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INFLUENCE OF Al DOPING ON STRUCTURE, MORPHOLOGY AND OPTICAL PROPERTIES OF TiO₂ NANOPARTICLES

Titanium dioxide (TiO₂) nanoparticles, both undoped and heterovalently substituted with aluminum ions, were synthesized using sol-gel routes. The influence of synthesis parameters, annealing temperature (500–900 °C), and Al³⁺ doping concentration on the phase composition, crystallographic parameters, crystallite size, defect structure, and optical properties of TiO₂ was systematically investigated. X-ray diffraction analysis revealed a temperature-driven anatase-to-rutile phase transformation in undoped TiO₂, while aluminum incorporation stabilized the anatase phase at moderate temperatures and suppressed rutile formation. At elevated temperatures and high dopant concentrations, a solubility limit of Al³⁺ in the TiO₂ lattice was observed, leading to the formation of secondary α -Al₂O₃ phases. Crystallite size analysis showed that increasing annealing temperature promotes grain growth and reduces lattice defect density, whereas Al³⁺ doping inhibits crystallite growth in anatase and increases defect concentration. In contrast, for rutile TiO₂ at high temperatures, aluminum incorporation enhances crystallite growth and lattice ordering. Photoluminescence studies demonstrated weak intrinsic emission of TiO₂ governed by defect-related states, with emission bands attributed to surface states, oxygen vacancies, and Ti³⁺ centers. Highly Al³⁺-doped samples exhibited additional red and near-infrared emission bands, which were assigned to trace Cr³⁺ impurities unintentionally introduced with aluminum precursors. The results demonstrate that synthesis conditions and heterovalent substitution provide effective tools for tuning the structural, morphological, and optical properties of TiO₂ nanoparticles. The findings highlight the critical role of defect chemistry, phase composition, and impurity-related effects in tailoring TiO₂-based materials for UV-blocking, cosmetic, and photonic applications.

Keywords: titanium dioxide (TiO₂), nanoparticles, Al³⁺-doping, crystal structure, optical properties.

1. Introduction

The global production of titanium dioxide (TiO₂) for practical applications amounts to several million tons annually. Nearly 70% of the total TiO₂ output is used as a pigment in paints, glazes, enamels, plastics, paper, fibers, food products, pharmaceuticals, cosmetics, and toothpastes [1–3].

In the early stages of TiO₂ pigment application, it was observed that surfaces coated with TiO₂

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Table 1. Determination of mass fraction of TiO₂ in (NH₄)₄[TiO₂(C₆H₅O₇)₂] · nH₂O

Crucible No.	Mass of empty crucible, g	Mass of crucible with the sample before annealing, g	Mass of crucible with the sample after annealing, g	Mass of the sample before annealing (mass of (NH ₄) ₄ [TiO(C ₆ H ₅ O ₇) ₂] · nH ₂ O), g	Mass of the sample after annealing (mass of TiO ₂), g	Mass fraction of TiO ₂ , %
1	18.3711	18.7778	18.4392	0.4067	0.0681	16.7445
2	18.6949	19.1058	18.7633	0.4109	0.0684	16.6464
3	16.7754	17.2000	16.8461	0.4246	0.0707	16.6510

faded more rapidly than others under solar irradiation. This behavior was attributed to the high photocatalytic activity of TiO₂. Surface modification with inorganic compounds such as aluminum oxide or silica effectively suppressed the surface catalytic activity and significantly improved weathering resistance, enabling the widespread use of TiO₂ as a white pigment [1, 4, 5].

Among synthesis approaches, the sol-gel method allows precise control over the structure and morphology of TiO₂ nanoparticles, offers relatively low energy consumption, and relies on simple and accessible equipment. However, it is a time-consuming process. Hydrothermal and solvothermal methods, although effective, require autoclaves operating at high pressures, which complicates their practical implementation. Sonochemical, electrodeposition, and microwave-assisted methods often fail to produce nanoparticles with sufficiently small and uniform sizes [1, 6–8].

An alternative strategy for controlling the photocatalytic activity of semiconductor materials is to dope their crystal lattices with foreign elements. Doping ZnO or TiO₂ nanoparticles with transition metals such as Mn, Co, or Fe has been shown to significantly reduce photocatalytic activity due to the formation of deep impurity levels within the band gap, which promote recombination of photogenerated charge carriers. However, the incorporation of transition metals often results in a dark coloration of the nanoparticles, limiting their suitability for sunscreen applications [9–11].

To overcome this limitation, Al³⁺ ions represent a promising dopant. As aluminum is a non-transition metal, Al-doped TiO₂ nanoparticles are expected to retain their bright color while providing improved aesthetic properties in sunscreen formulations [1, 6, 12].

The aim of this work was to investigate the effects of heat-treatment temperature and Al³⁺ doping on

the phase composition, structural and morphological characteristics, and optical properties of titanium dioxide nanopowders.

2. Synthesis and Experimental Description

2.1. Starting Components

For the synthesis of TiO₂ by the sol-gel method, a complex precursor, ammonium titanium citrate, (NH₄)₄[TiO₂(C₆H₅O₇)₂] · nH₂O, was selected. The primary reason for choosing this compound is its high solubility in water, which ensures uniform distribution of titanium-containing species within the reaction medium. This homogeneity enables effective control over the hydrolysis and condensation processes during sol formation, which are critical stages of the sol-gel method.

Prior to the main synthesis, the mass fraction of titanium dioxide in the initial precursor was determined by gravimetric analysis. A known mass of the precursor was placed in pre-weighed crucibles and calcined to constant mass to ensure the complete removal of volatile and organic components. After cooling to room temperature, the crucibles were reweighed, and the mass fraction of TiO₂ was calculated as the ratio of the residual oxide mass to the initial sample mass (Table 1). The obtained values were used for subsequent stoichiometric calculations in the synthesis procedures.

Based on these data, the mass fraction of titanium dioxide in the initial complex was determined to be 16.68%. This value was subsequently used to calculate the required amount of (NH₄)₄[TiO₂(C₆H₅O₇)₂] · nH₂O for the synthesis of TiO₂ nanopowders.

In addition, the thermal behavior of the precursor was investigated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The

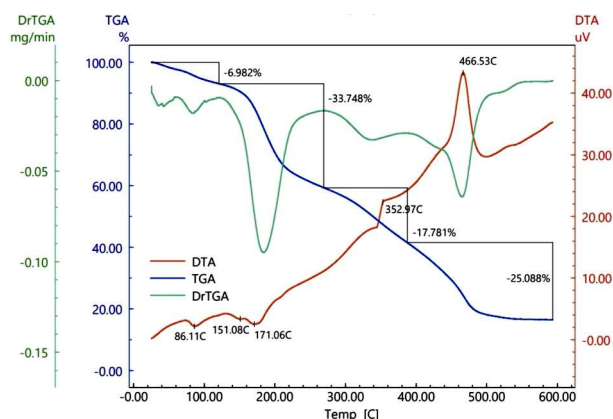


Fig. 1. Derivatogram of the $(\text{NH}_4)_4[\text{TiO}_2(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot n\text{H}_2\text{O}$

results revealed that the thermal decomposition of $(\text{NH}_4)_4[\text{TiO}_2(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot n\text{H}_2\text{O}$ proceeds through several distinct stages, as illustrated in Fig. 1.

Up to 171 °C, a mass loss of 6.982% is observed, which corresponds to the removal of physically adsorbed water and ammonia. In the temperature range of 150–350 °C, decomposition of the carboxyl groups of citric acid occurs, accompanied by a mass loss of 33.748%. The final intense exothermic peak at 466.53 °C reflects the complete combustion of residual organic components, resulting in an additional mass loss of 25.09%. The formation of nanodispersed TiO_2 is completed at temperatures above 500 °C.

For the synthesis of aluminum-doped titanium dioxide ($\text{Al}^{3+}:\text{TiO}_2$), aluminum nitrate, $\text{Al}(\text{NO}_3)_3$, with a concentration of 0.57 mol L^{-1} was used as the aluminum source. The concentration of the aluminum nitrate solution was determined by back complexometric (trilonometric) titration using xylenol orange as an indicator (0.01 wt.% in KNO_3). Aluminum nitrate was selected due to its high solubility in water, which ensures uniform distribution of Al^{3+} ions within the TiO_2 matrix [13].

Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was used as an organic ligand capable of coordinating with titanium and aluminum ions, thereby promoting homogeneous gel formation during the sol-gel synthesis. To catalyze the combustion process in all syntheses, several drops of concentrated nitric acid (HNO_3) were added to the solution. Nitric acid also facilitated the acid-catalyzed hydrolysis of the titanium complex and improved sol formation.

2.2. Synthesis of Samples by the Sol-Gel Method

The sol-gel method enables control over the structure and morphology of TiO_2 nanoparticles while optimizing energy consumption and employing relatively simple and accessible technological equipment [6].

Synthesis of the TiO_2 nanoparticles by the sol-gel method was carried out by dissolving $(\text{NH}_4)_4[\text{TiO}_2(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot n\text{H}_2\text{O}$ in distilled water, followed by the addition of several drops of concentrated HNO_3 . The resulting solution was intensively stirred on a magnetic stirrer with simultaneous heating, which ensured complete dissolution of the precursor and initiated hydrolysis and condensation reactions of titanium oxide species.

Gradual heating of the solution led to the formation of a viscous gel-like substance. Further heating resulted in dehydration of the gel and combustion of organic components, yielding a porous dry residue (Fig. 2). The obtained solid mass was thoroughly ground in an agate mortar to produce a homogeneous powder.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the resulting precursor powder were also performed (Fig. 3).

Water removal occurs up to 150 °C, accompanied by a mass loss of 4.32%. Subsequent combustion of organic residues proceeds in two distinct stages, characterized by intense exothermic peaks at 319.44 °C and 434.34 °C, with corresponding mass losses of 33.85% and 19.93%, respectively. The appearance of two exothermic peaks instead of a single one indicates an insufficient concentration of nitrate ions to fully oxidize the organic phase during the initial stage. As a result, an intermediate carbonized residue is formed, which subsequently burns out during the second stage under the action of atmospheric oxygen. Such two-stage thermal decomposition may influence the formation of structural defects in the resulting TiO_2 nanoparticles, particularly in samples calcined within the temperature range of 400–500 °C.

