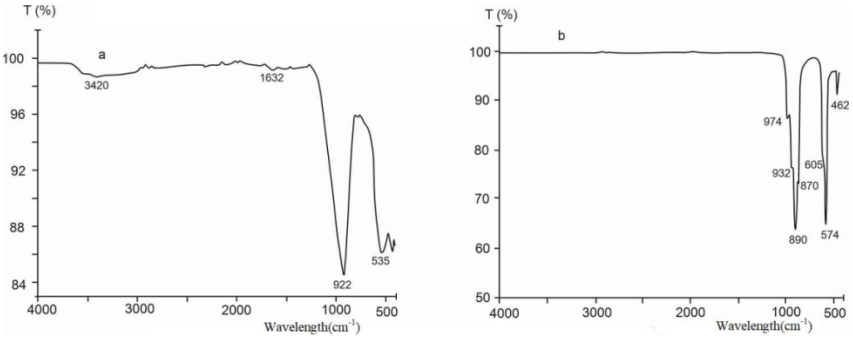

Fig.2. IR spectra of Zn_2SiO_4 synthesized (a) and heat-treated at 1000°C (b) zinc orthosilicate.

Comparison of DTA, TG data (fig. 3) from XRD showed what processes take place when heating samples. Fig. 1(b) shows the presence of crystal structure. On the TG curve there is a loss of mass with an endothermic effect at 240°*C* (by DTA), at which crystalline water disappears, at 670°*C* an exothermic process takes place (fig. 3), which, according to XRD, is associated with the formation of a nucleated crystalline phase (fig. 1b), which is also evidenced by the larger half-width of X-ray reflections. The exothermic peak at 866*oC*. and XRD data (fig. 1c) show that at this temperature the crystal formation of zinc orthosilicate (willemite) is completed.

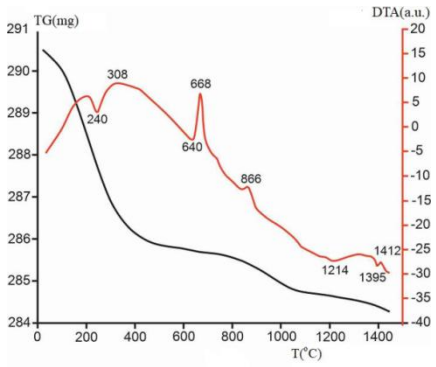

Fig.3. DTA-TG analysis of zinc orthosilicate.

This is evidenced by the narrowing of the X-ray reflection lines, as well as the narrowing of the 922 *cm-*^{1} IR absorption spectra and the appearance of new bands (574, 605, 890, 932, 974 *cm*$^{-1}$ (fig. 2b).

The average diameter- D of crystalline particles is calculated from XRD to the Scherrer equation: $D = K\lambda/\beta\cos\theta$, where K is the dimensionless particle shape factor, (Scherrer constant), for spherical particles it is assumed to be 0.9; λ is the wavelength of X—ray radiation (CuKa—0.154 *nm*); β is the width of the reflex at half-height (in radians and in units of 2θ); θ is the diffraction angle (Bragg angle).The results of the measurements of specific surface area, pore volume and particle size are shown in tabl.1.

Table 1

The results of measurements and calculations the volume of pores, specific surface area and the particles size of the synthesized Zn_2SiO_4.

Synthesis and heat treatment conditions	Specific surface area, m^2/g	Volume pores, cm^3/g	Particle sizes D, *nm*
			From XRD *nm*
MW synthesis at 100 ℃	58,6	0,39	26
Heat treatment at 700 ℃, 2*hr* in the air	19,3	0,26	53
Heat treatment at 1000 ℃ (Willemite), 2 *hr* in the air	6,0	0,15	94

The data in table 1 show that heat treatment leads to a decrease of specific surface area, a decrease of the volume of pores and an increase of the diameter of the crystals.

The nanoscale structure of the synthesized zinc orthosilicate is also visible on SEM images shown in fig.4. It can be seen that heat treatment of synthesized zinc orthosilicate leads to an increase in particle sizes.

