

## Article

# Microwave-Assisted Synthesis of Titanosilicates Using a Precursor Produced from Titanium Ore Concentrate

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**Abstract:** Titanosilicates comprise a broad class of materials with promising technological applications. The typical obstacle that restricts their industrial applicability is the high manufacturing cost due to the use of specific organotitanium precursors. We herein report a new approach to the synthesis of titanosilicates using an inexpensive inorganic precursor, ammonium titanyl sulfate (ATS or STA),  $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ . The latter is an intermediate in the processing of titanium-bearing concentrates produced from apatite-nepheline ores. In this paper, the new synthetic approach is exemplified by the microwave-assisted synthesis of IONSIVE-911, one of the most effective Cs-ion scavengers. The method can be modified to synthesize various titanosilicate compounds.

**Keywords:** microwave-assisted synthesis; sitinakite; functional material; sorbent; cesium; eco-friendly reagent



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## 1. Introduction

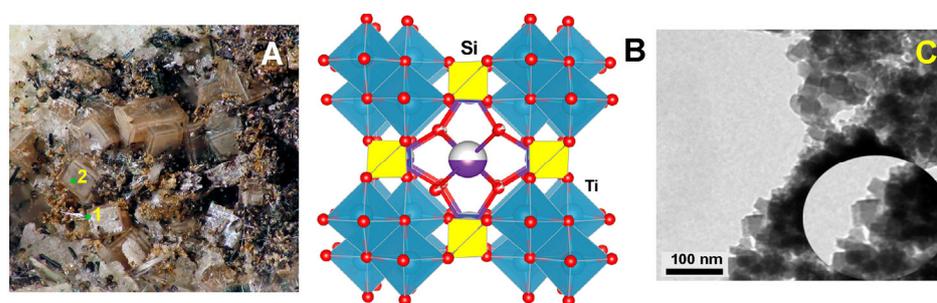
In modern science, microwave methods are closely related to definitions of hydrothermal synthesis and new functional materials, including aluminosilicates and titanosilicates, as synthetic analogs of natural minerals. Microwave techniques are used in both organic and inorganic chemistry [1], for example, for organometallic compounds [2], individual and multicomponent oxides and compounds with more complex structures [3]. In numerous instances, this technique helps to increase the speed of chemical reactions tenfold and preserve the fundamental reaction scheme for mixture components. This method has been used by scientists for a considerable amount of time, and the first manuscript on zeolites was published in 1988 [4]. It was a US patent of the “Mobil” company for the synthesis of NaA and ZSM-5 zeolites [5]. The paper focuses on the microwave synthesis of Y-type and ZSM-5 zeolites, which in 1993 [6] gave rise to a growing interest in this method and the development of different types of equipment. Microwaves have wavelengths between 0.01 and 1 m, and operate in the frequency range between 0.3 and 30 GHz (electromagnetic

spectrum between infrared and radio waves). Microwave experiments are currently conducted at 2450 MHz (the corresponding wavelength is 12.24 cm) [5]. The subject of all the sharp questions on special “microwave effects”, non-thermal effects and heating effects with increased temperatures in microwave closed synthesis systems is still a controversial matter and open for discussion and investigation nowadays [5,7]. In laboratory investigations, microwave ovens have some advantages over conventional laboratory ovens in terms of the speed of thermal effects [1,3]: (1) the introduction of microwave energy into a chemical reaction can lead to much higher heating rates than those achieved conventionally. Thereby, beta-zeolites can be produced in 4 h by the microwave method, while the standard method with conventional heating may take 60 h [7]. Engelhard titanosilicate (ETS-4) can be successfully synthesized by microwave heating at 235 °C within a very short time of 50 min [8]; (2) microwave energy enters into the chemical reactor without direct contact between the energy source and the reagents; (3) it involves closed-circuit heating and instantaneous (or rapid) heating with no barrier or heat-diffusion effects; (4) it can perform selective heating because chemicals and materials that enable chemical reactions do not interact with microwaves in the same way; (5) “hot spots” yielded at local boundaries as a result of reflections and refractions may result in a “superheating” effect, which can be described as local overheating and is similar to the slow boiling of overheated liquids under conventional conditions; (6) the reaction gel mixture can be dissolved quickly, and the product can also be crystallized quickly [7]. The range of important materials obtained by microwave methods includes LTA, MFI, AFI, FAU, SOD and ETS-4 types of zeolite membranes, zeolite A, MCM-41, beta-zeolites, ZMS-5, TS-2 and metal substituted aluminophosphates [3,8].

The microwave (microwave irradiation) method is often used not only for the synthesis of new materials but also for the post-synthesis treatment. It is possible to obtain a new mesoporous system by creating titanosilicates (ETS-10) [9]. In this way, high-purity ETS-10 crystals were produced in 24 h, while low crystallinity ETS-10 crystals were obtained after 96 h with conventional heating, as reported by the authors of the paper [10].

The Engelhard titanium silicates ETS-4 and ETS-10 are the two well-known examples of the part of the unique variety of molecular sieve materials first reported by S.M. Kuznicki [11–14].

Other interesting examples of materials with useful applications in the field of sorption are the synthetic analog of the sitinakite mineral [14,15]—CTS, the alkali cation analogs of the pharmacosiderite mineral ( $\text{KFe}_4(\text{AsO}_4)(\text{OH})_4 \cdot 7\text{H}_2\text{O}$ ) [16,17]—GTS-1 [18,19], and the ivanyukite mineral [20,21]—SIV [18,22–24]. All these synthetic materials have attracted interest in the fields of catalysis [25,26], adsorption [27], separation and ion exchange [15,20,28–31] due to their branched channel system in the crystal structure with sufficiently wide internal channels (Figure 1). All of these materials are of the pharmacosiderite type and have a similar crystalline structure and morphology.



**Figure 1.** Photomicrograph ivanyukite (A) 1—sitinakite; 2—a natural analog of IONSIVE-911. General view of their crystal structure (B). TEM image of synthetic crystals of the ivanyukite and sitinakite mixture (C) synthesized in this work. Reproduced with permission from references [32].