After drying, the precursor mixture was uniformly distributed among crucibles and subjected to calcination at various temperatures for 30 min. Since heat-treatment temperature has a decisive effect on the phase composition, morphology, and functional properties of TiO_2 , and taking into account the results of the thermal analysis of the dried gel, the following

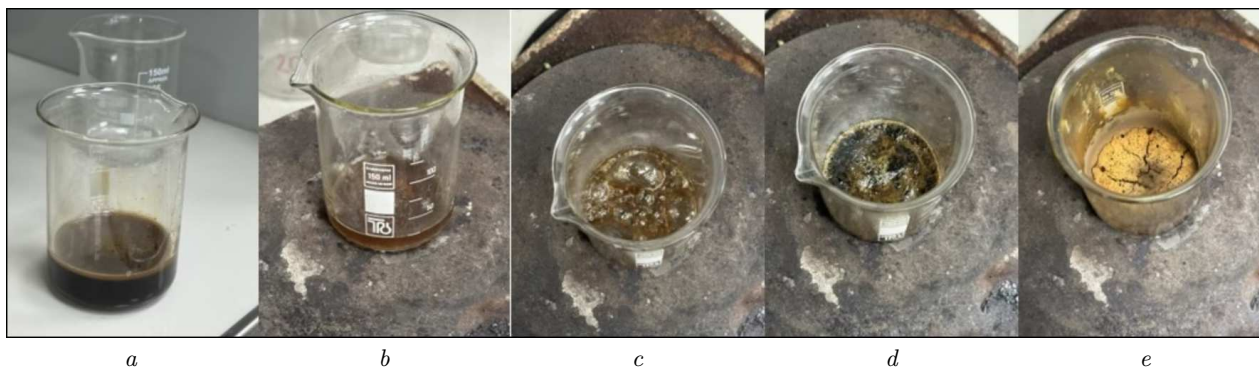


Fig. 2. Sequential stages of the sol-gel synthesis of TiO₂: initial precursor solution (a); sol formation after addition of HNO₃ and heating (b); gel formation and initial solvent evaporation (c); thermal decomposition and combustion of organic residues (d); formation of an intermediate product consisting of TiO₂ mixed with residual organic compounds (e)

calcination temperatures were selected: 400, 500, 600, 700, 800, and 900 °C. This temperature range enables controlled phase transformations that strongly influence the photocatalytic, mechanical, and thermal properties of the material.

At 400 °C, the material predominantly consists of the anatase phase, which exhibits high photocatalytic activity due to its large specific surface area and small crystallite size. Increasing the temperature to 500 °C initiates the anatase-to-rutile transformation, allowing partial retention of photocatalytic performance while improving mechanical stability. In the 600–700 °C range, coexistence of anatase and rutile phases is observed; this mixed-phase composition is often associated with enhanced photocatalytic efficiency. At 700 °C, rutile becomes the dominant phase, leading to improved thermal and mechanical stability. Calcination at 800 °C results in a pronounced reduction of surface area but provides increased structural strength and resistance to high-temperature conditions [19]. Complete transformation to the rutile phase occurs at 900 °C, ensuring maximum thermal stability required for applications under extreme conditions. After calcination, the obtained powders exhibited a characteristic white color (Fig. 4).

Sol-gel synthesis of Al_{0.2}Ti_{0.8}O₂, Al_{0.1}Ti_{0.9}O₂, and Al_{0.05}Ti_{0.95}O₂. To enhance the UV-blocking efficiency, TiO₂ nanoparticles doped with aluminum were synthesized using the sol-gel method. The syntheses of Al_{0.2}Ti_{0.8}O₂, Al_{0.1}Ti_{0.9}O₂, and Al_{0.05}Ti_{0.95}O₂ were carried out using an aqueous solution of a titanium citrate complex as the titanium precursor. Citric acid was added as a chelat-

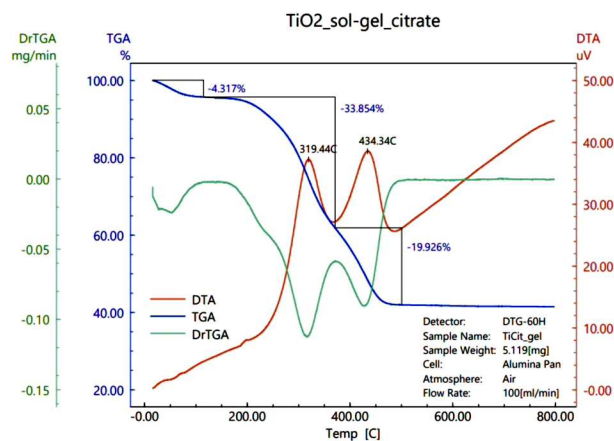


Fig. 3. Derivatogram of the blend after sol-gel synthesis of TiO₂

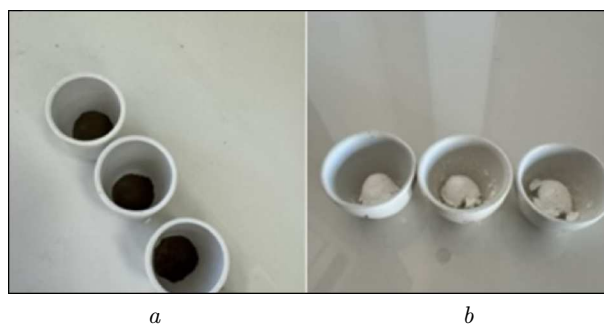


Fig. 4. Crucibles containing TiO₂ powders before (a) and after (b) calcination at different temperatures

ing agent to promote homogeneous complexation and uniform gel formation.

A critical step in the synthesis involved the introduction of aluminum in the form of aluminum nitrate, which served as the dopant source. The aluminum

concentrations were selected to optimize UV absorption while suppressing the photocatalytic activity of TiO₂. Aluminum contents of 5–10 mol% (corresponding to approximately 1.8–3.6 wt%) were employed, as previous studies have demonstrated that Al doping above 0.5 wt% leads to a significant reduction in TiO₂ photocatalytic activity without compromising its UV-shielding capability [6].

After the addition of the aluminum salt, the solution was intensively stirred on a magnetic stirrer and heated on a hot plate to initiate hydrolysis, condensation, and gel formation. Subsequently, several drops of concentrated nitric acid were added to catalyze the sol–gel process. The resulting gel was dried and ground into a fine powder.

Final heat treatment of the obtained powders was performed at 500 °C and 900 °C to stabilize the anatase and rutile phases of TiO₂, respectively, enabling investigation of the influence of aluminum doping on phase composition and functional properties.

2.3. Synthesis of TiO₂ from titanium(IV) isopropoxide (TTIP) by controlled hydrolysis

An alternative synthesis of titanium dioxide was carried out via acid-catalyzed hydrolysis of titanium(IV) isopropoxide (TTIP, 98+%, Thermo Scientific Chemicals). To obtain 5 g of TiO₂, the required amount of TTIP (18.7 mL, 0.0626 mol) was calculated based on reaction stoichiometry. Prior to hydrolysis, TTIP was dissolved in 30 mL of isopropanol, which reduced the hydrolysis rate and prevented premature particle aggregation.

Hydrolysis was performed in an acidic medium (pH 1–2), prepared by adding 1 mL of concentrated nitric acid (65%) to 50 mL of deionized water. The acidic environment facilitated the formation of stable colloidal TiO₂ particles and suppressed uncontrolled aggregation [14–16].

The hydrolysis process was conducted at 40–60 °C with slow, dropwise addition of the TTIP solution under intensive stirring (500 rpm) for 1–2 h. The resulting product was a highly viscous gel, which hindered efficient vacuum filtration. Therefore, solvent removal was carried out using a rotary evaporator at 80 °C and a reduced pressure of 30 kPa, enabling effective elimination of the mother liquor.

After drying, a crystalline white solid was obtained, which was subsequently ground and calcined

at 500 °C for 30 min in a muffle furnace. The final product, a fine white TiO₂ powder, was intended for cosmetic applications and is hereafter referred to as TiO₂-TTIP.

2.4. Physicochemical characterization methods

The phase composition and crystal lattice parameters of the synthesized samples were analyzed by X-ray powder diffraction (XRD) using a Shimadzu LabX XRD-6000 diffractometer with CuK_α radiation ($\lambda = 1.5406$ Å). Diffraction patterns for phase identification were recorded using the θ – 2θ scanning geometry with Bragg–Brentano focusing in the 2θ range of 5–70°, with a step size of $\Delta(2\theta) = 0.02^\circ$ and a counting time of 1 s per step. Measurements were performed at a tube voltage of 35 kV and a current of 30 mA. Phase identification was carried out using the JCPDS PDF-2 database. Processing of diffractograms, refinement of lattice parameters, and structural analysis were performed using the Match! and FullProf software packages.

The average crystallite size of nanostructured TiO₂ powders was estimated from XRD peak broadening using the Scherrer equation [5]:

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl} \cos \theta_{hkl}}, \quad (1)$$

where D_{hkl} (nm) is the average crystallite size perpendicular to the (hkl) plane, K is the shape factor ($K = 0.9$), λ is the CuK_α wavelength (0.15406 nm), β_{hkl} is the integral breadth of the diffraction peak corresponding to the (hkl) plane, and θ_{hkl} is the Bragg angle.

The true integral peak width was calculated according to:

$$\beta_{hkl} = (\beta_{\text{exp}}^2 - \beta_0^2)^{0.5}, \quad (2)$$

where β_{exp} is the experimentally measured full width at half maximum (FWHM), and β_0 is the instrumental broadening determined by the diffractometer configuration.

Rietveld refinement showed that the diffraction peak profiles in the 2θ range of 5–30° are well described by a pseudo-Voigt function, with the Lorentzian component contributing more than 90% ($\eta \rightarrow 1$). Therefore, a Lorentzian function was used to approximate peak shapes. For crystallite size determination, the (101) reflection of anatase and the (110)

reflection of rutile were selected as the most representative peaks.

Thermal analysis of the synthesized powders was performed using a Shimadzu DTG-60H synchronous thermal analyzer. Samples weighing 3–5 mg, together with Al₂O₃ as a reference material, were placed in alundum crucibles and heated in air from room temperature (20 °C) to 600 °C at a heating rate of 10 °C min⁻¹. The airflow rate was maintained at 100 mL min⁻¹. After reaching the maximum temperature, samples were allowed to cool naturally.

Thermal decomposition processes were additionally monitored using infrared (IR) spectroscopy. IR absorption spectra of annealed samples in the range of 400–4000 cm⁻¹ were recorded using a Spectrum BX FT-IR spectrophotometer (PerkinElmer) with KBr pellet preparation.

Diffuse reflectance spectra were recorded at room temperature using a UV-2600i spectrophotometer (Shimadzu) equipped with an integrating sphere, in the UV–Vis range of 200–900 nm. The diffuse reflectance data were analyzed using the Kubelka–Munk function:

$$F(R) = \frac{\alpha}{S} = \frac{(1 - R)^2}{2R}, \quad (3)$$

where R is the reflectance at a given wavelength, $F(R)$ is proportional to the absorption coefficient α , and the scattering coefficient S is assumed to be constant for sufficiently thick powder layers.

