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SYNTHESIS AND PROPERTIES OF NANO-POROUS TITANOSILICATES

Anatoly I. Nikolaev, Lidia G. Gerasimova, Marina V. Maslova, Daria V. Spiridonova,
Victor N.Yakovenchuk, Gregory Yu.Ivanyuk
Department for Advanced Study of Synthetic Nanoporous Materials, Kola Science Centre,
Russian Academy of Science, Fersman st 14, Apatity, 184209, Murmansk region, Russia,
e-mail: maslova@chemy.kolasc.net.ru

Abstract

In the last years the interest in new synthetic and natural titanosilicates has increased. Due to the tunable pore diameter and other distinct characteristics, these materials can be utilized for commercially important separations of gas mixtures of similar size molecules, catalysts and removal of radioactive elements from nuclear waste. However, from the point of view of industrial synthesis, scale-up complicated technology and high cost of the agents are limiting factors, hence it is of interest to research new materials to replace expensive pure titanium precursors and stimulate studies to develop an efficient technology. The results of synthesis of the new nanoporous titanosilicates using cost efficient ammonium oxysulphotitanate are presented. By carefully selecting the titanium sources and synthesis parameters, it is possible to obtain titanosilicate $Na_2K(Ti_4(OH)(SiO_4)_3$ analogue of the mineral pharmacosiderite.

Key words: *Titanosilicate, synthesis, ammonium oxysulphotitanate, ETS-4, ETS-10, ivanyukite*

1.INTRODUCTION

Zeolites are among the most valued commercial products finding use as ion exchangers because of thermal and radiation stability, high selectivity, and fairly good adsorption properties (Linssen et al., 2003). They have found a wide application due to the possibility of producing them in pelleted form acceptable for industrial usage. However, alumosilicates are chemically unstable in acidic and alkaline media, which limits both their service life and commercial uses. Hence is the importance of searching for new ion exchange materials.

From this point of view, hetero-polyhedra framework materials with nano- and microporous structures, and many of the rare mineral alkaline titanosilicates and their synthetic analogues, in particular, are of special interest to investigate (Rocha and Anderson, 2000). It is known that there are several families of titanosilicates with nano-porous structures. Their unique properties are due to tunable pore diameter and geometric parameters of the crystal lattice facilitating their selectivity to certain ions and molecules. These materials have high chemical stability and can be used for safe storage and removal of radioactive elements from nuclear waste. Other applications of nano-porous titanosilicates are based on modified titanosilicate matrixes.

One of the most widely studied titanosilicates is ETS-4 with a structure similar to that of the natural mineral zorite $(Na, Ca, Mn,)_8(K)(Ti, Nb)_5[(Si_6O_{17})_2(OH,O)_5]\cdot 12–14H_2O$ (Gruciani et al., 1998, Depmeier, 2009). The crystal structure of zorite (Fig. 1) is based upon an open framework of SiO_4 tetrahedrons, TiO_6 octahedrons, and TiO_5 pyramids; the cavities are occupied by Na^+ and K^+ cations, and H_2O molecules (Spiridonova et al., 2011). Large K^+ cations are located within the large octangular channels. The Na1 site is approximately at the center of a 6-membered ring formed by four

silicate tetrahedrons and two Ti octahedrons, whereas the Na2 site blocks a 7-membered ring formed by four silicate tetrahedrons and three Ti polyhedrons. The presence of extra-framework exchangeable cations (Na^+ and K^+) determines the ion-exchange properties of ETS-4 to mono-and divalent metal ions, including hazardous elements. This material can be used as a selective adsorbent suitable for commercially important separation of gas mixtures of molecules with similar sizes in the range of 4.0-3.0 Å such as N_2/CH_4, Ar/O_2 and N_2/O_2. Moreover, the presence of titania nanowires in the ETS-4 structure find potential applications in the area of nonlinear optics, semi-conductors and sensors.