At present, the most widespread method for obtaining the listed materials is hydrothermal synthesis based on reagents of a high purity class. Very often this list includes  $\text{TiCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{TiF}_4$ ,  $\text{Ti}(\text{SO}_4)_2$ ,  $\text{Ti}(\text{OC}_2\text{H}_4)_4$ ,  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ,  $(\text{NH}_4)_2\text{F}_6\text{Ti}$ ,  $\text{Na}_2\text{TiF}_6$ ,  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{K}_2\text{SiO}_3$  and  $\text{Si}(\text{OC}_2\text{H}_5)_4$  [10,33]. In the work [34], the authors suggest using by-products of the coal-fired power plants (coal fly ash) instead of pure reagents for zeolite synthesis. In this paper, we tried to reproduce the method of sitinakite synthesis developed for its production under hydrothermal synthesis conditions [35,36], under microwave synthesis, in a shorter time. In addition, the crystalline titanium salt, ammonium titanyl sulfate (ATS or STA)  $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , was added to the reaction mixture as a source of titanium [37,38]. STA is a semi-product of processing of multicomponent mineral and technogenic raw materials of mining enterprises in the Murmansk region. This precursor was first used for microwave synthesis in this experimental work. Previously, this salt was produced in close collaboration between the Tananaev Institute of Chemistry, Mining Institute of FRS KSC RAS and "Apatit" JSC for leather tanning. After the organization of industrial production, the product was introduced into the leather industry of the USSR jointly with the Central Research Institute of the Leather and Footwear Industry (Moscow, Russia) and tested in the cities of Novosibirsk, Chelyabinsk, Sarapul, Moscow, Ulyanovsk, and Bishkek. However, currently at the Kola Science Centre, the ammonium titanyl sulfate can be produced only with laboratory equipment or an enhanced laboratory facility [39]. The economic feasibility of STA as a substitute for expensive reagents as a source of titanium would be further supported by experimental verification of the potential of using this salt in the microwave synthesis of one of the modern zeolite-type adsorbents (IONSIVE-911). The main contribution of this research is to confirm the synthesis of a sitinakite analog using a specific salt, to establish the optimal parameters for the microwave synthesis of sitinakite and the potential profitability of processing titanium-bearing raw materials from the mining industry into modern IONSIVE-type sorbents. This research demonstrates the potential for the complex processing of non-traditional raw materials. For this reason, we specially synthesized an STA shipment sample from the titanite concentrate produced by the mining enterprise "Apatit" JSC (Apatity, Russia) with this instrumentation. The development of new applications of salt could help to substantiate the profitability of its production, and then use it as a precursor in the synthesis of a new functional material. In the case of sitinakite synthesis, the microwave method would significantly reduce the time needed to obtain the final product from a low-resolution source of titanium in the region.

## 2. Materials and Methods

In microwave synthesis, we used the semi-product (ammonium titanylsulfate  $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) of sulfuric acid titanite ore treatment (mining enterprise "Apatit" JSC, "PhosAgro", Apatity, Russia), titanium trichloride as a Ti source, sodium hydroxide and sodium metasilicate. The chemicals used were of reagent or analytical grade quality, obtained from commercial suppliers and used without further purification (Merck, Aldrich, and Neva reactive); distilled water was used as a solvent.

The samples were weighed on scales of special accuracy class AND HR-200, Japan (Kurnakov Institute of General and Inorganic Chemistry of RAS), electronic laboratory scales Massa—K VK-600, components were stirred using a magnetic stirrer PE-6600, "ECROS-Analitica" LLC, Moscow, Russia (Kurnakov IGIC RAS). Syntheses were carried out in 100 mL PTFE autoclaves using a microwave multitasking research laboratory autoclave sample preparation and synthesis station Milestone Ethos Up, USA (Kurnakov IGIC RAS). Synthesized powders were separated from the mother liquor in a Centurion Scientific Ltd. centrifuge, UK (Kurnakov IGIC RAS). The powder drying process was carried in a Memmert UF30 convection lab oven, Germany (Kurnakov IGIC RAS).

The phase composition of the powders was determined by X-ray phase analysis using a MiniFlex 600 (Japan, Centre for Collective Use of the Kola Scientific Centre of the RAS). The content of components in the mother liquor was determined by inductively coupled plasma atomic emission spectrometry using a Shimadzu ICPE-9000, Japan, (ICP

AES, I. V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, FRC KSC RAS). The chemical composition of the initial solutions before sorption experiments and after contact with the samples of the sorbent were determined by the Perkin Elmer ELAN 9000 DRC-e mass spectrometer (USA, I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, FRC KSC RAS). The content of the chemical composition of the STA salt was detected by inductively coupled plasma atomic emission spectrometry using a Perkin Elmer Optima 2100DV (USA, Institute of North Industrial Ecology Problems, FRC KSC RAS).

The morphology of the obtained powders was studied using a LEO-1450 scanning electron microscope (Germany) and the chemical composition was studied with an Oxford Instruments Ultim Max 100 analyzer (UK) at 20 kV, 500–1000 pA, 1–3  $\mu\text{m}$  beam diameter (Geological Institute of FRC KSC RAS).

The surface properties of the sitinakite phases were characterized by a surface area analyzer Micromeritics TriStar 3020 (USA, I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, FRC KSC RAS).

The morphology of synthetic samples of the ivanyukite–sitinakite phase (Figure 1) was studied using transmission electron microscopy (TEM) with a Jem 1001 device, Japan (Lomonosov Moscow State University) with an 80 kV accelerating voltage, copper grids and ultrasound.

Salt batches were obtained and produced at the pilot plant for titanium concentrate dissection and hydrothermal synthesis of “Sorbent” products (Nanomaterial Research Centre, FRC KSC RAS).

### 2.1. Abbreviations

GTS-1—Grace Titanium Silicate-1, titanosilicate synthetic analog of the mineral pharmacosiderite with the ideal formula  $(\text{KFe}_4(\text{AsO}_4)(\text{OH})_4 \cdot 7\text{H}_2\text{O})$  [33].

CTS—crystal titanosilicate structure analogous to the mineral sitinakite, initially referred to in papers as the TAM-5 material [33].

CST—crystalline silicotitanite materials proposed for use as ion exchangers [33].

TAM-5—silicotitanate first obtained at Texas A&M University [33].

ETS-4—titanosilicate, patented by “Engelhard Titano Silicate”. The synthetic analog of the mineral zorite with the ideal formula  $\text{Na}_8\text{Si}_{12}\text{Ti}_5\text{O}_{38}(\text{OH}) \cdot 8.5\text{H}_2\text{O}$  [33].

ETS-10—titanosilicate patented by “Engelhard Titano Silicate”; synthetic material with the formula  $(\text{Na,K})_2[\text{TiSi}_5\text{O}_{13}] \cdot n\text{H}_2\text{O}$ , which have not been found in nature [33].

SIV—synthetic analog of the natural ivanyukite mineral’s family with the initial formula  $\text{Na}_4(\text{TiO})_4(\text{SiO}_4)_3 \cdot n\text{H}_2\text{O}$  [23].

STA—ammonium sulfate oxytitanium,  $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ . It is a pre-product of titanite concentrate reprocessing (“PhosAgro” PJSC, Apatity, Russia) [23].

ZSM-5—Zeolite Socony Mobil-5—a synthetic analog of natural mutinaite, a silica zeolite with the MFI framework topology. It is of considerable significance as a catalytic material [40].

MFI—framework topology of mesoporous zeolites [41].

TS-2—porous titanium silicate with MEL topology [33].

ZSM-11—Zeolite Socony Mobil-11 (Mobil eleven or MEL), zeolite with the MFI framework topology [33].

$\beta$ -zeolite—a mesoporous zeolite with high silica content (**Beat-H**) commonly using in cracking [40,42].

