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Alkali titanosilicates from titanite. Production and properties

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Abstract

The study deals with synthesis of an alkali titanosilicate with a framework structure similar to the material known as ETS-10. The titanium source was an oxotitanium ammonium sulphate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (ASOT) obtained from a titanite mineral concentrate (CaTiSiO_5). The optimum component ratio and pH for the mixture ($\text{TiO}_2:\text{SiO}_2:\text{Na}_2\text{O}:\text{KF} = 1:4.5.:4:0.25$, pH – 10.8) of a gel-like precursor have been determined. As a result of hydrothermal synthesis, the precursor has been found to form an almost monophasic precipitate. Observance of the above conditions rules out the formation of zorite and quartz impurities. It is shown that heat-treated, dehydrated titanosilicate recrystallizes to an XRD-amorphous powder turning into a new, frameless, crystalline phase – narsarsukite. The material tends to vitrify at temperatures around 900 °C. Surface properties and sorption and photocatalytic activity of heat-treated titanosilicate are discussed.

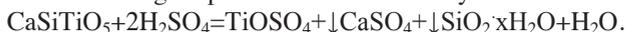
Keywords: Titanosilicate; Titanite; Ion-exchange capacity; Photocatalytic activity.

In recent years, much attention has been paid to safe handling and disposal of radioactive waste from civic and defence enterprises. Normally, radionuclides such as ¹³⁷Cs and ⁹⁰Sr are concentrated and immersed into stable matrixes to be buried in stable

geological formations. Searching for stable matrixes has been a challenge for both science and engineering. We propose making matrixes from mineral-like alkaline titanositicats with a framework structure, such as those known as ETS (ETS-4-zorite and ETS-10) (Kuznicki, 1989; Kuznicki & Thrush, 1990; Chapman & Roe, 1990). On heating, these titanositicats get restructured forming a monolithic ceramic, which isolates the adsorbed radionuclides as insoluble compounds. Another application for thermally treated titanositicats is as luminophores. The luminophores are characterized by intense glowing, stable processing behavior, and resistance to chemical and thermal attacks. Silicate luminophores are produced by mere roasting of a charge consisting of pure salts (or oxides) and silicon dioxide in a temperature range of 1150 – 1350 °C (Kachgikin et al., 1975). The process is power intensive because the solid-phase reactions therein proceed for a long time and at high temperatures.

In this work, we have synthesized several alkali titanositicats using a new titanium-containing precursor, an ammonium sulphate oxotitanate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (ASOT), and studied the product properties.

ASOT was obtained from a mineral titanium concentrate isolated from the process of apatite-nepheline ore concentration (the Khibiny deposit, Russia). Titanite interacted with a 6 mol/l sulphuric acid yielding titanium(IV) leached out to the liquid phase. The process occurs in a boiling suspension for 7-8 hours by the reaction:



Since the reaction occurs in a heterogeneous system, the leaching degree depends on the size of titanite particles, as demonstrated in Fig. 1.

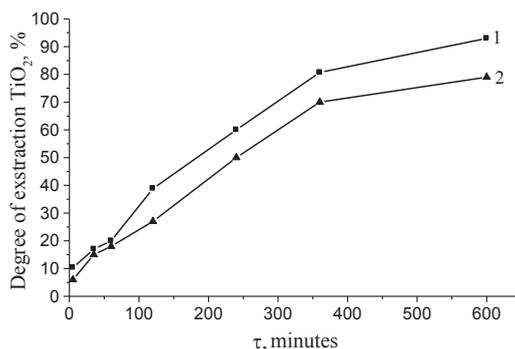


Fig. 1. Relationship between the grain size of sphene concentrate and the level of titanium extraction to solution. 1 – fraction of particles less than 40 μm ; 2 – fraction of particles of 63-80 μm .