Microporous titanosilicate ETS-10 ($(Na, K)_2TiSi_5O_{13}$) is a modified ETS-4 with large pores in the framework (Fig.2). The difference between the structures stems from the high amount of defect groups in ETS-4 and/or from the growth of various titanosilicate phases (Pavel et al., 2002). The presence of each tetravalent Ti atom in an octahedron generates two negative charges, which are balanced by non-framework and exchangeable cations Na^+ and K^+. Such a unique framework property has demonstrated unusual adsorption properties towards mono-, di-, and even tri-valent cations under chemically harsh conditions (Celestain and Clearfield, 2007, All-Attar et al., 2003, Lopes et al., 2007). Like zorite, ETS-10 contains monoatomic –O-Ti-O-wires embedded in an insulating SiO_2 environment that leads to a one-dimensional quantum confinement of electrons or holes within this wire which promotes the formation of optoelectronic and nonlinear optical properties. The oxidizing-reducing properties of ETS-10, being the result of reduction of a part of Ti^{4+} to Ti^{3+} using Na vapour, make ETS-10 attractive in battery technology (Bal et al., 2000, Krisnandi and Howe, 2006).

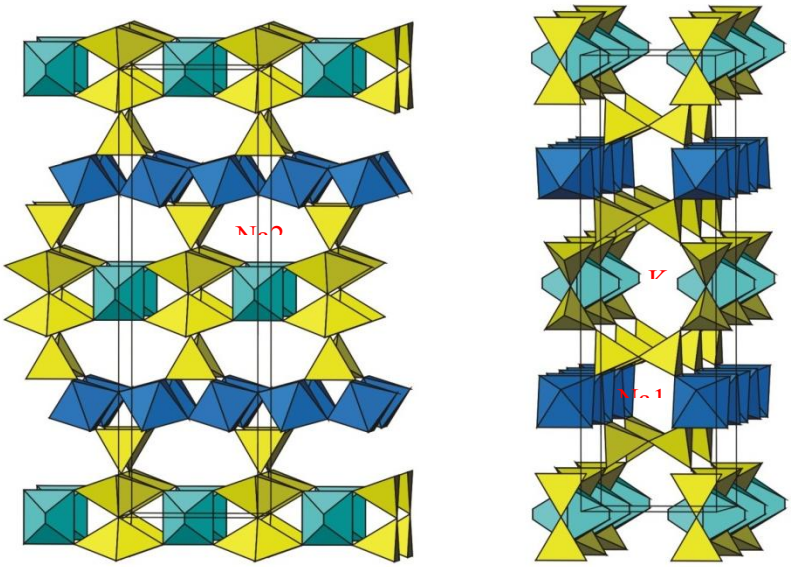


Fig. 1. Titanosilicate frameworks of zorite and ETS-4

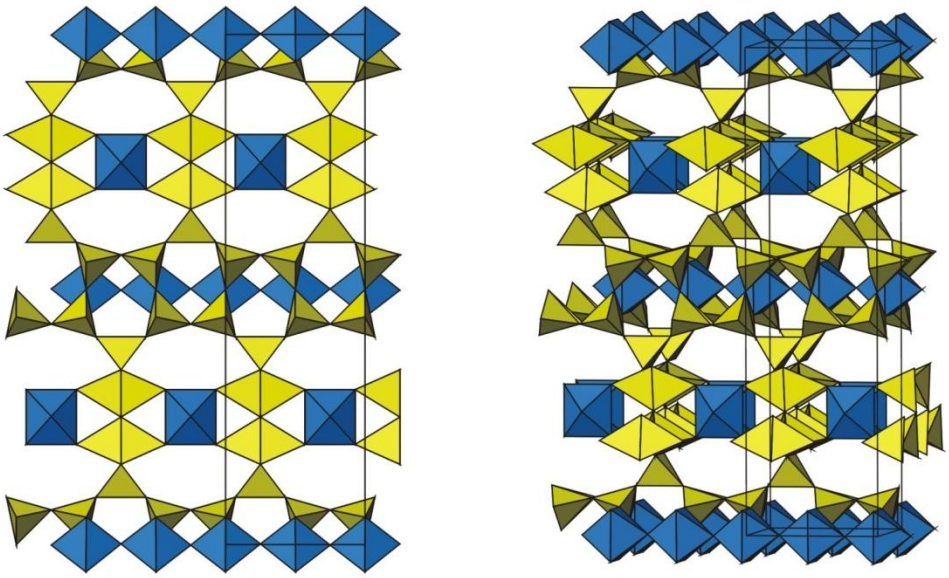


Fig. 2. Titanosilicate framework of ETS-10

Another promising ion-exchanger is ivanyukite-Na ($Na_2K[Ti_4(OH)O_3(SiO_4)_3]\cdot 7H_2O$) discovered in the Khibiny alkaline massif in 2009 (Yakovenchuk et al., 2009). Its crystal structure is based upon a 3-dimensional framework of the pharmacosiderite type (Yakovenchuk et al., 2011) and consists of fundamental building blocks of four edge-sharing TiO_6-octahedrons interlinked by SiO_4 tetrahedrons (Fig. 3). The resulting framework has a 3-dimensional system of channels defined by 8-membered rings occupied by Na^+ and K^+ cations and H_2O molecules.