The optical band gap energy (E_g) was determined using the Tauc method, based on the relation:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g), \quad (4)$$

where h is Planck's constant, ν is the photon frequency, A is a proportionality constant, and n depends on the type of electronic transition. For TiO₂, an indirect allowed transition was assumed ($n = 2$).

Substituting α with $F(R)$ yields:

$$(F(R)h\nu)^{1/n} = A(h\nu - E_g). \quad (5)$$

The optical band gap energy of both undoped and Al³⁺-doped TiO₂ samples was determined by extrapolating the linear portion of the $(F(R)h\nu)^{1/n}$ versus $h\nu$ plot to the energy axis.

The morphology and chemical composition of the synthesized TiO₂ nanoparticles were examined using a high-resolution field-emission scanning electron microscope (SEM) FEI Inspect S equipped with

the EDAX Element Detector. The SEM images and EDX spectra were collected at an accelerating voltage of 5 kV.

Photoluminescence (PL) properties were investigated using synchrotron radiation excitation at the PETRA III P66 beamline of the Deutsches Elektronen-Synchrotron DESY, where the detection monochromator is a 0.3 m Kymera 328i (Andor) spectrograph with an F/4.1 aperture (200–1100 nm) and 0.4 nm spectral resolution. The measured spectra were corrected for the spectral response of the equipment. Correction of the excitation synchrotron flux intensity as a function of photon energy was carried out using a sodium salicylate Ref. [17].

3. Results and Discussion

3.1. Phase composition and crystallographic parameters of undoped and Al³⁺-doped TiO₂: influence of temperature and dopant concentration

The X-ray diffraction (XRD) patterns of the synthesized TiO₂ powders are presented in Fig. 5. For XRD data analysis and Rietveld refinement, tetragonal titanium dioxide structures in the anatase modification (COD No. 96-900-8214, space group $I4_1/amd$) and rutile modification (COD No. 96-900-4142, space group $P4_2/mnm$) were selected as the initial structural models from the Crystallography Open Database.

The Rietveld-refined diffraction patterns of TiO₂ powders calcined at different temperatures are shown in Fig. 5. The diffraction pattern of the sample calcined at 500 °C is dominated by reflections of the anatase phase (>99%). In addition, a low-intensity peak marked by an asterisk (*) appears in the 2θ range of 27.5–28.0°, corresponding to the (110) reflection of the rutile phase, whose content does not exceed 1%. The formation of an absolutely pure anatase phase was not observed, since traces of rutile are already present even at relatively low calcination temperatures. This behavior can be attributed to the higher thermodynamic stability of rutile compared to anatase.

An increase in the calcination temperature to 600 °C leads to a gradual increase in the rutile content to 3.9%, while anatase remains the dominant phase (96.1%). At 700 °C, a pronounced phase transformation is observed: the anatase content decreases to

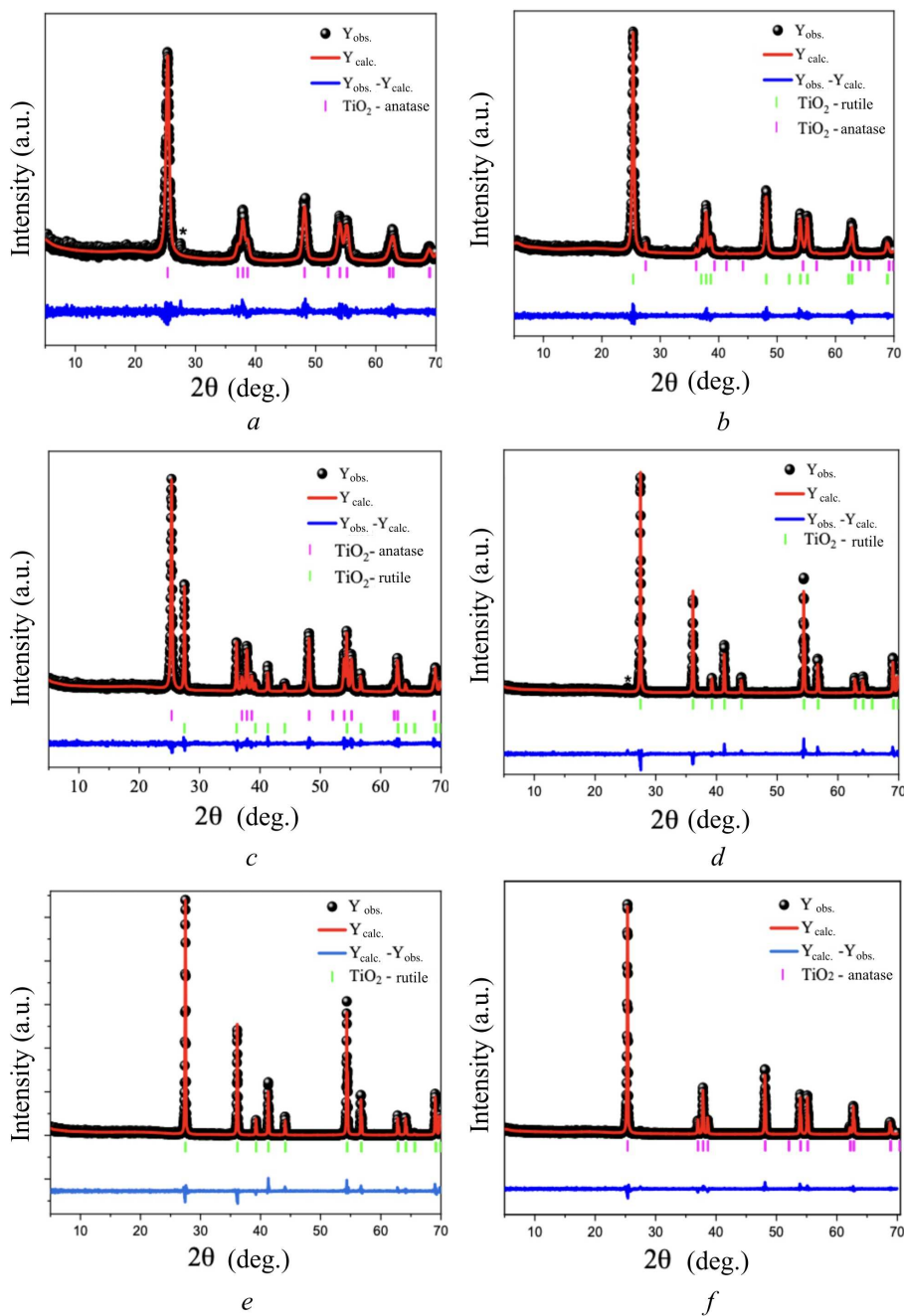


Fig. 5. XRD of TiO_2 nanopowder calcined at 500 °C (a), 600 °C (b), 700 °C (c), 800 °C (d), 900 °C (e) and commercial (f)

65.6%, whereas the rutile fraction increases to 32.4%, indicating the active progression of the anatase-to-rutile phase transition. Upon calcination at 800 °C, rutile becomes the dominant phase (>99%), and the anatase phase is preserved only as a weak residual reflection in the 2θ range of 25.2–25.4° (*). At 900 °C,

the anatase phase is completely transformed into rutile, confirming the metastable nature of anatase at elevated temperatures.

According to the phase analysis results, the diffraction peaks of the commercial TiO_2 reference sample fully coincide with those of standard anatase TiO_2 ,

Table 2. Crystallographic parameters of TiO₂, refined by the Rietveld method, synthesized at 500 °C (TiO₂-500), 600 °C (TiO₂-600) and 700 °C (TiO₂-700)

Sample	TiO ₂ -500		TiO ₂ -600		TiO ₂ -700	
Phase composition	TiO ₂ -anatase (<99 vol.%)	TiO ₂ -rutile (<1 vol.%)	TiO ₂ -anatase (96.10 vol.%)	TiO ₂ -rutile (3.90 vol.%)	TiO ₂ -anatase (67.57 vol.%)	TiO ₂ -rutile (32.43 vol.%)
Diffractometer	Shimadzu XRD-6000		Shimadzu XRD-6000		Shimadzu XRD-6000	
Radiation	CuK α , filtered		CuK α , filtered		CuK α , filtered	
Radiation, K α ₁ , K α ₂ (Å)	1.54051, 1.54433		1.54051, 1.54433		1.54051, 1.54433	
2 θ angular range (°)	5–70		5–70		5–70	
Scanning step (°)	0.02		0.02		0.02	
Background	Chebyshev polynomial		Chebyshev polynomial		Chebyshev polynomial	
Temperature (K)	293		293		293	
Crystal system	tetragonal		tetragonal	tetragonal	tetragonal	tetragonal
Space group	<i>I</i> 4 ₁ / <i>amd</i> (No. 141)		<i>I</i> 4 ₁ / <i>amd</i> (No. 141)	<i>P</i> 4 ₂ / <i>mnm</i> (No. 136)	<i>I</i> 4 ₁ / <i>amd</i> (No. 141)	<i>P</i> 4 ₂ / <i>mnm</i> (No. 136)
Lattice parameters <i>a</i> , <i>b</i> , <i>c</i> (Å)	<i>a</i> = 3.7806(2) Å <i>b</i> = 3.7806(2) Å <i>c</i> = 9.5024(12) Å		<i>a</i> = 3.7813(2) Å <i>b</i> = 3.7813(2) Å <i>c</i> = 9.5095(6) Å	<i>a</i> = 4.5891(10) Å <i>b</i> = 4.5891(10) Å <i>c</i> = 2.9570(11) Å	<i>a</i> = 3.7812(1) Å <i>b</i> = 3.7812(1) Å <i>c</i> = 9.5137(5) Å	<i>a</i> = 4.5915(1) Å <i>b</i> = 4.5915(1) Å <i>c</i> = 2.9578(2) Å
Lattice angles α , β , γ (°)	$\alpha = \beta = \gamma = 90^\circ$		$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$
Number of formula units, <i>Z</i>	4		4	2	4	2
Unit cell volume, <i>V</i> (Å ³)	135.82(2)		135.97(1)	62.27(3)	136.03(1)	62.36(1)
Crystallite size, <i>D_S</i> (nm)	13.9 ± 0.1		25.0 ± 0.2	68.2 ± 22.3	38.4 ± 0.4	82.4 ± 3.6
Dislocation density, $\delta \times 10^4$ (nm ⁻²)	51.5		16.2	2.2	6.8	1.5
X-ray density, <i>D_{XRD}</i> (g·cm ⁻³)	3.904		3.902	4.259	3.900	4.254
R _p (%)	12.1			11.2		11.5
R _w p (%)	17.2			16.5		18.1
R _{exp} (%)	15.2			15.16		15.31
χ^2 (%)	1.28			1.18		1.40

indicating the absence of secondary phases and high phase purity.