Zeolite A—a basic aluminosilicate with the chemical compound  $\text{Na}_{16}(\text{AlO}_2)_{16}(\text{SiO}_2)_{32} \cdot 16\text{H}_2\text{O}$  [40].

Zeolite Y—a zeolite with a higher Si/Al atomic ratio [40].

LTA—Linde Type A, Zeolite A (Linde Division, Union Carbide), a NaA zeolite membrane [40,42].

NaA—a hierarchical zeolite of cubic morphology with LTA framework structure, Na-modification of A-type zeolite [40].

MCM-41—a mesoporous molecular sieve with a hexagonal arrangement of uniformly sized mesopores [43].

AFI—Aluminophosphate-five  $\text{AlPO}_4\text{-5}$  (FIve), a type of aluminophosphate zeolite membrane [40].

FAU—a type of aluminosilicate zeolite membrane with a similar crystal structure to natural *faujasite*, [40].

SOD—the type of aluminosilicate zeolite membrane with a crystal structure of natural *sodalite* [40,41].

IONSIVE-911—the synthetic analog of natural titanosilicate *sitinakite* [44].

## 2.2. Methods for Analysis

### 2.2.1. Synthesis of a Titanium-Containing Precursor

The process of obtaining the sphene (titanite) concentrate to produce STA with the formula  $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  was carried out according to the procedure described in the work [45]. Into the solution of sulfuric acid (550 g/L  $\text{H}_2\text{SO}_4$ ) heated to 80–90 °C, the sphene concentrate (from the mining enterprise “Apatit” JSC, “PhosAgro”, Apatity, Russia) was added corresponding to the ratio T:V = 1:3. Further treatment of the sphene concentrate was carried out at 110–115 °C for 12 h. After treatment, the supernatant was separated by vacuum filtration. Then ammonium sulfate salt was added to the obtained liquid and left for 2 h with stirring. The precipitated STA was separated by filtration. The chemical compound of the STA salt includes K, Na, Al, Fe, Ti and Nb (% wt): 0.042; 0.038; 0.027; 0.023; 11.840; 0.001, respectively.

### 2.2.2. Microwave Synthesis of IONSIVE-911 Phase

In this work, crystalline powders of titanosilicates were prepared by hydrothermal method using microwave heating. The average weights of the initial components were as follows: 7.80 g of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ , 2.5 g of NaOH, 4.64 g of STA or 16.8 g of  $\text{TiCl}_3$ . Distilled water was used as the solvent and its amount was 50 mL in each system. The mixture for synthesis was obtained by mixing the initial components in the molar ratio of 9.0 Na:3.4 Si:1.0 Ti. The system was stirred for an average of 60 min. The obtained mixture was placed in 100 mL autoclaves with PTFE inserts and subjected to microwave heating. A total of 15 microwave synthesis experiments were performed. The treatment time varied from 5 min to 1 h, and the temperature—from 150 to 210 °C under autogenous pressures.

### 2.2.3. TGA and DSC Analysis

Thermogravimetric (TGA) and differential scanning calorimetry (DSC) curves were measured with the NETZSCH DSC 204F1 Phoenix (Germany) at the Institute of Chemistry of St. Petersburg State University (St. Petersburg, Russia). The samples of synthesized powders after the heating process based on the STA salt at 180 °C and microwave treatment for 1 h; 210 °C and treatment for 5 min, 20 min, 1 h and based on the  $\text{TiCl}_3$  precursor at 210 °C and treatment for 5 min were heated under an Ar atmosphere in the range of –80 to +100 °C with a rate of 10 K/10 min.

### 2.2.4. IR Analysis

Data for synthesized samples were detected using a SHIMADZU UV-2550PC IR spectrometer at the Institute of Chemistry of St. Petersburg State University (St. Petersburg, Russia) under atmospheric conditions with a step of 0.01 Abs. IR analysis was performed only for *sitinakite* samples confirmed previously by XRD analysis.

### 2.2.5. XRD Analysis

The quality of the solid powder of  $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  salt, the synthetic phases obtained after microwave synthesis and the samples of modification forms after sorption processes was characterized by means of powder X-ray diffraction using a MiniFlex 600 powder diffractometer (Centre for Collective Use of the Kola Science Centre of the RAS)

with the ASC-8 device prefix, under  $\text{CuK}\alpha$  radiation, 40 kV and 15 mA. The experiments were conducted in the  $2\Theta$  range of  $5\text{--}80^\circ$  with a step of  $0.02^\circ$  and exposure speed of  $5.00^\circ/\text{min}$ .

#### 2.2.6. BET Surface Properties

The BET surface properties of the sitinakite phases were characterized by the nitrogen and adsorption/desorption method at 77 K using a surface area analyzer Micromeritics TriStar 3020 at the Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of the Kola Science Centre (Apatity, Russia). The average pore diameter was calculated as 4 V/S. Prior to adsorption/desorption measurements, the sample was degassed at 393 K for about 24 h.

#### 2.2.7. Sorption of $\text{Cs}^+$ Cations from CsCl Model Solution

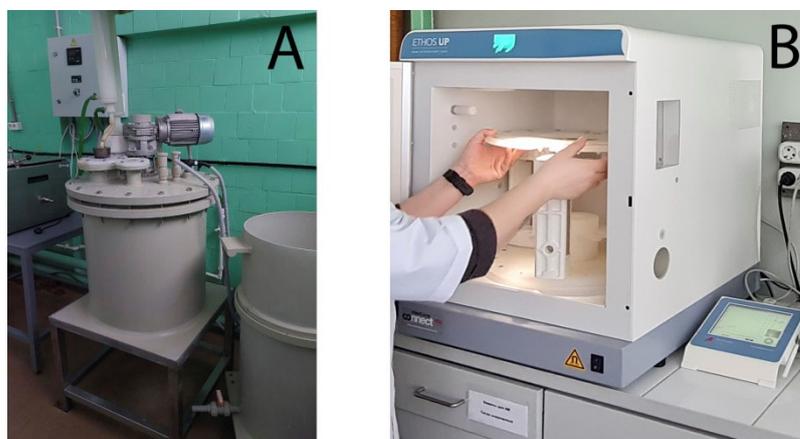
To determine the sorption capacity of products obtained by microwave synthesis, the following experiment was performed using a model solution of CsCl (1 g/L of  $\text{Cs}^+$ ) in 3 M  $\text{HNO}_3$ . Titanosilicate samples were left in the model solution under constant stirring for 2.5 h at room temperature (S:L ratio = 1:100 g/mL). After the experiment, the solutions were separated by filtration and solid powders were dried at  $70^\circ\text{C}$ . Solutions after sorption were analyzed for the content of  $\text{Cs}^+$  ions using the ICPE-MS method. According to the obtained data, the sorption capacity of the obtained sorbents was calculated according to the equation:

$$A_\tau = (C_0 - C_\tau) \cdot V/m;$$

$C_0$  and  $C_\tau$  correspond to the initial and equilibrium concentrations of ions in solution, mg/L;  $V$  is the volume of solution, mL; and  $m$  is the sorbent sample weight, g.