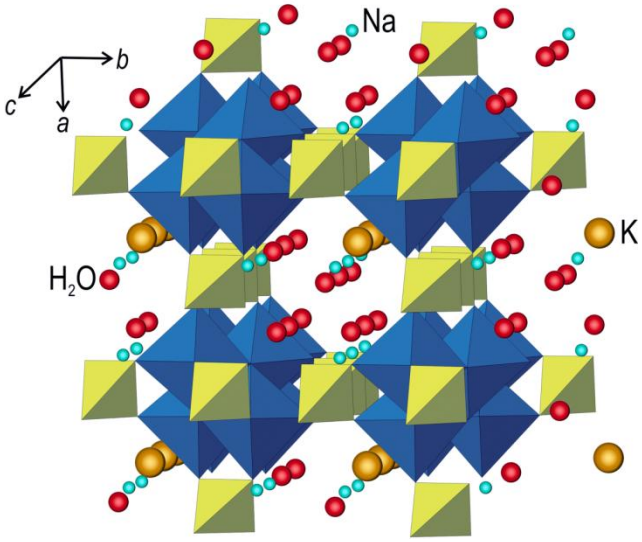


Fig. 3. Crystal structure of ivanyukite-Na-*T* (Yakovenchuk et al. 2011)

It was found that three atoms per formula unit of Na^+ and K^+ in original ivanyukite-Na can be replaced by 3 atoms of Tl^+, 2.8 anoms of $N_2H_5^+$, 2.5 atoms of Rb^+, 2.2 atoms of Cs^+, 1.8 atoms of NH_4^+, 0.8 atoms of Sr^{2+}, 0.7 atoms of Co^{2+}, 0.1 atoms of Ni^{2+} and 0.2 atoms of La^{3+}. Rb-, Cs-, Tl-, N_2H_5- and NH_4. These substituted phases are water-free and very stable over a wide range of pH and at high temperatures, which means that this compound can be used not only for the removal of radioactive and hazardous metals from waste solutions but also for their immobilization in the stable titanosilicate matrix (Yakovenchuk et al., 2009).

There are known several methods of titanosilicate synthesis, including mechanochemical synthesis, co-precipitation, and the sol-gel method. In a typical synthesis, chemically pure sodium silicate and titanium-containing solutions are mixed and stirred followed by the hydrothermal treatment at 150-230^{0}C in an autoclave for about 30 days. At present, the efforts of many investigators are directed towards titanium and silica precursors and alkali effect on crystallization and phase purity. $TiCl_3$ and $TiCl_4$ are a much-used titanium source. For example, using $TiCl_3$ Rocha reported (Rocha et al, 1998) a method for a rapid (less 20 h) synthesis of ETS-10. The studies carried out by Lv (Lv et al., 2004) have shown that under proper conditions the thermodynamically stable TiO_2 phases of anatase and rutile can be used as an alternative titanium source, but the synthesis of ETS is accompanied by the formation of anatase and quartz. In the work (Kim at al., 2003) the authors presented a comparative study of different silica precursors (sodium silicate, Ludox AS-40 and fumed silica). The presence of K^+ ion was found to facilitate converting of the titanosilicate gel to the crystalline phase of ETS-10 (Kim et al., 2002, Noh et al., 2006). As shown in (Lv et al., 2004, Pavel et al., 2002, Yang et al., 2001), the reactive titanium chlorides also initiate the formation of the ETS-10 structure, but their excessive sensitivity to moisture requires special equipment. When using titanium fluorides as TiF_4 or $(NH_4)_2TiF_6$, the ETS-10 phase can be obtained only at a molar ratio of $F/TiO_2<0.6$. Further increase of fluorine leads to the emergence of a quartz phase in the sample.

However, from the point of view of industrial synthesis, scale-up complicated technology and high cost of the agents are limiting factors, hence it is of interest to research new materials to replace expensive pure titanium precursors and stimulate studies to develop an efficient technology.

