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$KTaO_3$ a perovskite for water and air treatment

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ABSTRACT

Perovskites are inorganic compounds that exhibit dielectric properties. These minerals belong to the crystal ceramics family. These compounds are described by the formula: ABX_3 where, A and B are 2, 3 or 4 valuable metal ions, and X is an ion of oxygen or fluorine. An example of perovskite is the compound $KTaO_3$. There are many methods for producing $KTaO_3$, but the hydrothermal method is most commonly used. Perovskites can be characterized by magnetic, photocatalytic and electrical properties. For this reason, the most effective methods for obtaining perovskite structures are sought, and research methods for their characterization are developed. In this thesis, $KTa_{0.8}A_{0.2}O_3$ (A = Co, Fe, Ni) was obtained by hydrothermal method. The influence of dopants on the photocatalytic was verified. As a result of experiments, it was found that two samples had a single phase the pyrochlore structure ($KTaO_3$ and $KTa_{0.8}Fe_{0.2}O_3$). The Ni-doping increased photocatalytic activity, while Fe-doping reduced photocatalytic activity.

***Keywords*:** perovskite, potassium tantalate, hydrothermal method, photocatalytic activity, transitions metals

1. INTRODUCTION

Over the past few years, it can be observed that nanomaterials were became more and more popular. They no longer associate only with complicated engineering, but also with everyday life. This is due to the increasing use of nanomaterials for a variety of technologies that improve living conditions. Decreasing the particle size to several nanometers results in completely new properties, both chemical and physical.

$KTaO_3$, which is the subject of the following work, is a perovskite. Perovskites belong to the most common minerals in the earth's crust. It is estimated that about 50% of the Earth's crustal minerals have a perovskite structure [1]. These compounds exhibit very interesting properties that are determined by the structure of the atomic arrangement. $KTaO_3$ is a cubic structure that presents two possible forms: the $K_2Ta_2O_6$ pyrochloride phase which is formed at low temperatures and the $KTaO_3$ perovskite phase, which is formed at moderately high temperatures. It is less investigated than other perovskites [2]. Pure $KTaO_3$ exhibits the characteristics of an insulator, but doped exhibits the characteristics of the n-type semiconductor. In semiconductor form, it can be used in high-temperature gas sensors or in fuel cells. Doping with calcium, cobalt or manganese causes ferromagnetic properties. Niobium doped solutions ($KTa_{1-x}Nb_xO_3$) can be used in microwave devices. Literature studies show that $KTaO_3$ can be used for degradation of pollutants in the aqueous or gaseous phase due to good photocatalytic properties [3].