### 3. Results

Fifteen hydrothermal syntheses with microwave treatment were carried out (Figure 2B). STA salt (Figure 3) was previously synthesized at the “Sorbent” pilot plant (Figure 2A) and further used as a titanium precursor in the production of titanosilicate powders. The weight ratios for the syntheses were kept constant, and the data are presented in Table 1. The synthesis temperature range was 150, 180, and  $210^\circ\text{C}$ . The temperature treatment time varied from 5 to 60 min. Only in five experiments was it possible to obtain a crystalline product containing sitinakite with an admixture of ivanyukite and halite phases. The data of XRD analyses are presented in Table 2. The diffractograms of XRD analyses of successful syntheses are shown in Figure 4.



**Figure 2.** Reactor for STA salt synthesis (25 L volume) from titanite concentrate (FRS Kola Science Centre RAS) (A) and Milestone Ethos Up microwave synthesis station, USA (Kurnakov IGIC RAS) (B).

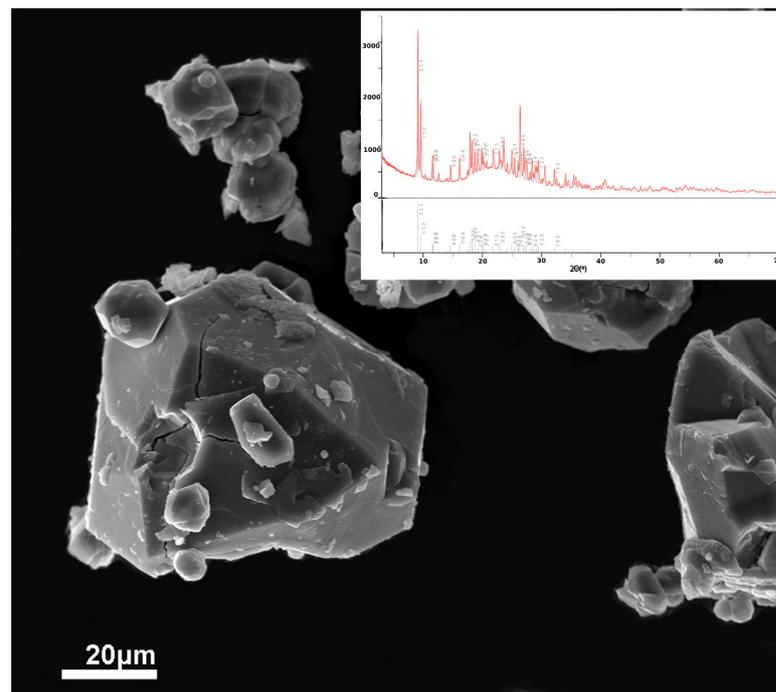


Figure 3. SEM image and XRD pattern of the initial STA salt (Ti-source) for synthesis.

Table 1. Initial components for the microwave synthesis with an IONSIVE-911 phase.

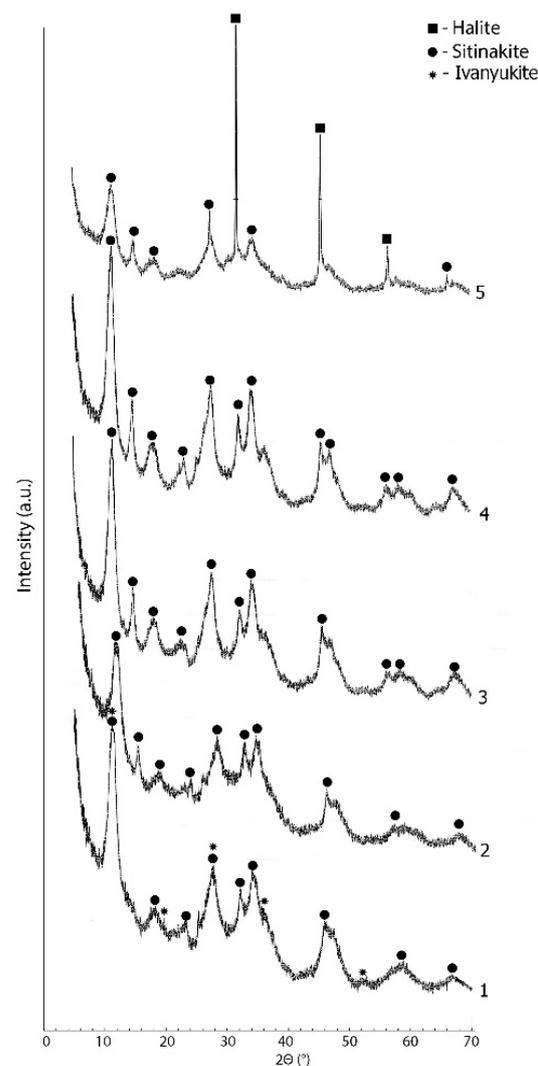
Initial Components for Synthesis with STA Salt	Treatment Time, Min			Initial Components for Synthesis with TiCl <sub>3</sub> , g	Treatment Time, Min		
	5	20	60		5	20	60
Temperature 150 °C							
Weight of Components, g							
<b>STA-Based Product</b>				<b>TiCl<sub>3</sub>-Based Product</b>			
Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	7.802	7.798	7.796	-	-	-	-
NaOH	2.520	2.528	2.530	-	-	-	-
STA salt	4.636	4.635	4.637	-	-	-	-
H <sub>2</sub> O <sub>distilled</sub>	50	50	50	-	-	-	-
Temperature 180 °C							
Weight of Components, g							
<b>STA-Based Product</b>				<b>TiCl<sub>3</sub>-Based Product</b>			
Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	7.797	7.799	7.796	Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	7.797	7.797	7.799
NaOH	2.520	2.519	2.521	NaOH	2.527	2.519	2.527
STA salt	4.634	4.635	4.635	TiCl <sub>3</sub>	16.800	16.800	16.800
H <sub>2</sub> O <sub>distilled</sub>	50	50	50	H <sub>2</sub> O <sub>distilled</sub>	25	25	25
Temperature 210 °C							
Weight of Components, g							
<b>STA-Based Product</b>				<b>TiCl<sub>3</sub>-Based Product</b>			
Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	7.796	7.797	7.798	Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	7.798	7.786	7.799
NaOH	2.560	2.522	2.600	NaOH	5.262	2.564	2.561
STA salt	4.637	4.636	4.637	TiCl <sub>3</sub>	16.800	16.800	16.800
H <sub>2</sub> O <sub>distilled</sub>	50	50	50	H <sub>2</sub> O <sub>distilled</sub>	25	25	25

Note: weights of reagents are indicated in the table in grams for convenience in tracking the experiment if necessary.