2. MATERIAL AND METHODS

2.1 Sample preparation

In this research, we planned to obtain the following titanium silicate products: ETS-4 (zorite); ETS-10 – $(Na, K)_2TiSi_5O_{13}$; naticite – Na_2TiSiO_5; ivanyukite -Na – $Na_2K(Ti_4(OH)O_3(SiO_4)_3$. The titanium precursors were cheap technical products of the Khibiny apatite-titanite-nepheline ore processing (Lazareva et al., 2006, Gerasimova et al., 2009) ammonium oxysulphotitanate in the monohydrate form $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ (AOST); titanium hydroxide containing 54% TiO_2, and also titanium dioxide of the anatase modification. The source of silica was hydrated SiO_2, fumed silica with SA-120m^2/g, and solutions of sodium silicate, potassium fluoride and sodium hydroxide. The titanium silicates were produced by hydrothermal synthesis, whereby the prepared mixtures of starting components (pH 10-11) were kept in an autoclave at the temperature of 200^{o}C for 2-4 days. The precipitate was washed with water and dried at 100^{o}C. The consumption of main components for titanium silicate synthesis was (moles): ETS-4 – $TiO_2 : 2.75SiO_2 : 2.6Na_2O : 1.25KF : 137H_2O$; ETS-10 - $TiO_2 : 5.5SiO_2 : 4.84Na_2O : 2.5KF : 250H_2O$; naticite – $TiO_2 : 0.8SiO_2 : 1.85Na_2O : 0.35KF : 50H_2O$; ivanyukite-Na – $TiO_2 : SiO_2 : 0.8Na_2O : 0.15KF : 20H_2O$.

2.2. Sample characterization

The obtained solid phases were dissolved in HF-HNO_3-HCl and the concentrations of the elements were determined using an ICPE-9000 spectrometer.

Powder X-ray diffraction studies of synthesized samples were performed using a Siemens D 500 diffractometer with a monochromatic Cu Kα radiation (λ=1.5418 Å).

A Micrometrics ASAP 2000 analyzer was used to characterize the surface properties and porosity of the materials obtained. All samples were degassed at 373 K for 4 h prior to N_2 adsorption/desorption measurements. The specific surface area was calculated using the BET equation. The total pore volumes of samples were determined by converting the amount of adsorbed nitrogen at a relative pressure 0.995 to the volume of liquid nitrogen. The external surface areas, micropore surface areas and micropore volumes were determined by the t-plot method. Pore size distributions were determined by the BJH method using the desorption branch of corresponding isotherms. The morphologies of the samples were studied using a Philips XL 30 scanning electron microscope (SEM) equipped with a LaB_6 emission source.

The adsorption measurement was conducted using a batch mode. The Cs^+, Sr^{2+} and Cu^{2+} ions obtained from the chloride salt were selected as adsorbates. The initial concentration of the metals was chosen as [Cs^+]-8mM, [Sr^{2+}]-8.5 mM, [Cu^{2+}]-5.5mM. About 0.2 g of the solid sample was added to the metallic solution with the volume-to-mass ratio of 200:1 (ml/g). The contact time was 24 h under constant shaking. The initial and final concentrations of the metal ion were determined using an AAS-300 (Perkin-Elmer) atomic absorption spectrometer. The results were reproducible within the range of experimental error.

3. RESULTS AND DISCUSSION

3.1 *Structural characterization of the titanosilicate samples*

The crystallinity and purity of titanosilicate products largely depend on the molar composition of the initial agents, sources of titanium and silica, and synthesis regime. In our work, the synthesis conditions were selected so as to obtain a desired titanosilicate. The molar ratio of the reaction mixture composition was chosen as an optimum from the previous results. The effect of the nature of components and hydrothermal regimes on crystallization of titanosilicates from gels with an optimized composition was examined.

The easiest-crystallizing material was a densely packed titanosilicate with the naticite structure (Fig.4). The compositional study was based on the molar composition previously described and aimed at determining the influencing factors, in particular, the effect of different titanium and silica sources (solutions of AOST ore sodium silicate, solid TiO_2 ore hydrated SiO_2) and the effect of alkali content, on crystallization regarding the crystallinity and purity phase. It was found that only excess alkalinity significantly affects the phase purity of naticite.