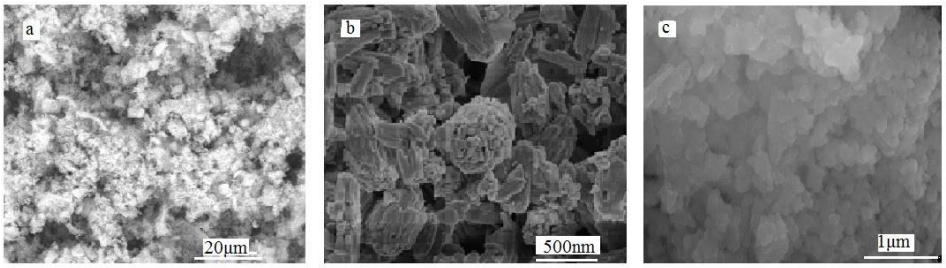

Fig.4. Electron microscopic images of zinc orthosilicate. a -100 ℃, b -. heat-treated at 700 ℃, c-. heat-treated at 1000 ℃.

Diffuse reflection measurements of willemite and willemite impregnated methylene blue- were carried out in the region of 220-950 *nm* before and after UV irradiation. The results are shown in fig.5.

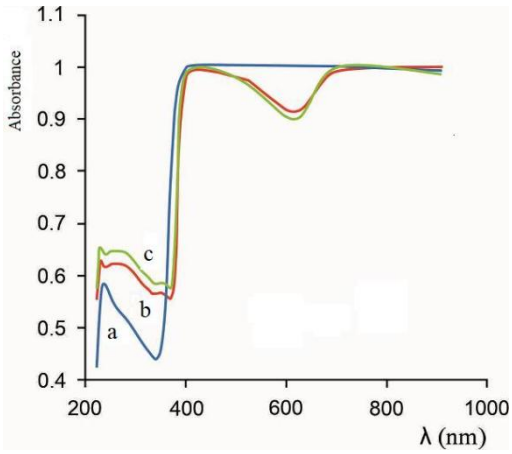

Fig.5. Diffuse reflection of samples: *1*- willemite, *2* and *3*-willemite with adsorbed MB before (*2*) and after (*3*) UV irradiation.

It can be seen from the figure that samples with an adsorbed MB layer actively absorb light with a wavelength of 600-700 *nm*. The band in the region 220-350 *nm* corresponds to absorption involving charge transfer. When a layer of MB is deposited on the surface of zinc orthosilicate (as indicated by the presence of a band at 664 *nm*), the absorption in this region (200–350 *nm*) decreases. The diffuse reflection of synthesized zinc orthosilicate (willemite) in the visible region of the spectrum is more than 95%. The band gap of crystalline zinc orthosilicate (willemite) equal to 3.75 *eV* was determined from the data of diffuse reflection spectrum: it is calculated from plot in Tauc coordinates (fig.6).

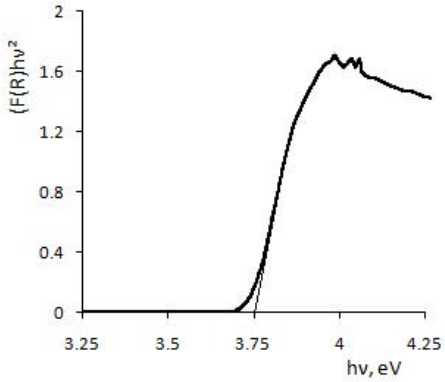

Fig.6. The plot in Tauc coordinates for calculate the band gap of willemite.

The spectrum of adsorbed MB on willemite showed that the maximum absorption is at 664 *nm*. This absorption wavelength has MB both in aqueous solution (fig.7) and adsorbed on willemite (fig. 5). In [34], the absorption spectra of MB adsorbed on various clays with different acidity in the visible region were studied. MB has the forms (MBH_2+, MB+)$_2$, (MB+)$_3$, MB+. It is shown that the form that has an absorption maximum of 670 *nm* is the MB^o and MB+ forms. Based on this, it can be assumed that the MB on the willemite surface is either in the form of a neutral MB^o or MB+. Our measurements of the zero-charge point of the surface by the method [35, 36] showed that the surface has a very weak acidity: pH = 5.3. On such a surface, a strong interaction between MB and the acid centers of zinc orthosilicate is impossible. Thus, MB on the surface of willemite is either in the form of MB+ or MB^o. Absorption at 664 nm (fig.5.3) UV irradiated zinc silicate sample impregnated with MB shows that water, or rather OH-ions, plays an important role in the catalytic oxidation of MB. About participation of water in the photocatalytic process can be assumed from fig. 5.3, where it can be seen that the irradiation of MB sorbed on the catalyst in the absence of water does not lead to a change in the spectrum.