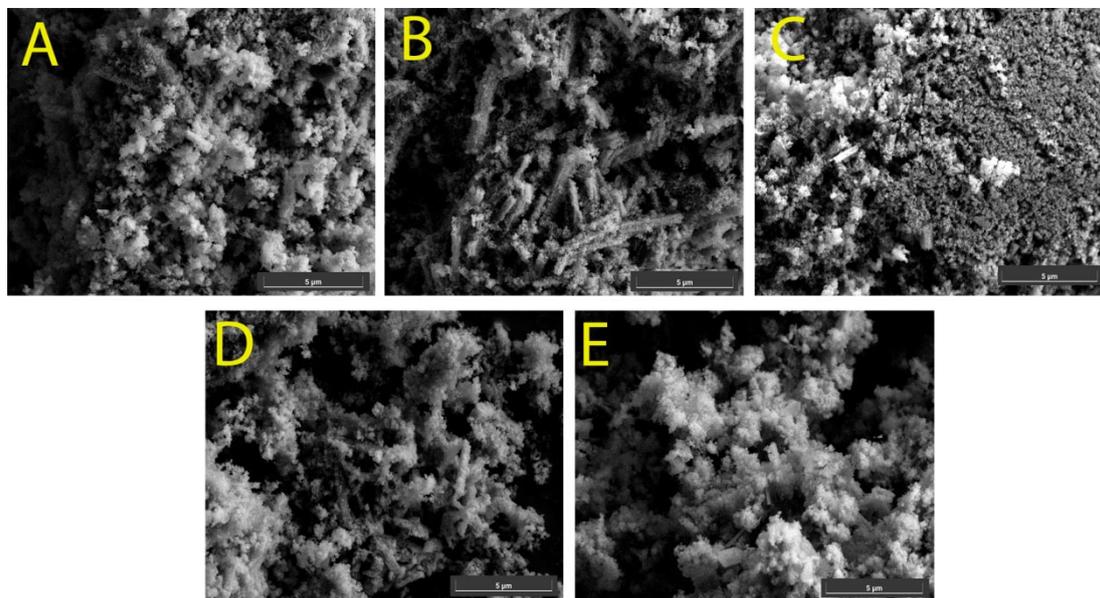
**Table 2.** XRD results of synthesis products and chemical composition of the mother solution after microwave synthesis.

Number of Synthesis	Ti Source	T, °C	Time, min	XRD Result	Chemical Composition of the Mother Solutions, g/L			
					Na	S	Si	Ti
1	STA	150	5	-	37.2	17.4	9.73	29.5
2	STA	150	20	-	38.1	18.1	9.97	26.0
3	STA	150	60	-	37.6	18.0	9.96	23.0
4	STA	180	5	4 reflects, no identification	38.1	18.4	9.82	24.0
5	STA	180	20	-	40.7	18.5	10.2	18.5
6	STA	180	60	IONSIVE + SIV	40.1	18.6	11.7	3.50
7	STA	210	5	IONSIVE	39.7	17.7	10.8	21.5
8	STA	210	20	IONSIVE	40.5	18.5	12.4	<2
9	STA	210	60	IONSIVE	40.4	17.9	12.2	<2
10	TiCl <sub>3</sub>	180	5	halite	47.8	<0.001	0.48	<2
11	TiCl <sub>3</sub>	180	20	halite	49.7	<0.001	0.07	<2
12	TiCl <sub>3</sub>	180	60	halite	51.8	<0.001	0.07	<2
13	TiCl <sub>3</sub>	210	5	halite + IONSIVE	66.0	<0.001	21.5	18.0
14	TiCl <sub>3</sub>	210	20	halite	47.9	<0.001	0.68	<2
15	TiCl <sub>3</sub>	210	60	halite	50.8	<0.001	0.04	<2

Note: crystallization of halite as a single or impurity phase can be caused by a high chlorine content in the reaction mixture and an insufficient number of separate washing cycles for the final synthesis product.

**Figure 4.** Synthesis of sitinakite phases based on: 1—STA salt at 1 h and 180 °C; 2—STA salt at 5 min and 210 °C; 3—STA salt at 20 min and 210 °C; 4—STA salt at 1 h and 210 °C; 5—TiCl<sub>3</sub> at 5 min and 210 °C.

All phases are fine-divided and with inclusions of elongated prismatic crystals, whose electron microscope chemical composition is difficult to determine due to the small size of prisms and uneven crystal surface (Figure 5).



**Figure 5.** SEM image of synthetic phases of sitinakite after microwave synthesis: (A) STA salt at 1 h and 180 °C; (B) STA salt at 5 min and 210 °C; (C) STA salt at 20 min and 210 °C; (D) STA salt at 1 h and 210 °C; (E) TiCl<sub>3</sub> at 5 min and 210 °C.

The analysis of the sitinakite samples' surface is shown in the Table 3. All products have a good developed surface, compared to modern promising sorbents such as ETS-4 (150 m<sup>2</sup>/g) [8] and ETS -10 (325 m<sup>2</sup>/g) [12].

**Table 3.** Surface properties of synthetic phases of sitinakite after microwave synthesis.

Conditions of the Synthesis of Sitinakite Phases	BET Surface Area, m <sup>2</sup> /g	BJH Adsorption Average Pore Diameter, nm
STA, 1 h, 180 °C	180.15	9.62
STA, 5 min, 210 °C	104.70	11.73
STA, 20 min, 210 °C	179.28	8.75
STA, 1 h, 210 °C	158.03	10.40
TiCl <sub>3</sub> , 5 min, 210 °C	131.12	13.00

The chemical composition of the sitinakite phases based on the STA salt at 210 °C is shown in the Table 4. The data are in good agreement with chemical analyses of the natural mineral reported in the literature. XRD analysis also confirms the synthesis of the sitinakite phase. The slight variations in values are due to the peculiar method of chemical composition determination of unpolished powders.

**Table 4.** Chemical composition of the sitinakite phases based on the STA salt at 210 °C.

Components	1	2	3	4
Na <sub>2</sub> O	17.31	16.45	14.17	10.79
SiO <sub>2</sub>	21.56	24.06	19.20	17.80
TiO <sub>2</sub>	36.67	38.66	38.45	43.22
Al <sub>2</sub> O <sub>3</sub>	0.97	0.49	0.44	0.08

Note: 1—microwave-assisted synthesis during 5 min; 2—20 min; 3—1 h; 4—sitinakite mineral [32].

Figures 6 and 7 demonstrated the results of TGA and DSC analyses of samples with a sitinakite phase and mixture phases of sitinakite and ivanyukite (Figure 4 (2)).