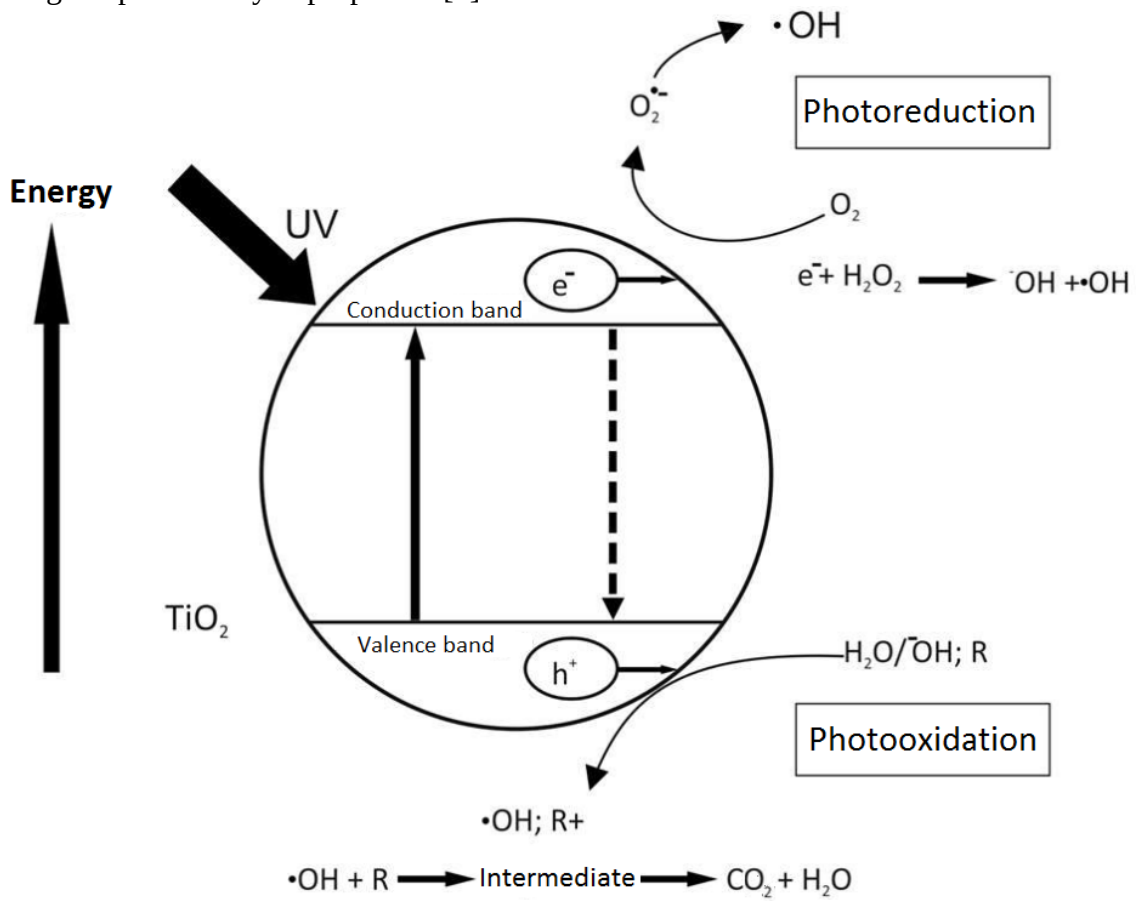

Figure 1. Scheme of photocatalysis on the TiO_2

Photocatalysis is the phenomenon of increasing the rate of chemical reaction with photons in the presence of a small amount of photocatalyst [4]. These substances interact chemically with the reactants but are not consumed. Most of the photocatalytic reactions are performed in a multiphase system of a gas – solid state or liquid – solid state.

Heterogeneous photocatalysis has been developing since Fujishima and Honda [5] have published results of photocatalytic degradation studies using titanium oxide (IV). TiO_2 is the most commonly used photocatalyst. In order to excite the electron and generate a hole in the TiO_2 valence band, there is a need for 3.2 eV, it is a photon about 388 nm wavelength. Thus, titanium dioxide can be activated in the range 300 – 388 nm (corresponding to UVA radiation) [6]. Figure 1 shows the scheme of photocatalysis taking place on the titanium oxide (IV) molecule. The photocatalyst molecule is exposed to wavelengths of 300 – 388 nm. Absorption of the photon results in the transfer of electrons from the valence band to the conduction band. Thanks to this, carriers of charges, i.e. holes (h^+) in the valence band and electrons (e^-) in the conduction band, are formed. Electrons can combine with oxygen to generate active oxygen ($O2^{\cdot-}$), while holes combine with water to generate hydroxyl radicals (·OH) [7].

Heterogeneous photocatalysis can be used in the following processes: cleaning water, cleaning air and removing odors, self-disinfecting materials, self-cleaning surfaces.

$KTaO_3$ belongs to the ABX_3 perovskite family. Many compounds of this family, such as $BaTiO_3$, $CaTiO_3$ and $SrTiO_3$, exhibit photocatalytic properties [8]. It can be concluded that $KTaO_3$ will also be a good photocatalyst [9]. Kato and Kudo [10] undertook to investigate the photocatalytic properties of $KTaO_3$. They investigated the photocatalytic properties of tantalans by the photocatalytic reaction of water. It turned out that many tantalans under the influence of UV radiation allows the degradation of H_2O to H_2 and O_2. In conclusion, $KTaO_3$ may prove to be another compound exhibiting promising photocatalytic properties. However, its potential has yet to be fully explored and exploited.

The aim of this work was to develop a method for obtaining pure and doped potassium tantalate and to investigate how dopants influence on the photocatalytic properties of the material.

2. EXPERIMENTAL

2. 1. Reagents

During the experimental research, following reagents were used:

• chemical reagents used for preparation of materials:
- potassium hydroxide (KOH, Chempur),
- tantalum (V), (99%, Ta_2O_5, Sigma-Aldrich),
- polyethylene glycol 400, (PEG-400, POCH S.A.),
- cobalt (II) hydrate, (99%, $CoCl_2 \cdot 6H_2O$, POCH S.A.),
- iron (III) hydrate, (99%, $Fe(NO_3)_3 \cdot 9H_2O$, POCH S.A.),
- nickel (II) hydrate, (99%, $Ni(NO_3)_2 \cdot 6H_2O$, POCH S.A.);

• model pollution subjected the photodegradation:
- phenol, (99%, C_6H_5OH, POCH S.A.);

• chemical compounds used for analytical determinations:
- p-nitroaniline, (98%, $C_6H_6N_2O_2$, POCH S.A.),
- sodium nitrate (98%, $NaNO_3$, POCH S.A.),
- sodium carbonate, (99.8%, Na_2CO_3, POCH S.A.).