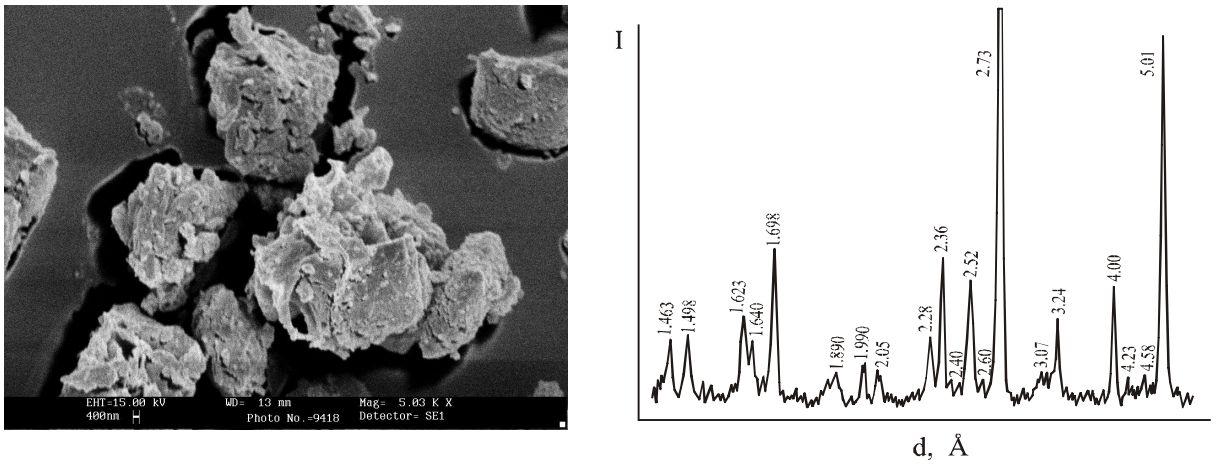


Fig. 4. SEM image of naticite particles and an XRD pattern of naticite powder.

For ETS-4, the final phase strongly depends on the Ti sources. It was observed that a solution obtained from cheap and local technical AOST was the best titanium precursor. Moreover, AOST can produce pure ETS-4 within a short crystallization time in the absence of seeds (Fig.5).

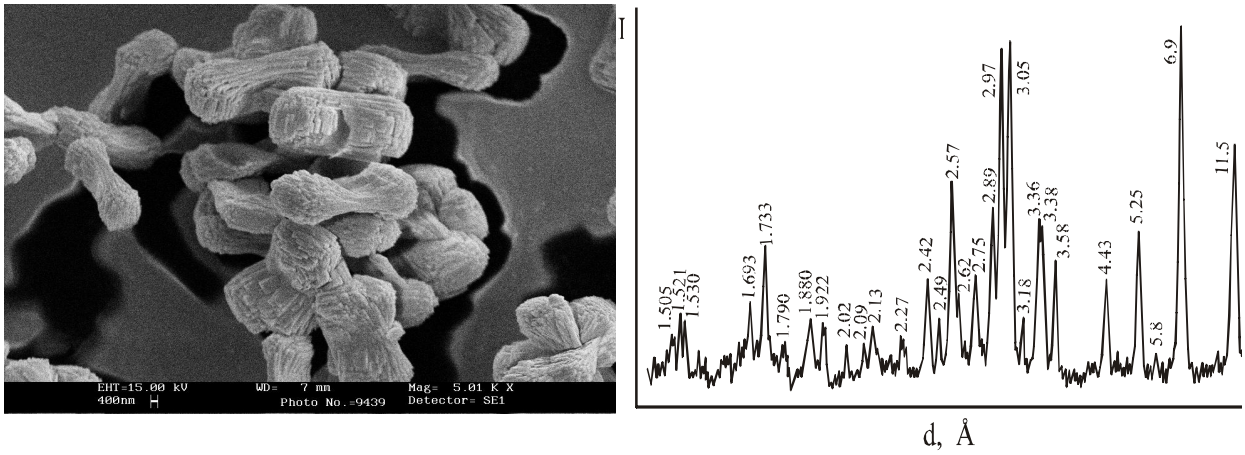


Fig. 5. SEM image of ETS-4 rosettes and an XRD pattern of ETS-4 powder

The synthesis of ETS-10 was carried out at 200˚C from the AOST, sodium silicate and an alkali reagent in the presence of potassium fluoride. The results have demonstrated that this titanosilicate with a high crystallinity and well-defined morphology can be successfully synthesized at high water contents and low alkalinity within 48 h of reaction. The rate of the crystalline phase formation from an AOST solution is faster due to higher activity of titanium (IV) compared to the ammonium-free $TiOSO_4$ solution.