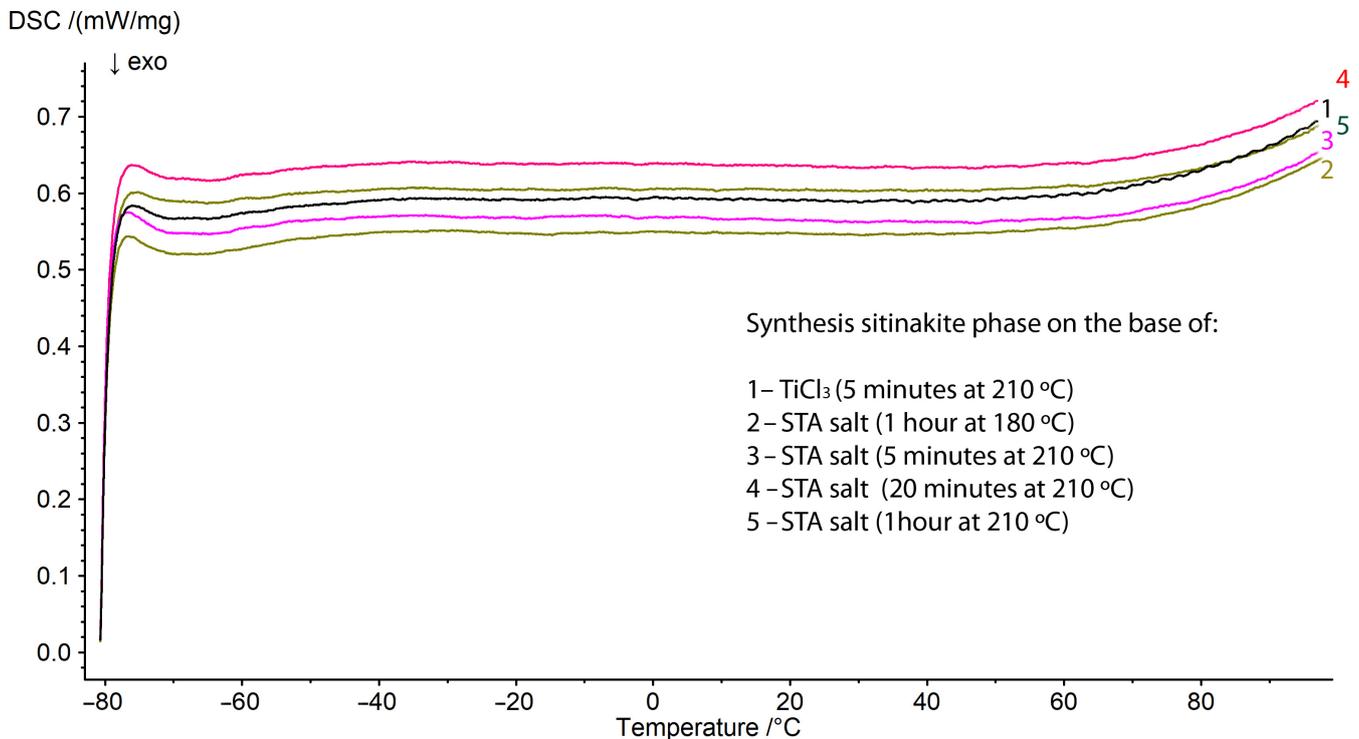


Figure 6. DSC curves of synthesized phases with sitinakite (Ar-atmosphere).

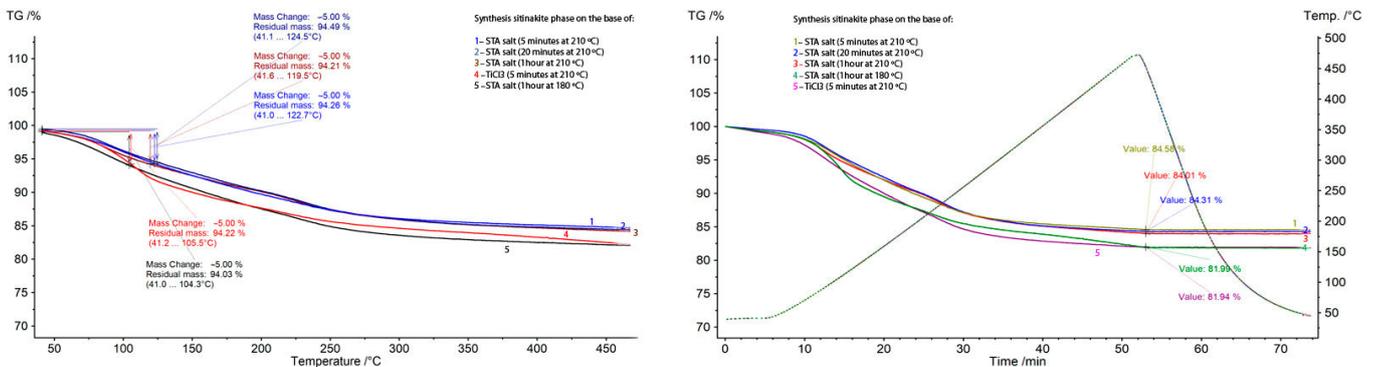


Figure 7. TGA curves of synthesized phases with sitinakite (Ar-atmosphere).

The heat flux curve (DSC analysis, Figure 6) of the obtained phases is characterized by a shift of the signal to the endoeffect in the 60 °C region, which is most likely associated with the removal of zeolite water from extra frame channels of the crystal structure of titanosilicate samples. TGA analysis also confirms this fact. According to the results of TGA analysis, all samples remain stable up to 41 °C. After reaching this temperature and increasing it up to 104.3 °C (sitinakite phase with halite), 105.5 °C (sitinakite phase with ivanyukite), 119.5 °C (sitinakite phase), 122.7 °C (sitinakite phase) and 124.5 °C (sitinakite phase), the total mass loss is observed for each sample in a volume of 5% that is also characteristic for compounds with a zeolite-like structure and is associated with the loss of zeolite water. After 125 °C, all samples retain their crystal structure and remain stable up to 450 °C, although the mass of the samples continues to decrease to 84.3% in the case of sitinakite with a halite admixture and 81.97% in the case of sitinakite with an ivanyukite admixture (Figure 7). Consequently, the average weight loss of the samples is 16.63%.

The infrared spectrum of synthesized sitinakite (Figure 8), in general, is similar to the spectrum of the natural mineral and agrees well with that of powder samples of sitinakite previously synthesized by the hydrothermal method at 210 °C from the work of Perovskii I. (Figure 9) [46,47].