2. 2. Sample preparation

Table 1. List of samples and quantity of reagents used.

Sample	Amount of the X reagent [g]
$KTa_{0.8}Co_{0.2}O_3$	5.2 g $CoCl_2$
$KTa_{0.8}Fe_{0.2}O_3$	4.4 g $Fe(NO_3)_2$
$KTa_{0.8}Ni_{0.2}O_3$	3.0 g $Ni(NO_3)_2$

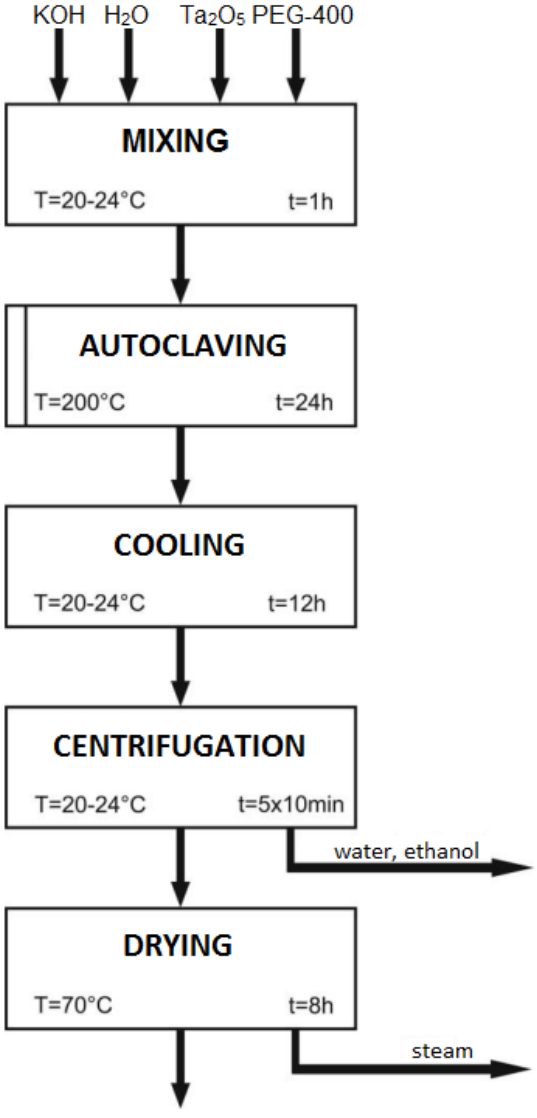

Figure 2. Schematic diagram of the process of obtaining $KTaO_3$

A hydrothermal method was used to produce pure samples of $KTaO_3$. This method consisted of adding to a solution of potassium hydroxide, tantalum pentoxide, and the PEG reagent (in the case of doped samples, the amount of Ta_2O_5 was reduced, and X g of the corresponding reagent was added in this space – Table 1). The suspension was stirred and then transferred to a Teflon-coated stainless-steel autoclave. The autoclave was sealed and heated in an oven (ED53 BINDER) at 200 °C for 24 h. After cooling to room temperature, the obtaining powder was washed several times with water and ethanol by centrifugation. Then the precipitate was placed in an oven at 70 °C for 8 h. Figure 2 shows the schematic diagram of the process of obtaining $KTaO_3$.

2. 3. Photocatalytic activity analysis

Photocatalytic activity was investigated in the phenol photooxidation reaction in the presence of UV-Vis radiation. A 25 cm^3 quartz reactor was used for the phenol photooxidation It was equipped with a cooling jacket to which water at 10 °C was fed. The source of the radiation was Oriel xenon lamp (1000 W). The measuring arrangement consisted of: a xenon lamp, a source of radiation, a cryostat (Polyscience), an optical filter, a magnetic stirrer that allowed continuous stirring of the slurry in a quartz reactor and an air cylinder from which the gas was fed to the reactor. The reactor was charged with 0.125 g of photocatalyst, 24 cm^3 of deionized water, 1 ml of phenol solution (c = 500 mg/dm^3). The resulting mixture was placed in a light-free measuring system where it was stirred for 30 minutes (450 rpm) and aerated (V = 5 dm^3/l) to determine equilibrium. After 30 minutes, a sample of 1 ml was taken using the syringe. The suspension was then irradiated with UV-Vis radiation for 1 h. Subsequent samples were collected every 20 minutes. Catalyst particles from samples were removed by Syringe Filters (Chromafil). The concentration of phenol in the solutions was determined by colorimetric method with p-nitroaniline and then the absorbance of the color complexes at 480 nm was measured on a UV-Vis spectrophotometer (Beckman DU520).