We failed to synthesize ivanyukite Na by the method described above (the resulting products of hydrothermal synthesis contained mostly anatase with amorphous silica as an impurity). This can be due to the difference of its molar composition from other titanosilicates. The nature of initial titanium

and silicon-containing precursors, ore loading or synthesis conditions prior to autoclave treatment did not significantly affect the pure phase crystallization. The main reason for the failure appears to be the higher activity of titanium sulfate in forming of hydroxocomplexes compared to silica precursors, which makes it difficult to prepare homogeneous titanium silicate gels as a Ti-O-Si-O-Ti bridge complex.

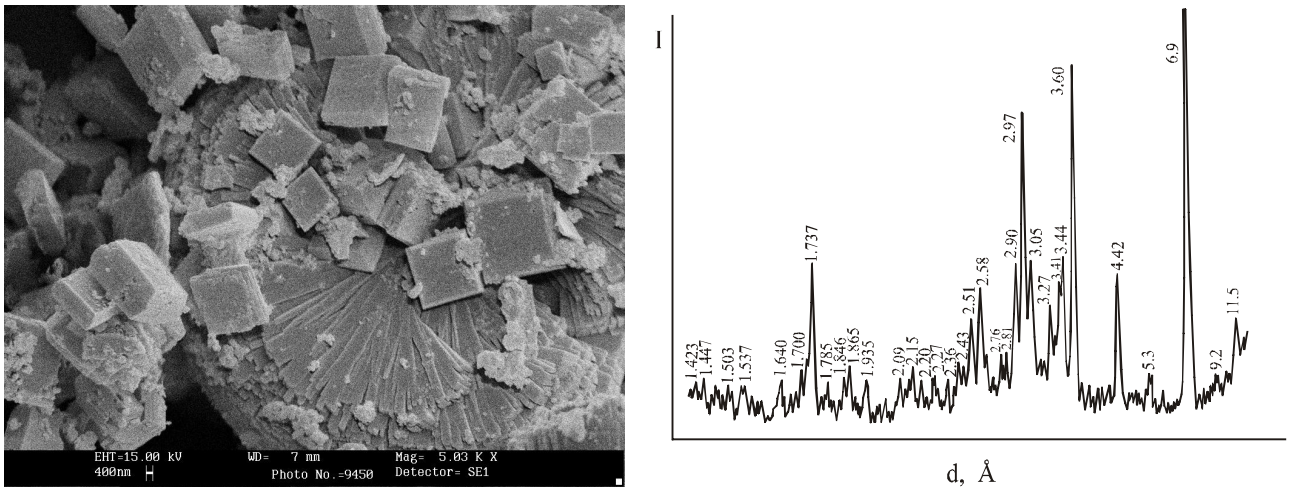


Fig. 6. SEM image of ETS-10 crystals and an XRD pattern of ETS-10 powder.

Based on the aforesaid, we synthesized ivanyukite (Fig.7) in the following manner. An AOST solution was mixed with a sodium silicate solution. The obtained translucent thick gel was stirred vigorously at room temperature for 12 h. The resulting gel was then filtered, washed with water and mixed with a NaOH+KF solution. The molar ratio of the components was stoichiometric to the chemical composition of ivanukite. The final reaction mixture was held in an autoclave for 2 days at 200 °C. After the reaction was completed, the solid product was washed with water and dried at 80 °C.