The obtained sitinakite phases are characterized by the presence of a zone from 3000 to 3500  $\text{cm}^{-1}$ , characteristic of the natural sample, and absorption bands at 3291  $\text{cm}^{-1}$ , characteristic of the valence vibrations of O-H bonds. However, the range of 3200–1600  $\text{cm}^{-1}$  is characterized by the absence of distinct peaks, i.e., the spectrum of synthetic material obtained in this work is much easier in this area compared to the hydrothermal synthesis sample from the work [46]. The peak of Si-O bond oscillations in the 600–500  $\text{cm}^{-1}$  region is also less pronounced. The intensity peaks at 1650  $\text{cm}^{-1}$  are due to the deformation vibrations of H-O-H in the  $\text{H}_2\text{O}$  molecule, the intensive absorption bands at 1520–1380  $\text{cm}^{-1}$  are the valence vibrations of amino groups and the absorption bands at 800 and 700  $\text{cm}^{-1}$  are also characteristic of the deformation vibrations of  $\text{NH}_2$  groups. The strong 872–750  $\text{cm}^{-1}$  band is characteristic of the valence vibrations of  $[\text{SiO}_4]^{4-}$  tetrahedrons in the range of 550–400  $\text{cm}^{-1}$ . The strongest absorption bands are observed at frequencies 3331.21, 3291.67, 1652.10, 1378.20, 1107.19, 872.83, 746.48, 564.20 and 404.10  $\text{cm}^{-1}$  for all the synthesized samples, which is fully consistent with the characteristic sitinakite model. Bands at 564.20  $\text{cm}^{-1}$  and bands in the range of 750–745  $\text{cm}^{-1}$  are characteristic of the valence vibration of the Ti-O group. It should be noted that the 1107.19  $\text{cm}^{-1}$  absorption band is less pronounced in the IR-spectrum of samples obtained from STA at 180 °C for 1 h and 5 min at 210 °C than in the case of more crystallized samples based on the same salt but obtained by microwave treatment at 210 °C for 20 min and 1 h. The investigated sample also showed a band at 1400  $\text{cm}^{-1}$  characteristic of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  group vibrations, which may be related to the admixture of the ammonia group in the obtained sitinakite due to the use of the STA salt.

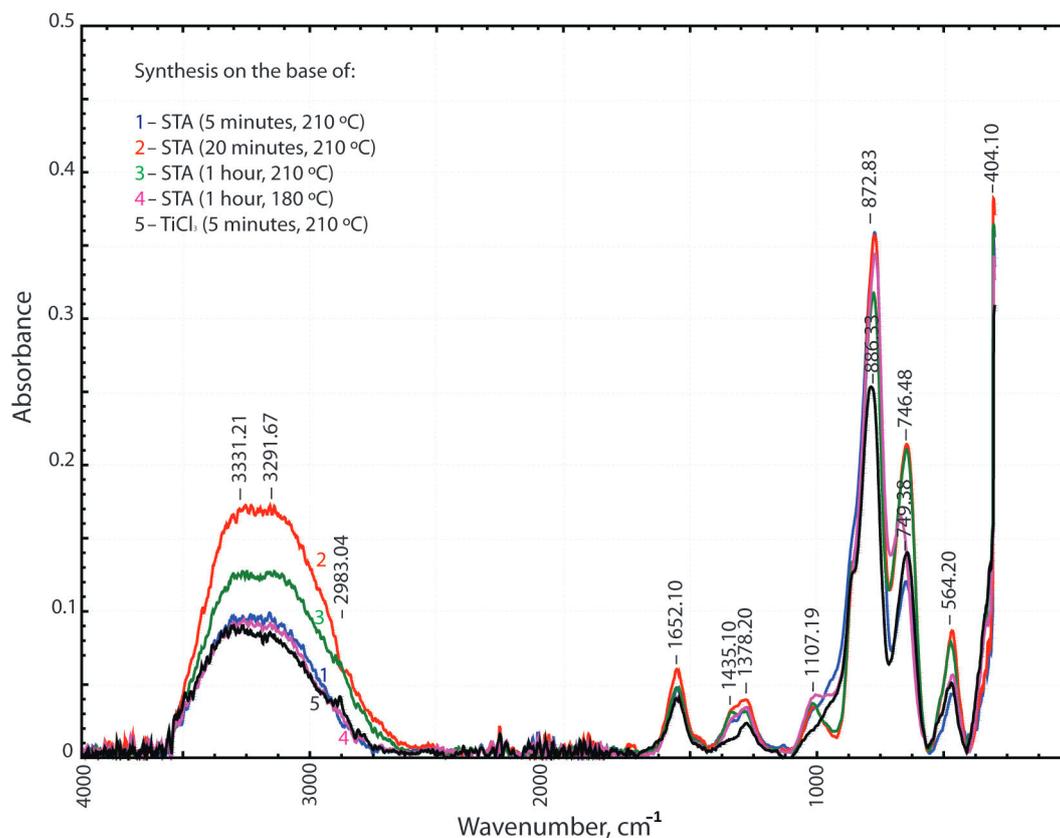
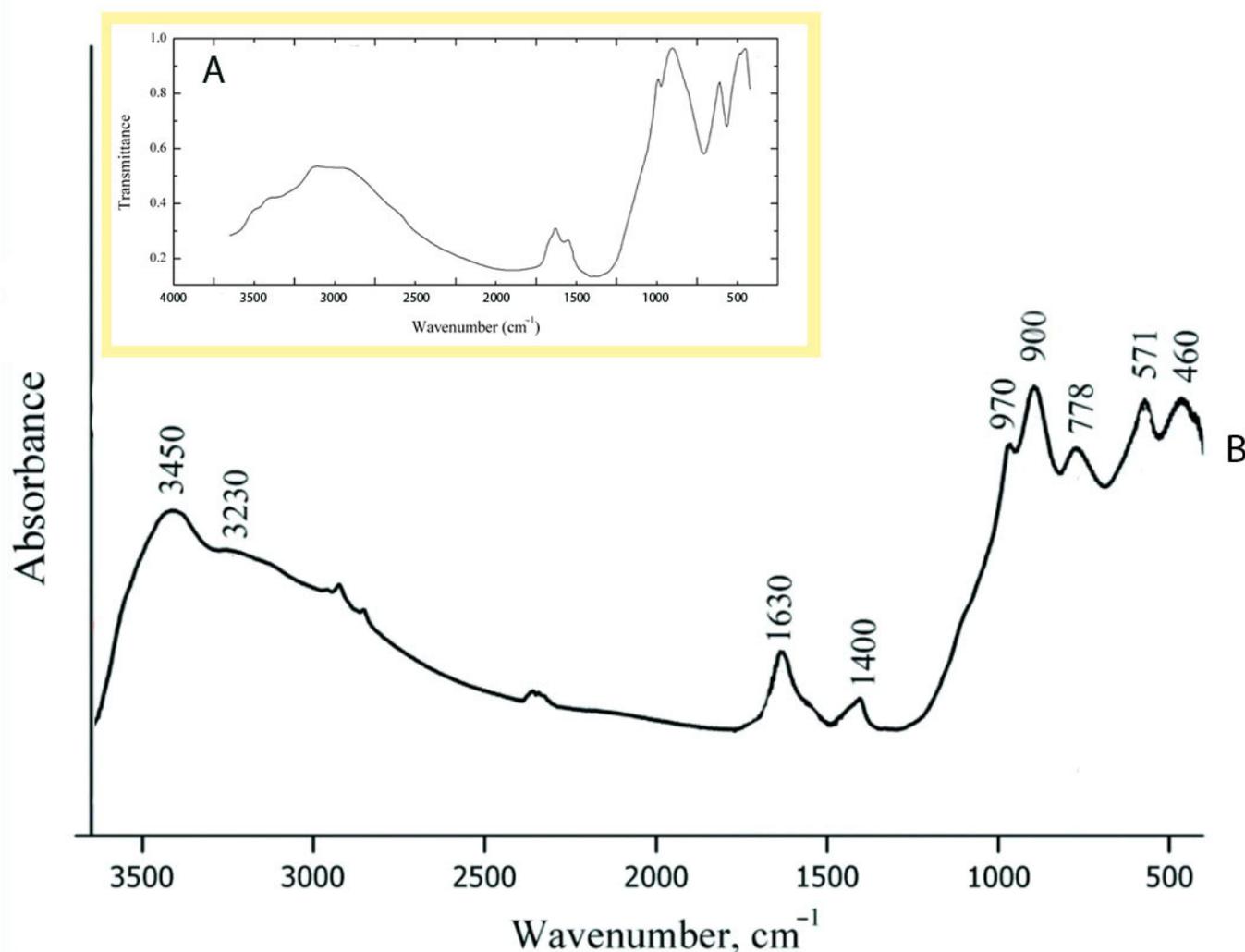