3. RESULTS

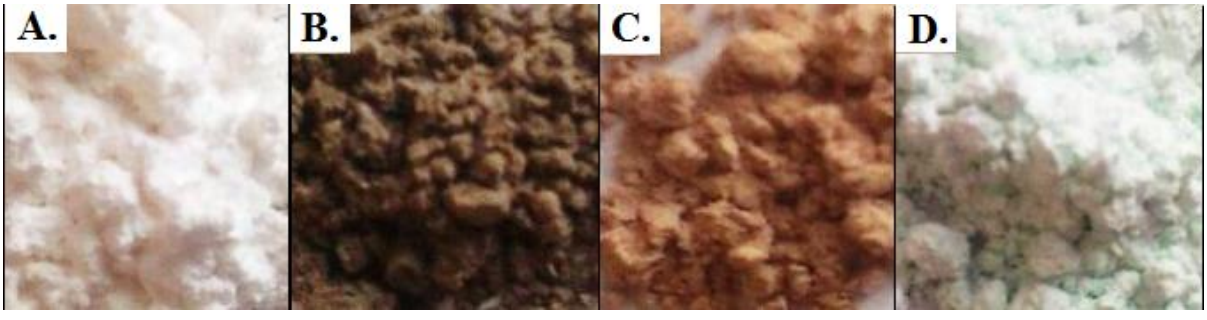

Figure 3. Photos of obtained powders: A. $KTaO_3$, B. $KTa_{0.8}Co_{0.2}O_3$, C. $KTa_{0.8}Fe_{0.2}O_3$, D. $KTa_{0.8}Ni_{0.2}O_3$

During the study four different types of compounds were obtained using the hydrothermal method: pure $KTaO_3$, $KTa_{0.8}Co_{0.2}O_3$, $KTa_{0.8}Fe_{0.2}O_3$ and $KTa_{0.8}Ni_{0.2}O_3$. Figure 3 shows photos of the obtained powders.

Comparison of the samples found differences in their colors. The pure $KTaO_3$ samples were white, and the admixtures introduced into it changed color of samples. Changing the color of the obtained samples may be attributable not only to the presence of the metals present in the dopants but also to the presence of unreacted oxides of these metals or other contaminating products.

3. 1. Photocatalytic activity

The photocatalytic activity of the obtained samples was estimated by determining the degradation of phenol under the influence of UV-Vis radiation. Effectiveness of phenol degradation after 60 min exposure was compiled in Table 2, while the dependence of phenol concentration on the exposure time is shown in Figure 4.