The activity of the obtained photocatalyst (crystalline form ortosilicate-willemite) was studied by the decomposition reaction of methylene blue under UV irradiation. The MB conversion is determined by the optical method. Figure 7 shows the optical densities of methylene blue solutions at different values of the wavelength of the spectrum before and after UV irradiation for 5 to 30 *min*. It has been experimentally established that the dependence of the optical density of the solution on the concentration (C) of MB is linear. Based on this, the concentrations of solutions are determined by the values of the optical densities of the MB solution at a wavelength of 664 *nm*, which corresponds to the maximum absorption of MB solution.

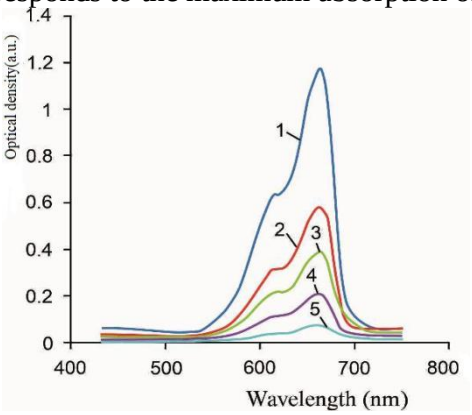

Fig.7. Optical density of methylene blue solutions at different values of the wavelength of the spectrum before (*1*) and after UV irradiation: *2*-5 *min*, *3*- 10 *min*, *4*- 20 *min*, *5*- 60 *min*.

The conversion curves of methylene blue under UV radiation under various conditions are shown in fig.8 Without a catalyst, the degree of decomposition of MB under UV irradiation is 36% in 45 *min*. In the presence of a catalyst, the conversion of MB reaches 85-93% after 25-30 minutes of irradiation. The decomposition reaction of methylene blue on the synthesized catalyst is almost completed in 30 minutes under UV irradiation. Experimental data of photocatalytic decomposition of MB under UV radiation show that the synthesized crystalline zinc orthosilicate-willemite has photocatalytic activity. The conducted studies have shown the effectiveness of the MW synthesis of the willemite zinc orthosilicate photocatalyst in comparison with traditional methods [7, 18-23, 37-38].

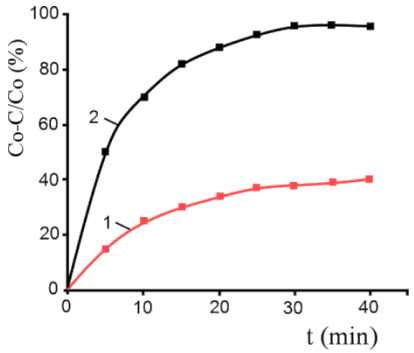

Fig.8. Conversion of MB vs time under UV irradiation *1*-without catalyst, *2*-in the presence of Zn_2SiO_4 (willemit) catalyst. The source of UV radiation is the Navigator lamp.

The photocatalytic decomposition of MB on the surface of the catalyst can be explained by the following mechanism. The process of heterogeneous photocatalytic decomposition of a substance in an aqueous medium can be divided into the following stages: transfer of a substance from an aqueous medium to the surface of the photocatalyst; adsorption of a substance; photocatalytic decomposition of the adsorbed substance; desorption and removal of decomposition products from the surface of the photocatalyst [1-5]. The proposed scheme of the processes occurring during the photocatalytic oxidation of MB is shown in fig.9.

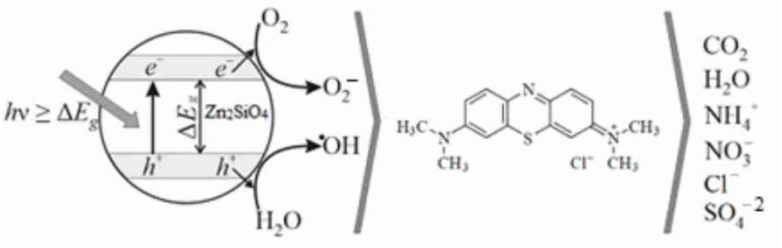

Fig.9. The scheme of the processes of photocatalytic oxidation of MB.

When UV radiation with an energy equal to or greater than the band gap width (for Zn_2SiO_4 $\Delta Eg = 3.75$) is applied to the willemite (photocatalyst), an electron-hole pair (e- h +) is generated. The photogenerated positive holes of the valence band (VB) react with adsorbed water on the surface of Zn_2SiO_4, or with hydroxyl groups. This process leads to the formation of a radical •OH, which has strong oxidizing properties. The electrons of the conduction band react with electron acceptors - oxygen adsorbed on the surface of dissolved in water. O_2^- radicals are formed.