The crystallographic parameters of TiO₂ powders synthesized at different temperatures and refined by the Rietveld method are summarized in Tables 2 and 3. These data provide quantitative insight into the evolution of lattice parameters and phase stability as a function of calcination temperature and dopant concentration.

The Rietveld-refined diffraction patterns and crystallographic parameters of Al³⁺-doped tita-

nium dioxide powders calcined at different temperatures – Al_{0.05}Ti_{0.95}O₂ (500 °C), Al_{0.1}Ti_{0.9}O₂ (500 °C), Al_{0.05}Ti_{0.95}O₂ (900 °C), and Al_{0.1}Ti_{0.9}O₂ (900 °C) – are presented in Fig. 6 and summarized in Table 4.

For the Al_{0.05}Ti_{0.95}O₂ and Al_{0.1}Ti_{0.9}O₂ samples calcined at 500 °C, the diffraction patterns are dominated by reflections of the anatase phase. Compared to undoped TiO₂ calcined under identical conditions, these samples exhibit a noticeable reduction in crystallite size, manifested by significant broadening of

Table 3. Crystallographic parameters of TiO₂, refined by the Rietveld method, synthesized at 800 °C (TiO₂-800), 900 °C (TiO₂-900) and commercial (TiO₂-commercial)

Sample	TiO ₂ -800		TiO ₂ -900	TiO ₂ -commercial
Phase composition	TiO ₂ -rutile (<99 vol.%)	TiO ₂ -anatase (>1 vol.%)	TiO ₂ -rutile (100 vol.%)	TiO ₂ -anatase (100 vol.%)
Diffractometer	Shimadzu XRD-6000		Shimadzu XRD-6000	Shimadzu XRD-6000
Radiation	CuK α , filtered		CuK α , filtered	CuK α , filtered
Radiation, K α ₁ , K α ₂ (Å)	1.54051, 1.54433		1.54051, 1.54433	1.54051, 1.54433
2 θ angular range (°)	5–70		5–70	5–70
Scanning step (°)	0.02		0.02	0.02
Background	Chebyshev polynomial		Chebyshev polynomial	Chebyshev polynomial
Temperature (K)	293		293	293
Crystal system	tetragonal		tetragonal	tetragonal
Space group	$P4_2/mnm$ (No. 136)		$P4_2/mnm$ (No. 136)	$I4_1/amd$ (No. 141)
Lattice parameters a , b , c (Å)	$a = 4.5907(1)$ Å $b = 4.5907(1)$ Å $c = 2.9576(1)$ Å		$a = 4.5901(1)$ Å $b = 4.5901(1)$ Å $c = 2.9574(1)$ Å	$a = 3.7822(1)$ Å $b = 3.7822(1)$ Å $c = 9.5081(3)$ Å
Lattice angles α , β , γ (°)	$\alpha = \beta = \gamma = 90^\circ$		$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$
Number of formula units, Z	2		2	4
Unit cell volume, V (Å ³)	62.33(2)		62.31(2)	136.02(1)
Crystallite size, DS (nm)	101.6 $\pm$ 2.8		104.8 $\pm$ 3.3	85.9 $\pm$ 1.7
Dislocation density, $\delta \times 10^4$ (nm ⁻²)	1.0		0.9	1.4
X-ray density, DXRD (g · cm ⁻³)	4.255		4.257	3.900
R _p (%)	13.6		10.7	9.8
R _{wp} (%)	19.3		16.9	16.6
R _{exp} (%)	15.14		12.82	12.62
χ^2 (%)	1.63		1.74	1.73

diffraction peaks. This behavior indicates that Al³⁺ incorporation inhibits crystallite growth and stabilizes the anatase modification, thereby suppressing the formation of the thermodynamically more stable rutile phase at moderate temperatures.

Upon calcination at 900 °C, the Al_{0.05}Ti_{0.95}O₂ sample undergoes a complete phase transformation to rutile. The diffraction peaks become narrow and well defined, reflecting pronounced crystallite growth and increased crystallinity. In contrast, the Al_{0.1}Ti_{0.9}O₂ sample calcined at 900 °C also predominantly consists of the rutile phase but exhibits additional reflections attributed to the corundum structure. This observation indicates that, at higher aluminum concentrations, Al³⁺ ions are not fully incorporated into the TiO₂ crystal lattice and instead segregate to form a secondary α -Al₂O₃ phase. Quantitative phase anal-

ysis reveals that α -Al₂O₃ accounts for 10.02% of the sample, while rutile constitutes the remaining 89.98%.

These results demonstrate that aluminum doping effectively stabilizes anatase at lower calcination temperatures but exhibits a solubility limit in TiO₂ at elevated temperatures, beyond which phase segregation occurs.

3.2. Effect of synthesis temperature and Al³⁺ doping on TiO₂ crystallite size

The calculated sizes of coherent scattering regions (Tables 2–4) demonstrate that both annealing temperature and aluminum doping have a pronounced influence on crystallite size and dislocation density in TiO₂ samples. For undoped TiO₂, increasing the annealing temperature from 500 to 900 °C results

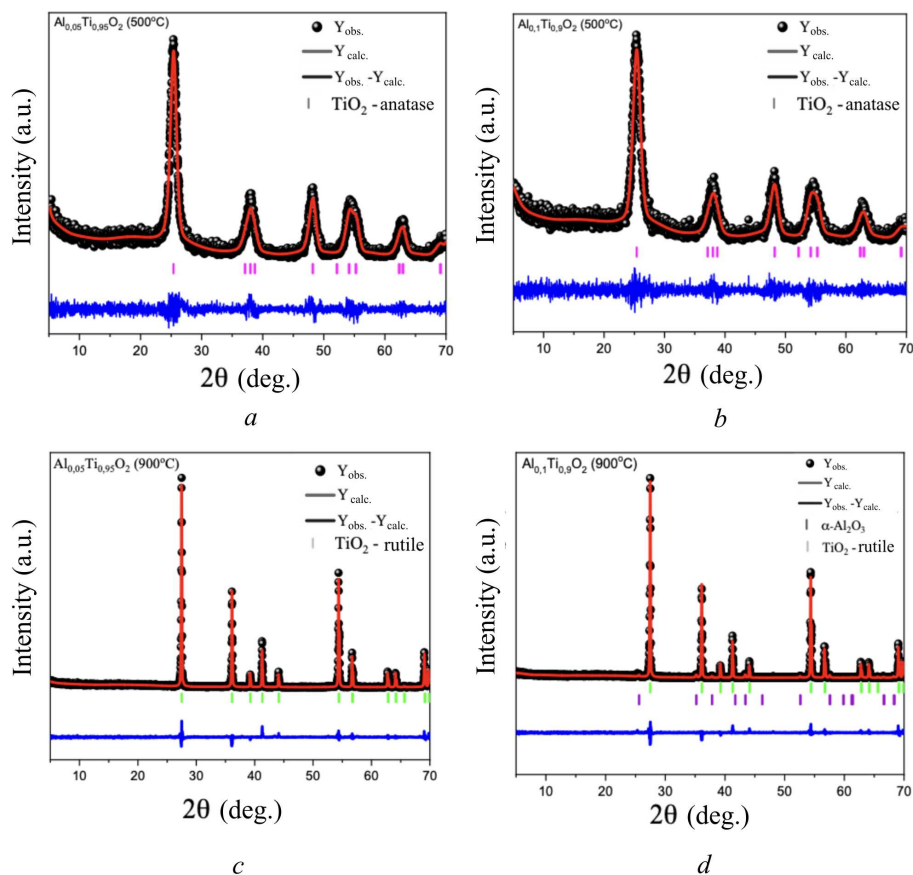


Fig. 6. XRD of Al³⁺-doped titanium dioxide powders calcined at 500 °C and 900 °C

in a systematic growth of crystallite size. This effect is particularly evident for the rutile modification, whose crystallites are significantly larger than those of anatase synthesized under comparable conditions. At elevated temperatures (≥ 700 °C), further crystallite coarsening occurs, accompanied by a reduction in structural defect density. The increase in temperature promotes improved ordering of the crystal lattice, which is reflected in a decrease in dislocation density, as summarized in Tables 2 and 3.

It is noteworthy that even at relatively low synthesis temperatures, the crystallite size of the rutile phase is approximately twice that of the anatase phase. This behavior can be attributed to the higher growth rate of nuclei belonging to the thermodynamically stable rutile modification of TiO₂, which favors rapid crystallite growth once nucleation has occurred.

The Al³⁺ doping also exerts a significant effect on crystallite size; however, its influence differs markedly between the anatase and rutile phases. For anatase samples calcined at 500 °C, aluminum incorporation

leads to a pronounced reduction in crystallite size, with higher Al³⁺ concentrations resulting in progressively smaller domains. Simultaneously, the dislocation density in Al³⁺ doped anatase is higher than that in undoped TiO₂, indicating an increase in structural defects. This behavior is consistent with the peak broadening observed in the XRD patterns (Fig. 7), where aluminum doping causes an increase in the full width at half maximum, reflecting reduced crystallite size and increased lattice distortion.

In contrast, for rutile samples calcined at 900 °C, aluminum doping produces the opposite effect. Under these high-temperature conditions, Al³⁺ incorporation promotes crystallite growth and leads to a reduction in dislocation density, as shown in Table 4. This suggests enhanced lattice ordering and defect annihilation during high-temperature annealing in the presence of aluminum.