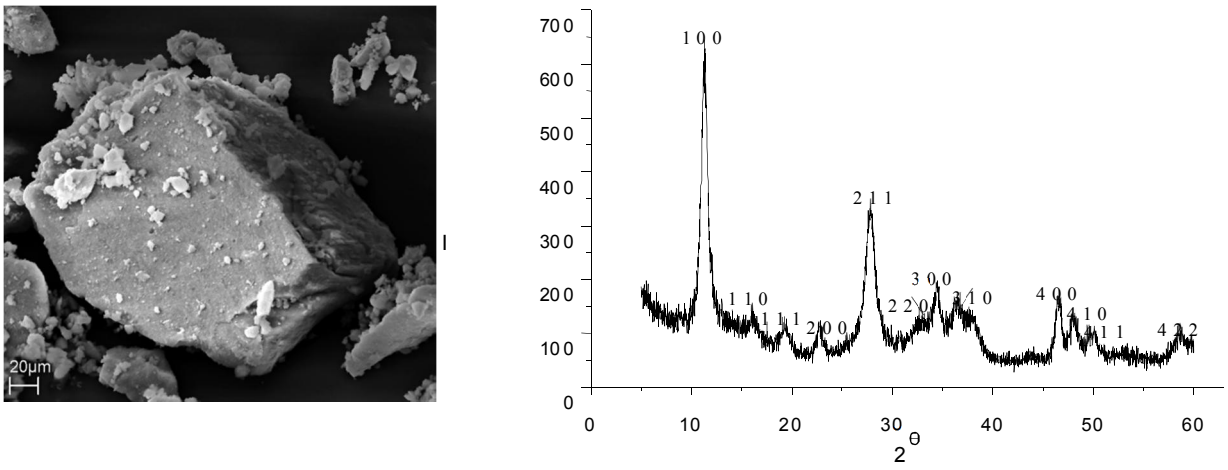


Fig. 7. SEM image of a crystal of synthetic ivanyukite and its XRD pattern

3.2 *Surface and adsorption properties of the final products*

The adsorption properties of titanosilicates depend on their structure. Table 1 presents the data on porosity of the products synthesized. In comparison with ivanyukite, the total pore volume of both ETS-4 and ETS-10 titanosilicates is smaller by an order of magnitude. According to the data of pore volume and pore diameter, both the ETS-4 and ETS-10 have narrow mesapores, whereas amorphous titanium silicates have large mesapores. The adsorption capacity of crystalline titanosilicates diminishes in the series ETS-10>ETS-4>naticite (Table 2).

Table1. Surface properties of different titanosilicates

Sample	SA, m^2/g	Pore volume,cm^3/g	Micropore volume, cm^3/g	Pore diameter, Å
Naticite analogue	26.81	0.087	0.00495	115.3
ETS-4	17.5	0.023	0.00345	71.8
ETS-10	164.2	0.078	0.0569	80.9
Ivanyukite+impurity	115.4	0.479	0.00221	180.5

Table 2.Adsorption capacity (E) of tanosilicates to different cations

Sample	E, mg/g		
	Cs^+	Sr^{2+}	Cu^{2+}
Naticite analogue	23.9	86.1	62.0
ETS-4	42.7	143.4	68.5
ETS-10	200.8	132,4	78.0
ivanyukite +impurity	27.3	38,0	45.8

CONCLUSIONS

Both titanosilicates of the ETS (ETS-4, ETS-10) type and the naticite analogue are stably formed in the process of hydrothermal synthesis during less than 2 days. Stability of the crystalline structure, as well as of the surface and adsorption properties of the final products, is achieved by adding excess amounts of silica (relatively titanium (IV)) to an alkaline medium (pH 10-11). The average pore diameter does not exceed 12 nm, so the material is classified as mesoporous.

Titanosilicates with the ivanyukite structure, differing from the listed above compounds by higher titanium (IV) contents, should be synthesized under conditions suppressing the titanium (IV) activity, for instance, by passing it to the colloid state.

For synthesis of titanosilicates, it is possible to use cheap and local technical initial components such as ammonium oxysulphotitanate obtained from titanite concentrate.

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REFERENCES

1.Al-Attar L., Dyer A., Paajanen A., Harjula R. (2003) Purification of nuclear wastes by novel inorganic ion-exchangers. . J. Mater. Chem., 13, pp.2969-2974.

2. Bal R., Chaudhari K., Srinivas D., Sivasanker S., Ratnasamy P. (2000) Redox and catalytic chemistry of Ti in titanosilicate molecular sieves: an EPR investigation. J.Molecul. Cat. A: Chemical, 162, pp.199-207.

3. Celestain J., Clearfield A. (2007) The origin of ion-exchange selectivity in a porous framework titanium silicate. J. Mater. Chem., 17, pp.4839-4842.

4. Cruciani G., De Luca P., Nastro A., Pattison P. (1998) Rietveld refinement of the zorite structure of ETS-4 molecular sieves. Micropor. Mespor. Mat. 21, pp.143-153.

5. Depmeier W (2009) Minerals as advanced materials. Cryst.Res.Technol., 44, 10, pp1122-1130.

6. Gerasimova L.G., Maslova M.V., Shchukina E.S.(2009) The technology of sphene concentrate treatment to obtain titanium salts. Theoretical Foundations of Chemical Engineering, 43(4), pp. 464-467.