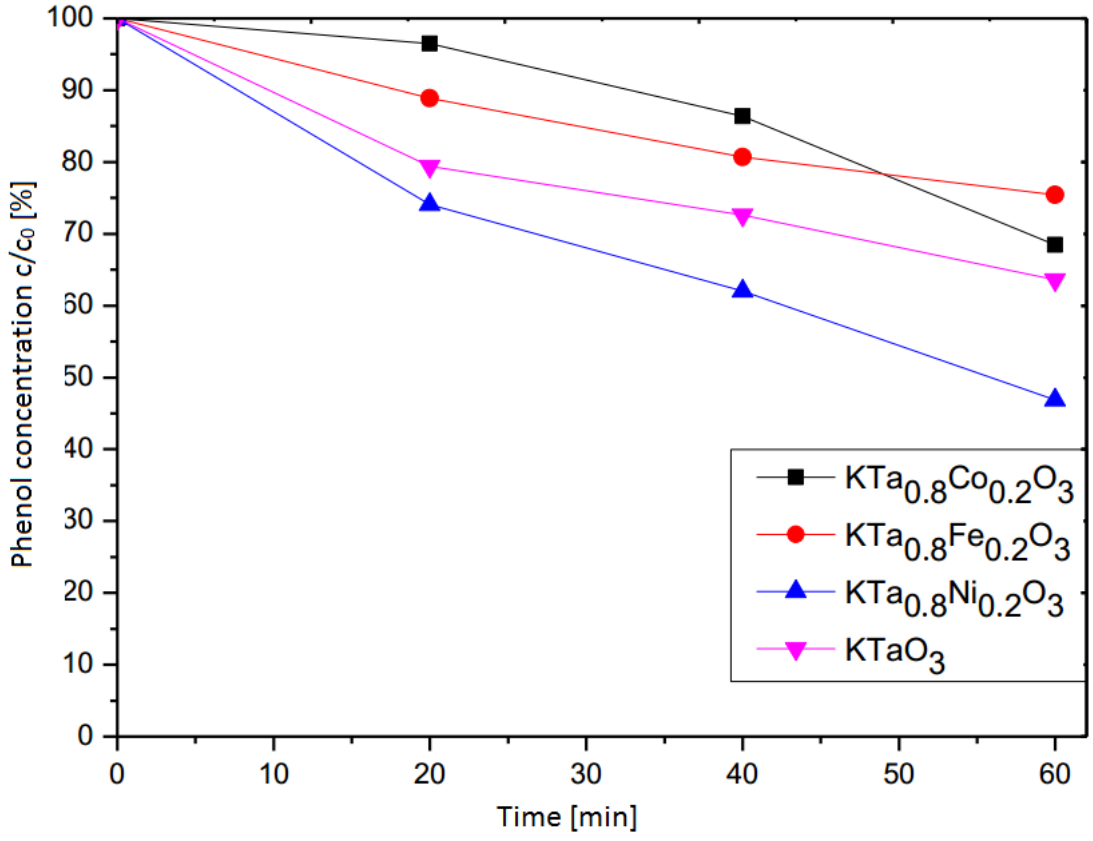

Figure 4. Phenol degradation efficiency as a function of the exposure time of the samples obtained by the hydrothermal method

By comparing the results for obtained samples by hydrothermal method, the best photocatalytic properties showed nickel doped tantalate (53% degradation value of phenol).

Both doping of potassium tantalate with iron as well as cobalt resulted in a reduction in photocatalytic activity (values of phenol degradation were 25 and 32%, respectively).

Table 2. Photocatalytic efficiency of the samples

Sample	Phenol degradation efficiency after 60 min exposure [%]
$KTaO_3$	36
$KTa_{0.8}Co_{0.2}O_3$	32
$KTa_{0.8}Fe_{0.2}O_3$	25
$KTa_{0.8}Ni_{0.2}O_3$	53

By analyzing the results in Table 2, it was found that transition metal doping may increase photocatalytic activity but also decrease it. Increasing photocatalytic activity was observed with nickel doping. Unfortunately, in the doping with iron and cobalt, results were lower than that of photocatalytic activity of pure $KTaO_3$ (36%).

4. CONCLUSIONS

By using the hydrothermal method, one-phase potassium tantalate, un-doped and iron-doped can be obtained. The obtained phase is a phase of pyrochlorium. In the case of nickel-doped tantalate and cobalt, multiphase substances were obtained. For this reason, obtaining nickel and cobalt doped tantalate using hydrothermal method requires additional research. Further studies should include determining the impact of the amount of introduced dopant and the duration of the process. Measurement of the photocatalytic activity of single-phase samples showed that iron doping significantly reduced the photocatalytic capacity of potassium tantalate. 60 min exposure of aqueous phenol in the presence of Fe-$KTaO_3$ resulted in degradation of 25% phenol while pure $KTaO_3$ resulted in degradation of 36% phenol. Measurement of photocatalytic activity of multiphase samples showed that phenol tantalate doped with nickel (53%) showed the highest photodegradation activity of phenol. This may be due to the high photoactivity of nickel oxide as a separate phase.

In conclusion, $KTaO_3$ and Fe-$KTaO_3$ are substances with promising photocatalytic properties. In the future, they can be used in water purification and air treatment.

References

[1] Smyth D.M., *Cryst. Latt. Def. and Amorph. Mat*. 18, 355-375 (1989).

[2] Zhang P., Zhang J., Gong J., *Chem. Soc. Rev.* 43, 4395-4422 (2014).

[3] Weber I. T., Audebrand N., Bouquet V., Guilloux-Viry M., Perrin A., *Solid State Sci.* 8, 602-612 (2006).

[4] Serpone N., Emeline A.V., *Int. J. Photoenergy* 4, 91-131 (2002).

[5] Foujishima A., Honda K., *Nature* 238, 37-38 (1972).

[6] Hoffmann M.R., Martin S.T., Choi W., Bahnemann D.W., *Chem. Rev.* 95, 69-94 (1995).

[7] Ahmed S., Rasul M.G., Martens W.N., Brown R., Hashib M.A., *Desalination* 261, 3-18 (2010).

[8] Ludwiczak M.: Characterization and photocatalytic activity of modified titanate based perovskites in photocatalytic splitting of water, AMUR, 2012.

[9] Zou Y., Hu Y., Gu H., Wang Y., *Mater. Chem. Phys.* 115, 151–153 (2009).

[10] Kato H., Kudo A., *Catal. Today* 78, 561-569 (2003).

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