Additional confirmation that diffraction peak broadening is predominantly governed by finite crystallite size rather than microstrain is provided by

Table 4. Crystallographic parameters of Al-doped TiO₂, refined by the Rietveld method, synthesized at 500°C (Al_{0.05}Ti_{0.95}O₂-500, Al_{0.1}Ti_{0.9}O₂-500) and 900°C (Al_{0.05}Ti_{0.95}O₂-900, Al_{0.1}Ti_{0.9}O₂-900)

Sample	Al _{0.05} Ti _{0.95} O ₂ -500	Al _{0.1} Ti _{0.9} O ₂ -500	Al _{0.05} Ti _{0.95} O ₂ -900	Al _{0.1} Ti _{0.9} O ₂ -900	
Phase composition	TiO ₂ -anatase (100 vol.%)	TiO ₂ -anatase (100 vol.%)	TiO ₂ -rutile (100 vol.%)	TiO ₂ -rutile (89.98 vol.%)	α-Al ₂ O ₃ (10.02 vol.%)
Diffractometer	Shimadzu XRD-6000	Shimadzu XRD-6000	Shimadzu XRD-6000	Shimadzu XRD-6000	
Radiation	CuKα, filtered	CuKα, filtered	CuKα, filtered	CuKα, filtered	
Radiation, Kα ₁ , Kα ₂ (Å)	1.54051, 1.54433	1.54051, 1.54433	1.54051, 1.54433	1.54051, 1.54433	
2θ angular range (°)	5–70	5–70	5–70	5–70	
Scanning step (°)	0.02	0.02	0.02	0.02	
Background	Chebyshev polynomial	Chebyshev polynomial	Chebyshev polynomial	Chebyshev polynomial	
Temperature (K)	293	293	293	293	
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal (hexagonal axes)
Space group	<i>I</i> 4 ₁ / <i>amd</i> (No. 141)	<i>I</i> 4 ₁ / <i>amd</i> (No. 141)	<i>P</i> 4 ₂ / <i>mm</i> (No. 136)	<i>P</i> 4 ₂ / <i>mm</i> (No. 136)	<i>R</i> -3 <i>c</i> (No. 167)
Lattice parameters <i>a</i> , <i>b</i> , <i>c</i> (Å)	<i>a</i> = 3.7775(5) Å <i>b</i> = 3.7775(5) Å <i>c</i> = 9.4801(24) Å	<i>a</i> = 3.7767(6) Å <i>b</i> = 3.7767(6) Å <i>c</i> = 9.4742(31) Å	<i>a</i> = 4.5897(1) Å <i>b</i> = 4.5897(1) Å <i>c</i> = 2.9582(1) Å	<i>a</i> = 4.5904(1) Å <i>b</i> = 4.5904(1) Å <i>c</i> = 2.9582(1) Å	<i>a</i> = 4.7567(7) Å <i>b</i> = 4.7567(7) Å <i>c</i> = 2.9582(36) Å
Lattice angles α, β, γ (°)	α = β = γ = 90°	α = β = γ = 90°	α = β = γ = 90°	α = β = γ = 90°	α = β = 90°, γ = 120°
Number of formula units, <i>Z</i>	4	4	2	2	6
Unit cell volume, <i>V</i> (Å ³)	135.28(4)	135.14(6)	62.31(2)	62.33(2)	254.59(9)
Crystallite size, DS (nm)	7.0 ± 0.1	5.6 ± 0.1	137.1 ± 6.3	224.9 ± 22.1	–
Dislocation density, δ · 10 ⁴ (nm ^{−2})	206	317	0.5	0.2	–
X-ray density, DXRD (g · cm ^{−3})	3.922	3.926	4.256	4.255	3.992
R _p (%)	11.7	11.3	12.8	12.8	
R _{wp} (%)	15.9	15.3	18.8	18.4	
R _{exp} (%)	14.62	14.58	15.29	14.96	
χ ² (%)	1.18	1.11	1.50	1.52	

analysis of the half-width ratio $\beta_{\text{II}}/\beta_{\text{I}}$ for different orders of reflection from the same crystallographic plane. For Al³⁺-doped rutile TiO₂, the ratio of peak widths for the (110) and (220) reflections closely matches the ratio $\cos \theta_{\text{I}}/\cos \theta_{\text{II}}$, where θ_{I} and θ_{II} are the corresponding Bragg angles. This agreement indicates that size broadening is the dominant contribution to line broadening in these samples.

3.3. Study of morphology and uniformity of dopant distribution using scanning electron microscopy

The synthesized samples were examined using SEM to analyze the changes in nanoparticle morphology with annealing temperature and to investigate the uniformity of dopant distribution. The SEM images

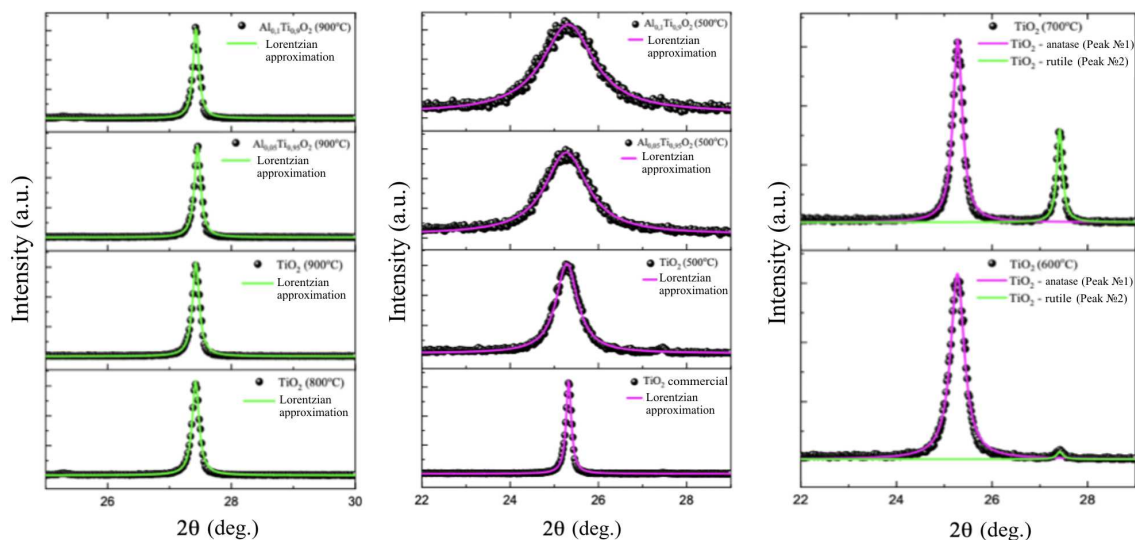


Fig. 7. The (011) peak of the anatase phase (left panels) and the (110) peak of the rutile phase (right panels) of Al³⁺-doped and undoped TiO₂ nanostructured powders (fitted using a Lorentzian function)

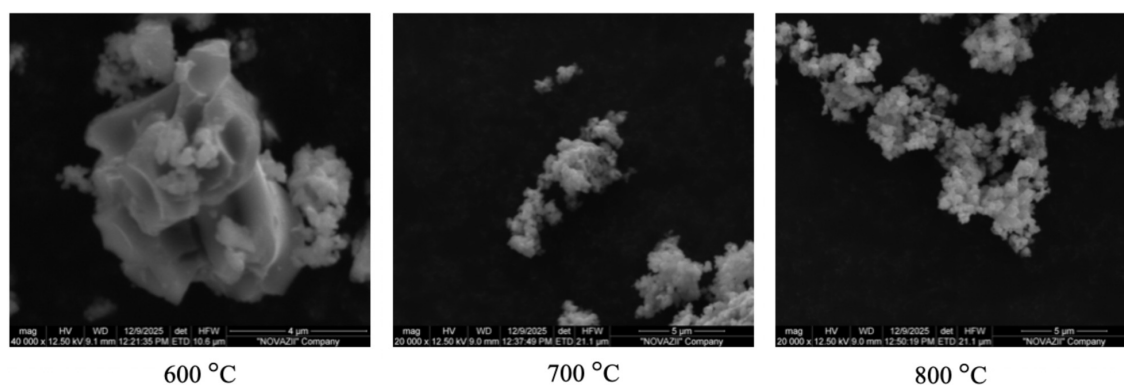


Fig. 8. SEM images of TiO₂ obtained after calcination at different temperatures

showed that the nanoparticle sizes reach up to 100–200 nm. These nanoparticles are agglomerated into micro-sized clusters that can reach several micrometers in diameter.

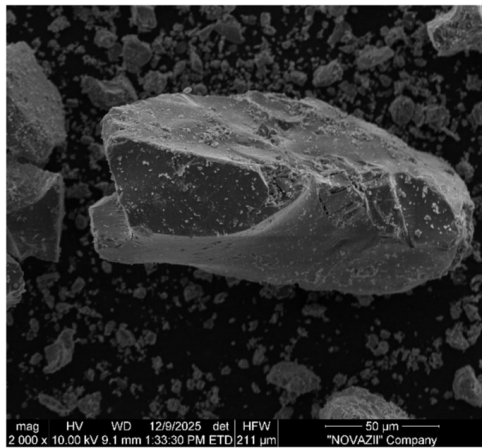
SEM images of TiO₂ nanoparticles, both in the as-prepared powder and in the annealed samples, demonstrate changes in the structure of these agglomerates with increasing annealing temperature (Fig. 8). The nanoparticles exhibit a dense structure and a smooth surface with isolated small regions showing a granular structure before annealing (Fig. 9). With the onset of annealing, surface erosion is observed along with the formation of cavities inside the particles. Most likely, these cavities form due to the expansion of air trapped within the parti-

cles. In addition, the surface becomes porous, which can be interpreted as the formation of gas escape channels. A further increase in the annealing temperature causes the entire particle surface to acquire a granular structure.

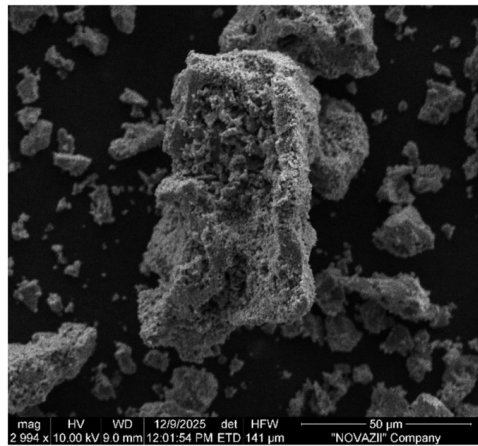
This transition is particularly clearly observed for the smallest particles (Fig. 10).

A different behavior is observed for Al_xTi_{1-x}O₂ powders during annealing. The formation of a granular structure does not occur, while surface erosion of the nanoparticles is still observed at 500 °C and 900 °C (Fig. 11).

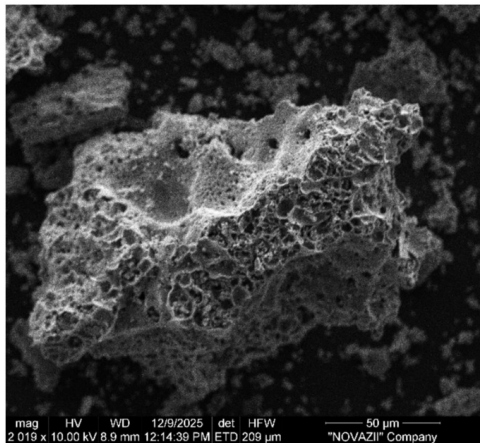
The elemental composition analysis showed a uniform distribution of aluminum dopants in all samples (Fig. 12).



