Synthetic analogues of natural titanosilicate mesoporous minerals as potential functional materials. Synthesis and application

A I Nikolaev, L G Gerasimova, M V Maslova and E S Shchukina
Federal Research Centre “Kola Science Centre of the Russian Academy of Sciences”
Apatity 14 Fersman street. Russia

E-mail: nikol_ai@chemy.kolasc.net.ru

Abstract: Phase formation upon hydrothermal crystallization in the Na₂O-TiO₂-SiO₂-H₂SO₄-H₂O system has been studied in depth. The obtained results provided the basis for the development of technology for new types of ion-exchangers with the structure of the mineral ivanyukite - Na₄(TiO)₄(SiO₄)₃·4·6 H₂O. It was shown that an excessive amount of Na and Si with respect to Ti (mol) and an alkaline medium up to pH 12 affect the rate of the ivanyukite crystallization. The optimal conditions producing the pure ivanyukite phase with designed structure, chemical composition and morphology have been found. The framework composes corner-sharing SiO₄ tetrahedra and TiO₆ octahedra linked through bridging oxygen atoms and provide pore system with channels containing H₂O molecules and exchangeable Na⁺ cations. The synthetic ivanyukite with wide-pore microporous framework is considered to be perspective cation-exchanger.

1. Introduction
The focus on natural synthetic alkali titanosilicates (Ti-Si) is explained by their versatile properties. Specifically, Ti-Si outperform zeolites, widely used for sorption, not only in terms of higher sorption extent, but also due to thermal stability and selectivity. Determination of conditions for generation of such minerals in nature allows for selection of components and parameters for streamlined synthesis of their analogues with mesoporous particles. Titanosilicates are used for immobilization of radioactive isotopes from aqueous solutions, removal of nonferrous heavy metals from water, separation of gas mixtures and as carrying sorbent agents in medicine. The synthesis of mineral-like Ti-Si is a relative newcomer [1], but in foreign countries many R&D products have been already implemented, e.g. Ti-Si of ETS-4 type [2, 3] or IONSIVIE-911 with a sitinakite mineral texture [4]. New types of Ti-Si minerals – ivanyukites – have been found in the urtites of the Koashva deposit (Kola Peninsula) [5, 6].

2. Main Body
This article describes the ivanyukite technology and its physical and chemical basis. The authors have developed the ivanyukite technology, which in many aspects outperforms the known methods, since it is based on the use of available titanium-containing raw material and innovative processing techniques, providing for high physical and engineering properties of the final products.

2.1. Research objects
Titanium salt (ammonium-titanyl-sulfate (ATS) – (NH₄)₂TiO(SO₄)₂·H₂O) obtained from titanite recovered from tails of Khibiny apatite-nepheline ore processing was used for the experiments [7]. Silicone was obtained from soluble glass with mass (%) concentrations: SiO₂ – 31.5; Na₂O – 10. Silicone density: 1.43 g/dm³. During synthesis the pH value (equal to 11.5) was adjusted by adding NaOH alkali. ATS solution (concentration, mol/L: TiO₂ – 1, H₂SO₄ – 1.1–1.5) and alkaline agents have been mixed in set proportions and the mixture was held up for 2 hours. The resulting jellylike
precursor was placed into an autoclave and incubated at 200°C within 72 hours. The composition of residual matter resulting from the hydrothermal synthesis was determined with the help of Shimadzu XRD-6000 diffractometer.

Judging from the formula Na₄(TiO)₄(SiO₄)₃·6H₂O, the molar ratio in ivanyukite Si/Ti and Na/Ti is equal to 0.7 and 1.0 respectively. Synthesis with stoichiometric consumption of components does not allow for generation of ivanyukite. To figure out the optimum synthesis conditions, ensuring generation of ivanyukite, the study was conducted in the system Na₂O-TiO₂-H₂SO₄-SiO₂-H₂O with changes of Na and S molar discharge relative to Ti, which determines the salt mass of the system and induces its “oversaturation” as a key condition for crystal phase formation. Ti, water content and pH value were non-variable.