7. Kim J.W., Kim S.D., Jung H.S., Hayhurst D.T. (2002) Compositional and kinetic studies on the crystallization of ETS-10 in presence of various organics. Micropor. Mesopor. Mater., 56, pp.89-100.

8. Kim S.D., Noh S.H., Kim W.J. (2003) Alkali effect and kinetic studies on the crystallization of a small pores titanium silicate molecular sieve, ETS-4 using different sources of silica and titanium under stirring. Micropor. Mesopor. Mater., 65, pp.165-175.

9. Krisnandi Y.K., Howe R.F. (2006) Effect of ion-exchange on photoreactivity of ETS-10. Appl Cat. A: General, 307, pp.62-69.

10. Lazareva I.V., Gerasimova L.G., Maslova M.V., Okhrimenko R.F. (2006) Sphene interaction with sulphuric acid solution. Rus. J. Appl. Chem., 79, 1, pp.18-21.

11. Linssen T., Cassiers K., Cool P., Vansant E.F (2003) Mesoporous template silicates: an overview of their synthesis, catalytic activation and evaluation of their stability. Adv. Coll. Interface Sci., 103, pp.121-147.

12. Lopes C.B., Otero M., Coimbra J., Peteira E., Rocha J., Lin Z., Duarte A. (2007) Removal of low concentration Hg^{2+} from natural wates by microporous and layered titanosilicates. Micropor. Mesopor. Mater., 103, pp.325-332.

13. Lv L., Su F., Zhao X.S. (2004) A reinforced study on the synthesis of microporous titanosilicate ETS-10. Micropor. Mesopor. Mater., 76, pp.113-122.

14. Noh S.H., Kim S.D., Chung Y.J., Park J.W., Moon D.K., Hayhurst D.T., Kim W.J. (2006) The effect of (Na+K)/Na molar ratio and kinetic studies on the rapid crystallization of a large pored titanium silicate, ETS-10 using cost efficient titanium oxysulfate, $TiOSO_4$ under stirring. Micropor. Mesopor. Mater., 88, pp.197-204.

15. Pavel C.C, Viono D., Catanzaro L., De Luca P., Bilba N., Nastro A., Nagy J.B. (2002) Synthesis and characterizastion of microporous titanosilicates ETS-4 and ETS-10. Micropor. Mesopor. Mater., 56, pp.227-239.

16. Rocha J., Anderson M.W. (2000) Microporous titanosilicates and other novel mixed octahedral-tetrahedral framework oxides. Eur. J. Inorg. Chem., pp.801-818.

17. Rocha J., Ferreira A., Lin Z., Anderson M.W. (1998). Synthesis of microporous titanosilicate ETS-10 from $TiCl_3$ and TiO_2: a comprehensive study. Micropor. Mesopor. Mater., 23, pp.253-263.

18. Spiridonova D.V., Krivovichev S.V., Britvin S.N., Yakovenchuk V.N. (20011) Crystal chemistry of ion-exchanged forms of zorite, a natural analogue of the ETS-4 titanosilicate material. Minerals as Advanced Materials II (Ed. S.V.Krivovichev). Springer, pp. 199–204.

19. Yakovenchuk V.N., Nikolaev A.P., Selivanova E.A., Pakhomovsky Ya.A., Korchak J.A., Spiridonova D.V., Zalkind O.A., Krivovichev S.V. (2009) Ivanyukite-Na-T, ivanyukite-Na-C, ivanyukite-K, and ivanyukite-Cu: New microporous titanosilicates from the Khibiny massif (Kola Peninsula, Russia) and crystal structure of ivanyukite-Na-T. American Mineralogist, 94, pp. 1450–1458.

20. Yakovenchuk V.N., Selivanova E.A., Krivovichev S.V., Pakhomovsky Ya.A., Spiridonova D.V., Kasikov A.G., Ivanyuk G.Yu. (2011) Ivanyukite-group minerals: crystal structure and cation-exchange properties. Minerals as Advanced Materials II (Ed. S.V.Krivovichev). Springer, pp. 205–211.

21. Yang X., Paillaud J.-L., Breukelen H.F.W.J., Kessler H., Duprey E. (2001) Synthesis of microporous titanosilicates ETS-10 with TiF_4 and TiO_2. Micropor. Mesopor. Mater., 46, pp.1-11.