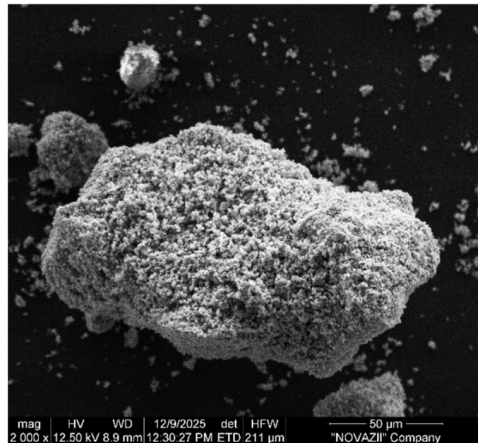
a



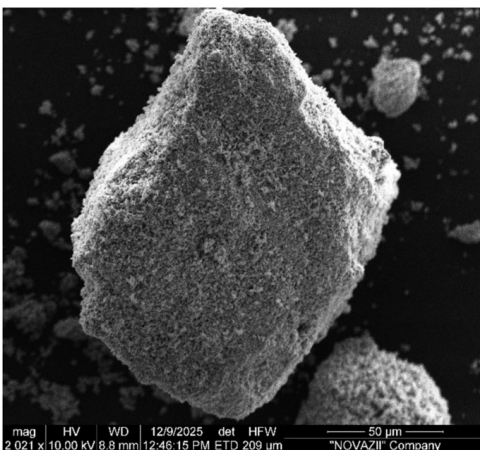
b



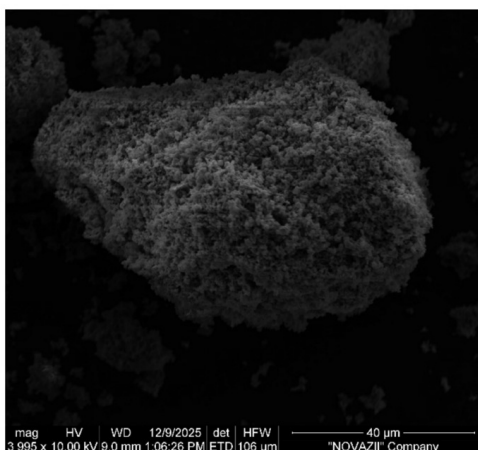
c



d



e



f

Fig. 9. SEM images of TiO_2 nanoparticles without annealing (*a*); 500°C (*b*); 600°C (*c*); 700°C (*d*); 800°C (*e*); 900°C (*f*)

3.4. Optical Characteristics of the Samples in the UV–Vis Range

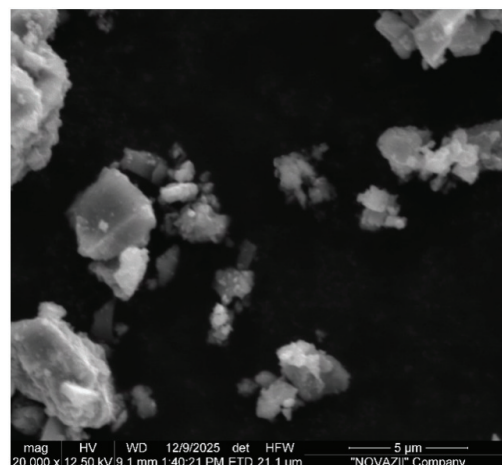
Spectral measurements of the investigated samples in the UV–Vis range were carried out to determine the band gap energy. The results of the band gap energy calculations (E_g , eV) for TiO₂ samples synthesized at different temperatures indicate that this parameter depends on the phase composition of the material (Table 5, Figs 13, 14 a).

Commercial TiO₂ (anatase) exhibits the largest band gap energy (3.2 eV) (Figs 13, 14, a). The lower E_g value of the sample calcined at 600 °C is explained by the influence of a small amount of rutile impurity on its electronic properties. TiO₂ obtained at 500 °C, despite the near absence of the rutile phase, shows an even smaller E_g value. This may be associated with the formation of impurity defect levels caused by the presence of carbon-containing residues. When the anatase-to-rutile phase transition is completed at 700–900 °C, the band gap energy stabilizes at 2.96–2.98 eV (Table 5). This is in good agreement with the E_g value of pure rutile (~3.0 eV) (Fig. 14, a).

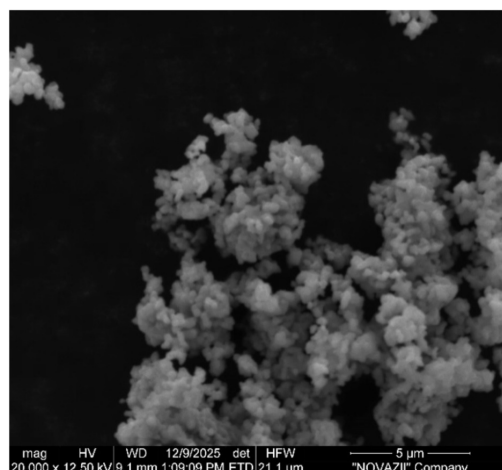
Aluminum doping also affects the E_g value. The band gap of Al_{0.05}Ti_{0.95}O₂, Al_{0.1}Ti_{0.9}O₂, and Al_{0.2}Ti_{0.8}O₂ samples synthesized at 500 °C is significantly higher than that of undoped TiO₂ (3.01 eV). This indicates band gap widening due to the incorporation of Al³⁺ ions, which can modify the electronic structure of the material. However, with increasing temperature up to 900 °C, the band gap decreases to 2.94–2.95 eV, which is consistent with the increased rutile content (Fig. 14, b).

Table 5. Band gap width (E_g) of undoped and Al-doped TiO₂ samples determined by the Tauc method

Sample, annealing temperature	E_g , eV
TiO ₂ , 500 °C	3.01
TiO ₂ , 600 °C	3.10
TiO ₂ , 700 °C	2.97
TiO ₂ , 800 °C	2.98
TiO ₂ , 900 °C	2.96
TiO ₂ commercial (anatase)	3.20
Al _{0.05} Ti _{0.95} O ₂ , 500 °C	3.12
Al _{0.1} Ti _{0.9} O ₂ , 500 °C	3.09
Al _{0.05} Ti _{0.95} O ₂ , 900 °C	2.94
Al _{0.1} Ti _{0.9} O ₂ , 900 °C	2.95
Al _{0.2} Ti _{0.8} O ₂ , 500 °C	3.12
TiO ₂ –TTIP	2.91



a



b

Fig. 10. SEM images of small TiO₂ particles: without annealing (a); annealed at 900 °C (b)

From the perspective of application in sunscreens, the samples synthesized at 500 °C, especially those doped with aluminum, may be more effective in absorbing UV-B radiation due to the band gap widening. At the same time, samples obtained at higher temperatures, with a greater rutile content, may exhibit improved absorption of longer UV-A wavelengths. This makes the combined use of these materials promising for broad-spectrum protection.

3.5. Luminescent properties of the synthesized TiO₂ nanoparticles

The photoluminescence (PL) spectra of the synthesized TiO₂ nanoparticles are characterized by

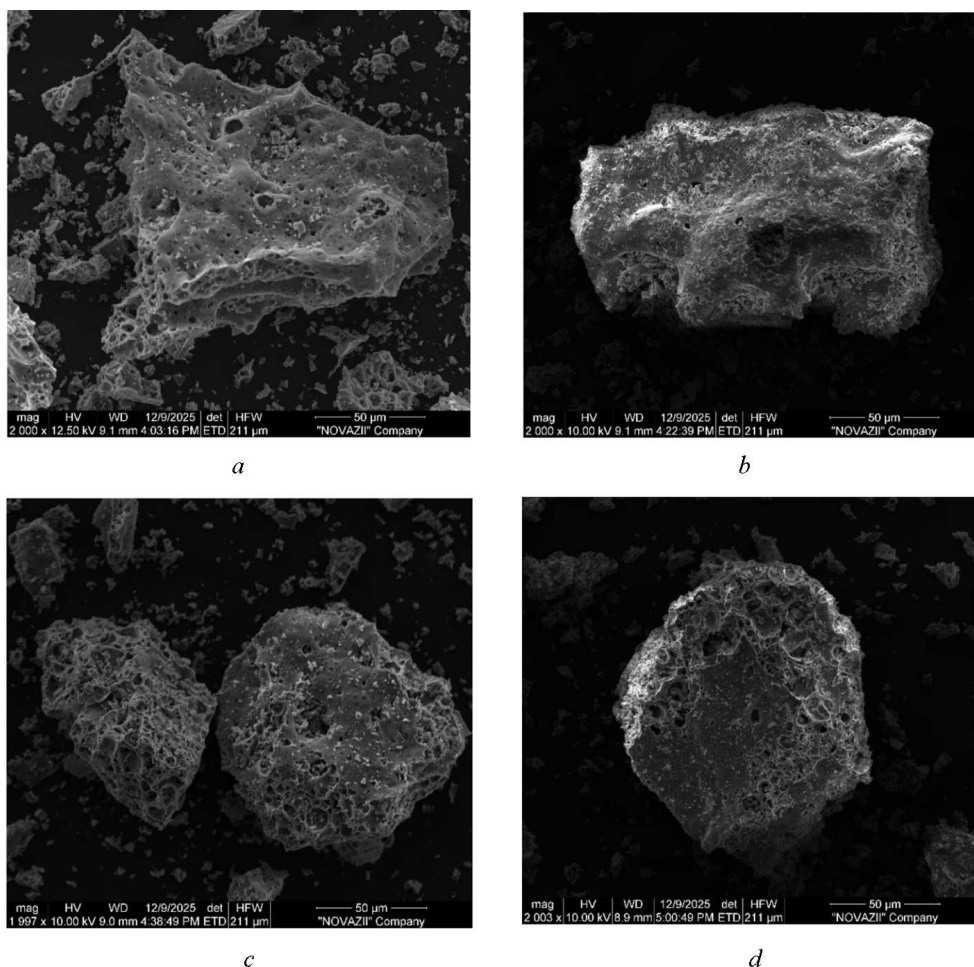


Fig. 11. SEM images of $\text{Al}_{0.05}\text{Ti}_{0.95}\text{O}_2$ nanoparticles annealed at 500 °C (a); 600 °C (b) and $\text{Al}_{0.1}\text{Ti}_{0.9}\text{O}_2$ nanoparticles annealed at 500 °C (c) and 900 °C (d)

very weak emission, which can be efficiently excited only by high-energy photons. The emission spectra of TiO_2 samples annealed at 500 °C exhibit two main broad bands centered at approximately 430 and 560 nm. The intensity of these bands increases for samples annealed at 700 °C and decreases significantly for samples annealed at 900 °C (Fig. 15).

An increase in the annealing temperature also leads to the appearance of a weak near-infrared emission band around 850 nm. In addition, temperature-dependent shifts of the short-wavelength edge are observed for both undoped and Al-doped TiO_2 nanoparticles. These shifts indicate the presence of an additional weak emission band near 375 nm, which gradually disappears with increasing annealing temperature.