2.2. The experimental part
Based on the study of phase formation in the system, the “system composition – solid phase property” plot was built [8]. The obtained crystallization field consists of nine zones (Figure 1). We noticed that in zone VI limited by the change of Si and Na molar ratios relative to Ti from 3.9 to 5.5 and from 3.5 to 4.8 respectively, the solid phase is generated in the form of two structural versions of ivanyukite: with trigonal crystal structure (T)-Na₄(TiO)₄(SiO₄)₃·6H₂O and with cubic structure (C) – Na₃H(TiO)₄(SiO₄)₃·4H₂O. In zone III, a monophasic sediment crystallizes with the zorite structure – Na₅Ti₃Si₁₂O₃₄(O,OH)₅·11H₂O. In other zones of the system, generation of polycomponent sediments containing various amounts of titanosilicate phases (natisite, sitinakite, zorite, ivanyukite, as well as TiO₂ anatase and quartz) takes place.

XRD patterns of samples in zone VI obtained under conditions specified in Table 1 are almost identical (Figure 2). Structural varieties of ivanyukite include slight displacement of the main peak (100) for the samples with mixed structure 1 and 2. The same samples are noted for a much higher peak intensity (211) as compared to sample 3, which is an evidence of its monophasic composition. Surface behavior was determined by nitrogen adsorption/desorption (BET method) using TriStar 3020 analyzer (Table 1).

![Figure 1. Crystallization field of alkali titanosilicate solids in Na₂O-TiO₂-H₂SO₄-SiO₂-H₂O system](image)

High BET surface area of ivanyukite (135–150 m²/g), its porosity (gross pore volume: 0.75–0.81 cm³/g) and availability of fluent off-scaffold cations Na⁺ and water molecules positively affect the speed and efficiency of exchange processes taking place in sorption systems. Sorption capacity (E) of ivanyukite was determined for sample 2 relative to cations Cs⁺, Sr²⁺ and Co²⁺, mg eq/g: ECs⁻ 2.9; ESr – 4.5; ECo – 3.2. A patent for the invention was received [9].
Table 1. Surface behavior of ivanyukite samples

| Sample No. | Consumption of agents during ivanyukite synthesis in zone VI | Surface behavior |
|------------|-------------------------------------------------------------|------------------|
|            |                                                              | SG, m²/g | Vpore, cm³/g | Dpore, nM |
| 1          | 4.1 Na:Ti:5.0Si:160H₂O ivanyukite-T+ ivanyukite-C           | 150.2±1.3 | 0.75        | 15.0      |
| 2          | 4.5Na:Ti:4.2 Si:160H₂O ivanyukite-T+ ivanyukite-C           | 137.6±1.0  | 0.78        | 16.0      |
| 3          | 3.9Na:Ti:5.5Si:160H₂O ivanyukite-C                           | 134.9±1.1  | 0.81        | 15.5      |

Figure 2. XRD patterns of samples

Titanosilicate precursor granulation technique using no additional agents and providing for high stability of granules during long-term dynamic impact, while maintaining their sorption characteristics, was developed (Figure 3).

Figure 3. Granular ivanyukite. Grain size: 1–1.3 mm

3. Conclusion
Derivatization methods of other structural types of titanosilicates using sulphate titanium salts are currently being developed. In particular, a diagram of stepwise synthesis of layered titanosilicate AM-4 (Na₃NaTi₂[Si₄O₁₃]·2H₂O) with a structure similar to lintisite and tundrite minerals was proposed. It has been established that in acidic media AM-4 is converted into a layered titanosilicate SL3 which
selectively extracts monovalent cations allowing for its use for silver recovery from complex process solutions and $^{137}$Cs from LRW [10]. Argentic form SL3-Ag exhibits photocatalytic properties.

Spent radioactive sorbent agent can be turned into a stable titanate ceramic corresponding to a solid highly reactive porcelaneous mass, similar to Synroc ceramics by composition [11].

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