$Zn_2SiO_4 + h\nu \rightarrow h^+_{VB} + e$

$O_2 + e \rightarrow O_2^-$

$OH(s) + h^+ \rightarrow$ •OH

The highly active radicals O_2^- and •OH formed in this way oxidize the MB adsorbed on the surface of the photocatalyst to form intermediate compounds, which decomposing form inorganic ions, as shown in fig. 9.

•OH + MB→ oxidized products →degradation

O^-_2 +MB→ oxidized products →degradation

Conclusion

1. The zinc orthosilicate photocatalyst was synthesized first time by the MW method from the aqueous solutions.
2. Synthesized and heat-treated zinc orthosilicate-willemite has a band gap of about 3.75 *eV*. The UV lamp used for photocatalysis has a maximum radiation energy approximately in this area.
3. The synthesized zinc orthosilicate –willemit exhibits high activity in the photocatalytic degradation of methylene blue and can successfully work as a photocatalyst under UV irradiation.
4. The conducted studies have shown the effectiveness of the MW synthesis of the willemite zinc orthosilicate photocatalyst in comparison with traditional methods.

Acknowledgement

The authors are grateful for the collaboration with the Institute of Chemical Physics after A.B. Nalbandyan, National Scientific Laboratory after A.E. Alikhanyan and Institute for Physical Research.

Funding

The research was carried out with the financial support Science Committee of the Ministry of Education, Science, Culture and Sports, of the Republic of Armenia within the framework of scientific project No. 21T-1D146 “Microwave synthesis of composites with photocatalytic properties”.

Conflicts of interest or competing interests:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ՑԻՆԿԻ ՍԻԼԻԿԱՏԻ ՄԻԿՐՈԱԼԻՔԱՅԻՆ ՍԻՆԹԵԶ ՖՈՏՈԿԱՏԱԼԻԶԻ ՀԱՄԱՐ

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Այս աշխատանքի նպատակն է մշակել նոր մեթոդ՝ ֆոտոկատալիզատորի համար ցինկի օրթոսիլիկատի միկրոալիքային սինթեզ: Մշակվել է ցինկի օրթոսիլիկատի սինթեզի հիդրոթերմալ-միկրոալիքային մեթոդ ջրում լուծելի ցինկի աղերից և նատրիումի սիլիկատից, և փորձարկվել է դրա ֆոտոկատալիտիկ ակտիվությունը: Սինթեզված Zn_2SiO_4-ի ֆիզիկաքիմիական հատկություններն ուսումնասիրվել և որոշվել են ֆիզիկաքիմիական անալիզի տարբեր մեթոդներով: Սինթեզված և ջերմամշակված ցինկի օրթոսիլիկատի՝վիլեմիտի արգելված գոտու լայնությունը 3,75 էՎ է: Ստացված վիլեմիտի ֆոտոկատալիտիկ ակտիվությունը որոշվել է ուլտրամանուշակագույն ճառագայթման տակ մեթիլեն կապույտի քայքայման ռեակցիայով: Մեթիլեն կապույտի քայքայման աստիճանը որոշվել է օպտիկական մեթոդով: Ստացվող ցինկի օրթոսիլիկատն ունի բարձր ֆոտոկատալիտիկ ակտիվություն և կարող է հաջողությամբ աշխատել որպես ֆոտոկատալիզատոր ուլտրամանուշակագույն ճառագայթման տակ: Կատարված ուսումնասիրությունները ցույց են տվել ցինկի օրթոսիլիկատի միկրոալիքային սինթեզի արդյունավետությունը ավանդական մեթոդների համեմատ:

МИКРОВОЛНОВЫЙ СИНТЕЗ СИЛИКАТА ЦИНКА ДЛЯ ФОТОКАТАЛИЗА

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Целью данной работы является разработка нового метода – микроволнового синтеза ортосиликата цинка для фотокатализатора. Разработан гидротермально-микроволновой метод синтеза ортосиликата цинка для фотокатализа из водорастворимых солей цинка и силиката натрия и проверена его фотокаталитическая активность. Физико-химические свойства синтезированного Zn_2SiO_4 изучены и определены различными методами физико-химического анализа. Синтезированный и термообработанный ортосиликат-виллемит цинка имеет ширину запре-

щенной зоны около 3,75 *эВ*. Фотокаталитическую активность полученного виллемита определяли по реакции разложения метиленового синего под УФ-облучением. Конверсию метиленового синего определяли оптическим методом. Полученный ортосиликат цинка обладает высокой фотокаталитической активностью и может успешно работать в качестве фотокатализатора при УФ-облучении. Проведенные исследования показали эффективность микроволнового синтеза ортосиликата цинка по сравнению с традиционными методами.

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