At lower annealing temperatures and low aluminum concentrations, Al^{3+} doping does not signif-

icantly affect the emission bands at 375, 430, and 560 nm. However, substantial changes are observed for highly doped $\text{Al}_{0.1}\text{Ti}_{0.9}\text{O}_2$ nanoparticles. In this case, a pronounced enhancement of the 430 nm emission band is detected, along with the emergence of an intense near-infrared band centered around 850 nm. This band is accompanied by a less intense, relatively narrow spectral component near 695 nm (Fig. 15).

3.6. Origin of the emission bands and correlation with structural properties

The observed photoluminescence of TiO_2 nanoparticles is governed by defect-related electronic states, whose population and radiative efficiency strongly depend on crystallite size, phase composition, annealing temperature, and dopant concentration. The weak in-

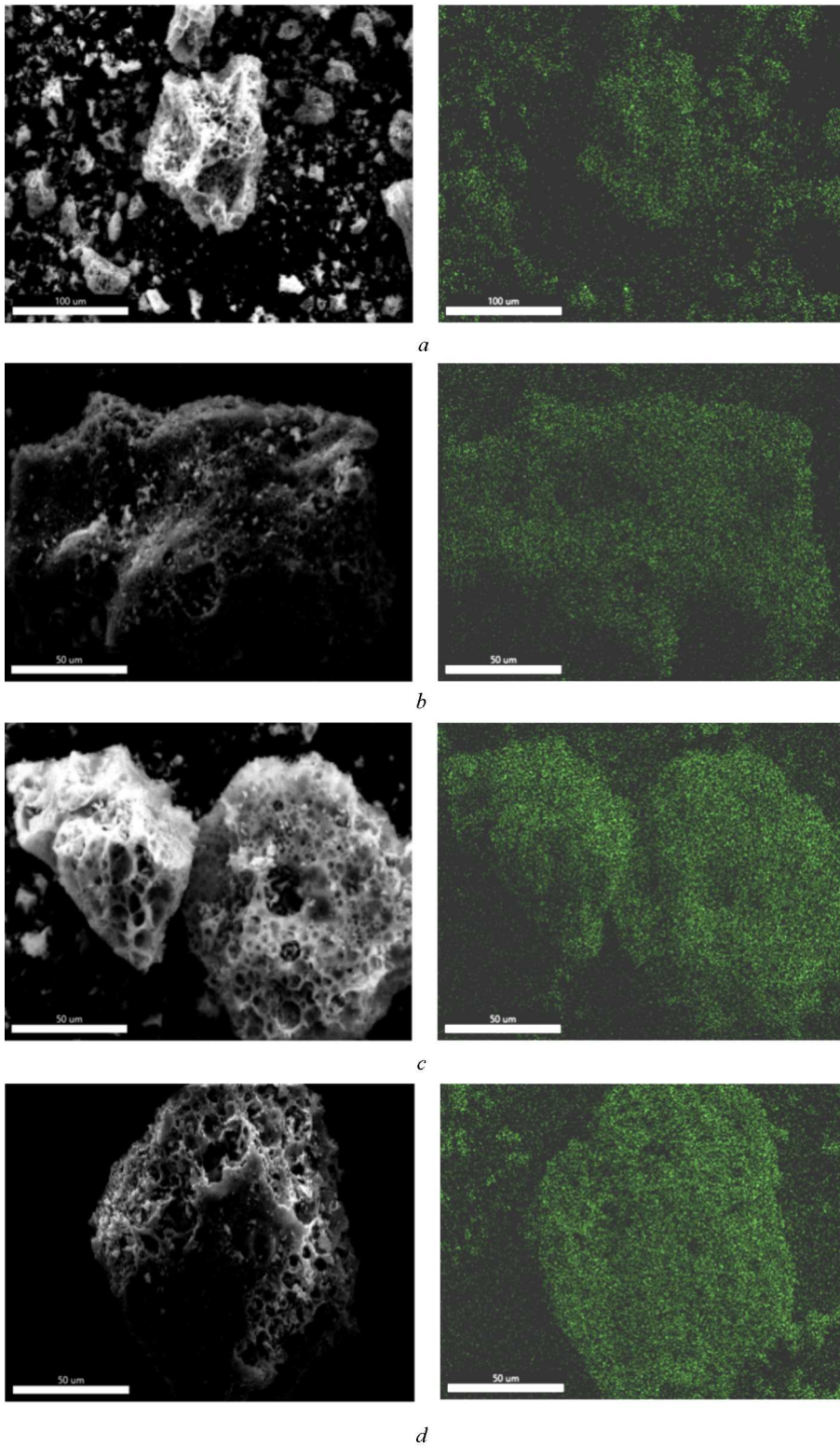


Fig. 12. SEM images of Al_{0.05}Ti_{0.95}O₂ annealed at 500°C (a); 900°C (b) and Al_{0.1}Ti_{0.9}O₂ annealed at 500°C (c) and 900°C (d), and the distribution of aluminum within them

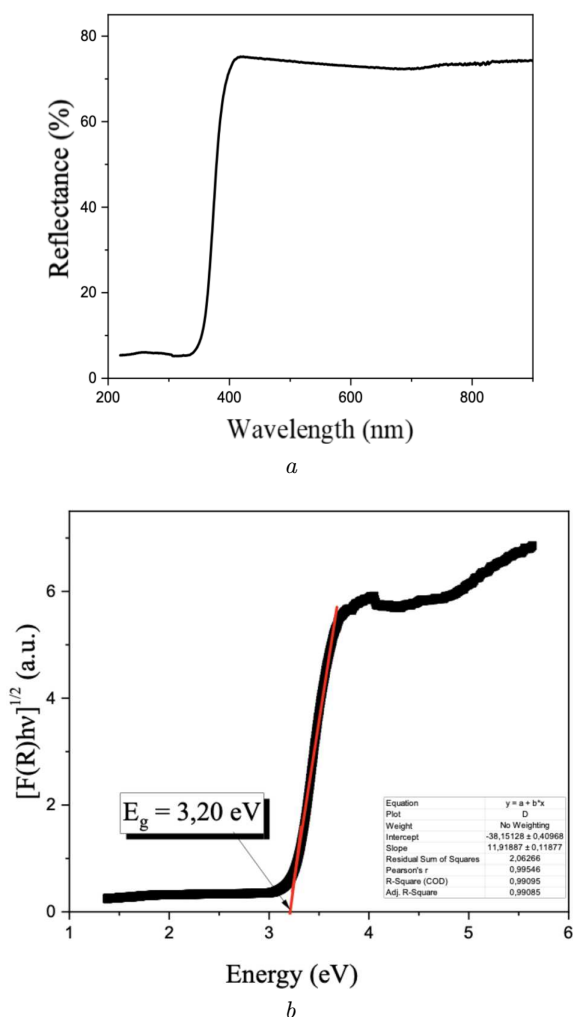


Fig. 13. Dependence of the diffuse reflectance coefficient (R) of commercial TiO_2 on the wavelength of electromagnetic radiation (a). Tauc plot for determining the band gap energy of commercial TiO_2 (b)

trinsic emission of TiO_2 reflects its indirect band gap nature and the predominance of non-radiative recombination pathways.

The weak ultraviolet emission band observed near 375 nm is attributed to near-band-edge recombination involving excitonic states or shallow defect levels [18–21]. Its presence at lower annealing temperatures and subsequent disappearance with increasing temperature indicate a surface-related origin. As the annealing temperature increases, grain growth and surface area reduction lead to annihilation of surface states, suppressing this emission.

The broad blue emission band centered around 430 nm is commonly associated with radiative recombination via shallow oxygen vacancy states and Ti^{3+} -related donor levels [21–25]. These defects are preferentially stabilized in the anatase phase and are more abundant in smaller crystallites due to their higher surface-to-volume ratio. Consequently, the intensity of the 430 nm band increases for samples annealed at intermediate temperatures ($\approx 700^\circ\text{C}$), where both anatase and rutile phases are present. The same effect was observed earlier for other two-phase crystalline oxide nanoparticles based on LaVO_4 dimorphic composition, where two-phase samples demonstrated the highest emission intensity [26–28]. In Al^{3+} -doped samples, particularly $\text{Al}_{0.1}\text{Ti}_{0.9}\text{O}_2$, this band is significantly enhanced, which can be attributed to charge compensation effects accompanying Al^{3+} substitution for Ti^{4+} , leading to an increased concentration of Ti^{3+} centers and oxygen vacancies.

The green-yellow emission band around 560 nm is attributed to deep-level defect states related to oxygen vacancy clusters and bulk defect complexes. This emission is typically observed in nanocrystalline anatase and diminishes with increasing annealing temperature as defect recombination occurs and the material transforms toward the more thermodynamically stable rutile phase. The reduction of this band at 900°C correlates with crystallite growth, defect annihilation, and phase transformation.

The near-infrared emission bands observed at approximately 695 nm and 850 nm cannot be satisfactorily explained by intrinsic TiO_2 defect states. These bands are most plausibly attributed to trace amounts of Cr^{3+} impurities, which are commonly present as uncontrolled contaminants in aluminum nitrate and other aluminum precursors and can exhibit luminescence at extremely low concentrations [29]. The characteristic Cr^{3+} electronic transitions, particularly ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ and ${}^2\text{E} \rightarrow {}^4\text{A}_2$, fall within the red and near-infrared spectral regions and are well known to produce emissions near these wavelengths [30]. The appearance of these bands exclusively in highly Al-doped samples and their absence in undoped TiO_2 strongly support this interpretation. Furthermore, the pronounced intensity of the 850 nm band in $\text{Al}_{0.1}\text{Ti}_{0.9}\text{O}_2$ suggests efficient incorporation of Cr^{3+} ions into octahedral sites, likely within Al-