Figure 8. IR spectra of the synthesized IONSIVE-911 phases.



**Figure 9.** IR spectra of natural sitinakite (A) [47] and the sitinakite sample synthesized at 210 °C in I.A. Perovskii's investigation [30] (B).

To confirm the sorption properties of the obtained sitinakite phases, the samples with the highest crystallinity quality obtained at 210 °C based on the STA salts (Samples 2, 3, 4 in XRD Figure 4) and  $\text{TiCl}_3$  (Sample 5 in XRD Figure 4) were tested as sorbents for  $\text{Cs}^+$  cations and compared with the data of I.A. Perovskii's paper (Table 5) [30].

**Table 5.** Chemical composition of the initial solution and solutions after sorbent treatment.

Sample	$\text{Cs}^+$ Concentration, $\text{g}/\text{dm}^3$	Sorption IONSIVE Capacity Synthesized from Titanite Concentrate, $\text{mg}/\text{g}$ [Current Paper]	Sorption IONSIVE Capacity Synthesized from Leucoxene Concentrate, $\text{mg}/\text{g}$ [30]	Sorption IONSIVE Capacity o Synthesized from Loparite Concentrate, $\text{mg}/\text{g}$ [30]
Method of synthesis		microwave-assisted synthesis	hydrothermal synthesis	hydrothermal synthesis
Initial solution	1.10	-	-	-
After treatment with Sorbent 2 (Figure 4)	0.85	25		
After treatment with Sorbent 3 (Figure 4)	0.53	57	170	297
After treatment with Sorbent 4 (Figure 4)	0.63	47		
After treatment with Sorbent 5 (Figure 4)	0.69	41		

The data of the sorption capacity of the sitinakite phase obtained as a result of microwave synthesis showed that the substance synthesized by this method is characterized by a decrease in sorption capacity by 127.5% and 254.5% compared to similar phases obtained by hydrothermal synthesis based on leucoxene and loparite concentrates, respectively.

#### 4. Discussion

The results of the work on the microwave synthesis of the sitinakite analog based on the STA salt showed that this titanium precursor is suitable for the transfer of the hydrothermal synthesis technique previously used by the authors of the paper to the conditions of microwave treatment of the reaction mixture. Synthesis in the case of the microwave treatment of the required reagents can significantly reduce the time for obtaining the sitinakite phase. This fact makes it possible to obtain the required titanosilicate in an extremely short time, which is important for the development of the material for the necessary number of studies of its properties on real objects of the industry. For example, the rapid development of a sorbent to eliminate the man-made contamination of natural water bodies in case of emergencies. However, this method greatly limits the yield of the technique to scalable conditions, since at this stage of research the reproducibility of the method is only 30% (percentage of successful syntheses of total experiments) in the presence of risks of obtaining multiphase products, where other titanosilicates with a crystal structure close to sitinakite, as well as sulfate or chloride salts of elements accompanying the main precursors, can act as impurity phases. At this stage of the investigative work, the microwave synthesis method is significantly inferior to the traditional synthesis of the sitinakite analog in hydrothermal conditions. It should also be noted that during the synthesis of the sitinakite phase based on STA at the same temperature (210 °C), but at different time intervals, there is a dependence on the improvement in the crystallinity of the substance. Thus, the sample obtained after treatment for 5 min has broader reflections in the range of 50–70° of the 2° angle; for the sample obtained after treatment for 20 min, there is still a broadening of the peaks in the range of 20–30° of the 2° angle; and the sample obtained after one hour of treatment has clearer, more intense and narrower reflections. The temperature changing in the synthesis process does not significantly change the morphology of the product (for example, the appearance of cubic sitinakite-like crystals). For this reason, it is necessary to continue research on the selection of the most optimal conditions for obtaining the sitinakite monophase, taking into account the accumulation of the required statistical data.

#### 5. Conclusions

In the present work, the synthesis of the sitikatite phase by means of microwave synthesis based on STA salt, which is a semi-product of titanite concentrate processing, was carried out for the first time. Studies of the crystallinity quality of the obtained samples showed that the microwave synthesis makes it possible to reduce the synthesis time by 1000 times (from 96 h to 5 min) compared to the hydrothermal method of the same titanosilicate phase synthesis. Nevertheless, it should be noted that the crystallinity quality of the samples and their sorption properties when obtained using microwave equipment are significantly inferior to the sitinakite phases obtained after hydrothermal treatment of the reaction mixture. The synthesis of the sitinakite phase utilizing the hydrothermal method enables crystal growth under the influence of convective flows in the reaction mixture's temperature. This aspect of hydrothermal synthesis could also account for the production of a product with reduced crystallinity. It has been experimentally confirmed that a monophase of a good crystalline sitinakite (IONSIVE-911) can be obtained by microwave-assisted synthesis using a precursor produced from titanium ore concentrate at 210 °C for 1 h. In this case, the synthesized sitinakite phase also has a SiO<sub>2</sub>/TiO<sub>2</sub> ratio (1/2) similar to the natural mineral. In order to produce a product with an improved surface area of 180 m<sup>2</sup>/g, it is essential to carry out microwave synthesis based on the STA salt at 210 °C for 20 min, which significantly reduces the time and energy required for the method. The sorption capacity of the sitinakite analog obtained by hydrothermal synthesis (average

value for Cs<sup>+</sup>—200 mg/g) is significantly higher than that of the product obtained by the microwave method (average value for Cs<sup>+</sup>—42.5 mg/g). The microwave method for the synthesis of the sitinakite analog allows fast phase crystallization on the base of ammonium titanyl sulfate (NH<sub>4</sub>)<sub>2</sub>TiO(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, as a new source of titanium, but further research is needed to correct the methodology.

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