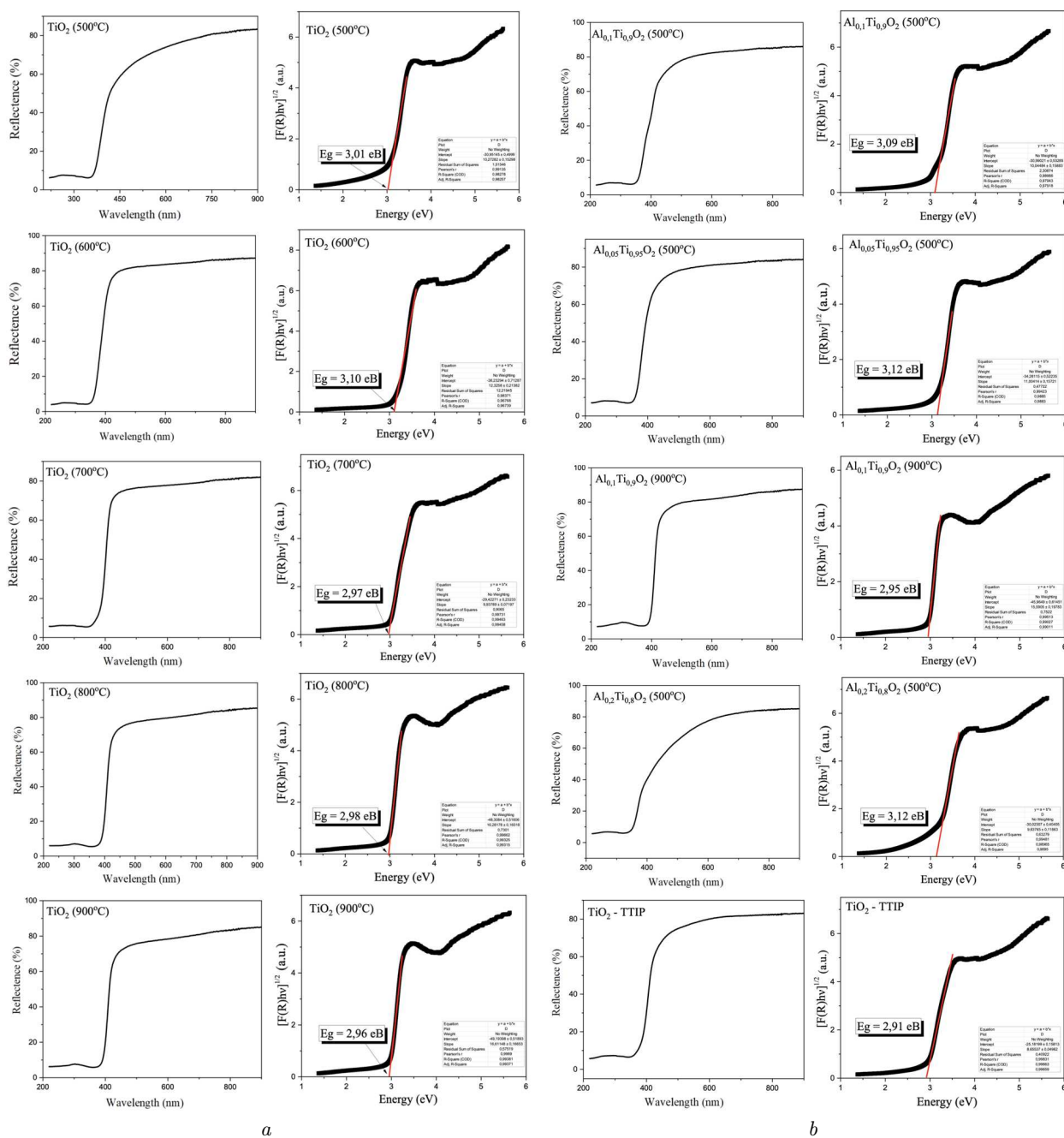


Fig. 14. (a) dependence of the diffuse reflectance coefficient (R) on the wavelength of electromagnetic radiation (left); Tauc plot for determining the band gap energy (right). (b) dependence of the diffuse reflectance coefficient (R) on the wavelength of electromagnetic radiation (left); Tauc plot for determining the band gap energy (right)

rich regions or secondary phases formed at high dopant concentrations.

Overall, the photoluminescence behavior of the synthesized TiO₂ nanoparticles reflects a complex

interplay between intrinsic defect states, extrinsic dopant-induced defects, crystallite size evolution, and phase composition. Aluminum doping stabilizes defect-related visible emission at moderate temper-

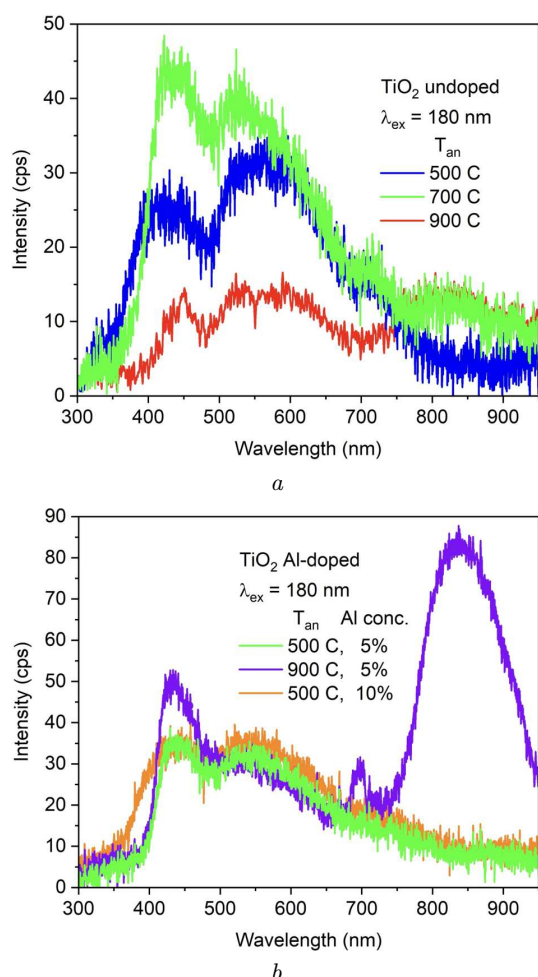


Fig. 15. PL spectra of undoped (a) and Al-doped TiO₂ nanoparticles excited by 180 nm synchrotron radiation (b)

atures, while high-temperature annealing suppresses intrinsic TiO₂ luminescence and promotes impurity-related near-infrared emission.

4. Conclusions

The TiO₂ nanopowders, both undoped and Al³⁺-doped, were successfully synthesized using sol-gel routes based on titanium citrate and titanium(IV) isopropoxide precursors, followed by controlled thermal treatment in a wide temperature range. Thermal analysis revealed multistage decomposition of organic components, with the formation of TiO₂ completed above 500 °C. The applied calcination temperatures enabled systematic control over phase composition, crystallite size, and defect structure.

The XRD analysis demonstrated that undoped TiO₂ undergoes a gradual anatase-to-rutile phase transition with increasing annealing temperature. Anatase dominates at 500 °C, mixed anatase-rutile compositions are observed at 600–700 °C, and complete transformation to rutile occurs at 900 °C. Aluminum doping stabilizes the anatase phase at moderate temperatures and suppresses rutile formation, while at high temperatures it exhibits a solubility limit, leading to the formation of the rutile phase.

Crystallite size analysis showed that increasing annealing temperature results in significant crystallite growth and a reduction in dislocation density, particularly for rutile TiO₂. Aluminum doping exerts a phase-dependent effect: in anatase, Al³⁺ incorporation reduces crystallite size and increases defect density, whereas in rutile at high temperatures it promotes crystallite growth and improved lattice ordering. These effects were confirmed by XRD peak broadening analysis and coherence-length calculations. The SEM and EDX analyses confirmed the homogeneous distribution of the Al ions in the doped samples.

The PL studies revealed that TiO₂ nanoparticles exhibit weak intrinsic emission dominated by defect-related states. Emission bands at ~375 nm, ~430 nm, and ~560 nm were assigned to near-band-edge surface states, shallow Ti³⁺/oxygen vacancy-related states, and deep oxygen vacancy complexes, respectively. The intensity of these bands strongly depends on crystallite size, phase composition, and annealing temperature, with maximal defect-related emission observed in nanocrystalline anatase at intermediate temperatures.

Highly Al³⁺-doped samples exhibited additional red and near-infrared emission bands at ~695 nm and ~850 nm. These bands cannot be attributed to intrinsic TiO₂ defects and are most plausibly associated with trace Cr³⁺ impurities unintentionally introduced with aluminum precursors. The enhanced intensity of these bands at high annealing temperatures is facilitated by the formation of rutile TiO₂ and Al-rich phases, which provide favorable crystal-field environments for Cr³⁺ luminescence.

Overall, the results demonstrate that the structural, optical, and luminescent properties of TiO₂ nanoparticles can be effectively tuned through controlled synthesis conditions, annealing temperature, and aluminum doping. The study highlights the crit-

ical role of defect chemistry, phase composition, and impurity incorporation in determining luminescent behavior, which is essential for optimizing TiO₂-based materials for UV-blocking, cosmetic, and photonic applications.

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ВПЛИВ ЛЕГУВАННЯ АЛЮМІНІЄМ НА СТРУКТУРУ, МОРФОЛОГІЮ ТА ОПТИЧНІ ВЛАСТИВОСТІ НАНОЧАСТИНОК TiO_2

Недоповані та гетеровалентно модифіковані йонами алюмінію наночастинки діоксиду титану (TiO_2) отримано методом золь–гель синтезу. Досліджено вплив параметрів синтезу, температури відпалу (500–900 °C) і концентрації допувальних елементів Al^{3+} на фазовий склад, кристалогра-

фічні параметри, розмір кристалітів, дефектну структуру й оптичні властивості TiO_2 . Рентгенофазний аналіз показав фазове перетворення анатазу в рутил, зумовлене підвищенням температури в недопованому TiO_2 , тоді як введення алюмінію стабілізувало фазу анатазу за помірних температур і призупиняло утворення рутилу. За вищих температур і високих концентрацій домішки спостерігалася межа розчинності Al^{3+} у кристалічній ґратці TiO_2 , що зумовлювало утворення вторинної фази $\alpha\text{-Al}_2\text{O}_3$. Аналіз розміру кристалітів показав, що підвищення температури відпалу сприяє росту зерен і зменшенню густини дефектів кристалічної ґратки, тоді як допущання Al^{3+} сповільнює ріст кристалітів в анатазі та підвищує концентрацію дефектів. Натомість для фази рутилу TiO_2 за високих температур введення алюмінію сприяє зростанню кристалітів і впорядкуванню кристалічної ґратки. Дослідження спектрів фотолюмінесценції показало слабе власне світіння TiO_2 , зумовлене дефектними станами, зі смугами світіння, пов'язаними з поверхневими станами, кисневими вакансіями та центрами Ti^{3+} . У зразках з високим вмістом Al^{3+} виявлено додаткові смуги світіння в червоному та ближньому ІЧ-діапазонах, пов'язані із домішками Cr^{3+} , випадково внесеними разом із прекурсорами алюмінію. Отримані результати показують, що умови синтезу й гетеровалентне заміщення є ефективними інструментами керування структурними, морфологічними й оптичними властивостями наночастинок TiO_2 . Результати свідчать про важливу роль хімії дефектів, фазового складу та впливу домішок на модифікацію матеріалів на основі TiO_2 для застосування як УФ-блокаторів, у косметичці та фотоніці.

Ключові слова: діоксид титану (TiO_2), наночастинки, допущання Al^{3+} , кристалічна структура, оптичні властивості.