After filtration, the titanium sulphate solution had the following composition: TiO_2 - 100 g/l, H_2SO_4 - 450 g/l. The solution was then slowly stirred for 1 - 1.5 h with addition of crystalline ammonium sulphate up to a concentration of 350 g/l in $(\text{NH}_4)_2\text{SO}_4$. The contents of titanium and impurities in the resulting salt, wt %, are listed below:

TiO_2	Fe_2O_3	CaO	Nb_2O_5	CeO_2	SiO_2
21.2	0.10	0.03	0.05	0.12	0.02

ASOT was dissolved in water to obtain an ammonium-sulphate solution with a concentration, mol/l: TiO_2 - 1; H_2SO_4 - 1.15; $(\text{NH}_4)_2\text{SO}_4$ - 1.1. The source of silicon was a liquid glass solution ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) containing 4 mol/l as SiO_2 . Synthesis of a

titanosilicate gel with a monophasic structure was performed using a sodium alkali solution of 2.5 - 3 mol/l, in terms of Na_2O , and a potassium fluoride solution.

To obtain a framework titanosilicate of the ETS-10 type, we prepared a gel-like compound by mixing the starting components at the molar ratios of $\text{TiO}_2:\text{SiO}_2:\text{Na}_2\text{O}:\text{KF} = 1:4 - 6:3.8 - 4,5:0.25$. The mixture with a $\text{pH} = 10.5 - 11.5$ was corrected by adding a NaOH solution. The resulting gel-like compound was placed into an autoclave for hydrothermal treatment during 24 hours at 200°C . Next, the suspension was filtered, the residue washed from the mother liquor with water and dried in air. The final product was a white crystalline powder. The data of XRD and NMR analysis are given in Fig. 2a, 2b.

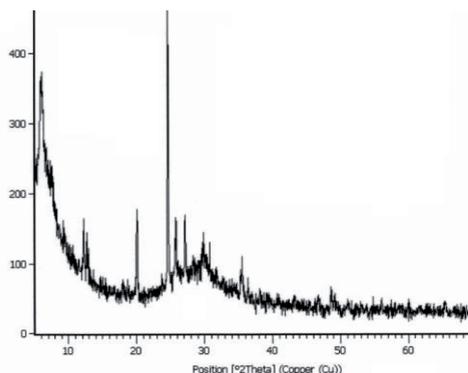


Fig. 2a. XRD pattern of titanosilicate powder.

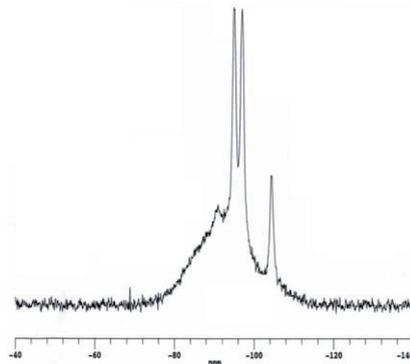


Fig. 2b. NMR spectrum of ^{29}Si of titanosilicate powder (air-dried).

The peaks corresponding to $d = 11.45; 6.96 \text{ \AA}$ in the XRD pattern of a titanium silicate sample are related to the main phase ETS-10 - $\text{Na}_9\text{Ti}_5\text{Si}_{13}\text{O}_{38}(\text{OH})(\text{H}_2\text{O})_{18}$. The data of ^{29}Si NMR spectroscopy indicate the presence of ETS - 4 impurity (-90.68 ppm) in the sample. It was noted that the impurity content in ETS - 4 was greater when the silica component was less than 4.5 mol relatively TiO_2 . At silica contents higher than 5 mol the titanosilicate sample contained more individual groups = $\text{Si}(\text{OH})_2$ (-87.4 ppm). The main chemical shifts at -94.93 and -97.01 ppm are attributed to the $3\text{Si}1\text{Ti}$ environment. This signifies that 3 silicon atoms are bonded with titanium and the SiO_4 tetrahedra are perpendicular to Ti-O-Ti chains. The chemical shift at -104.25 ppm is attributed to $4\text{Si}0\text{Ti}$ environment, where the central silicon atom is bonded tetrahedrally with 4 other silicon structural units. It was also found that the silica component started to increase at pH values in the gel higher than 11, replacing the ETS-10 phase and deteriorating the titanosilicate properties.

According to TG analysis, the total weight loss for a titanosilicate sample was 12.3% (Fig. 3); free water was removed up to 117°C , structural water – up to $240\text{-}250^\circ\text{C}$. Due to water removal, the mass loss was 10.2%. As shown by TG data, mass losses continued up to the temperature of 500°C . Evidently, recrystallization in the material, exposed to thermal treatment, proceeds up to the total decay of the crystal lattice at 500°C (Table 1). Further heating causes the formation of a new crystalline phase, i.e. narsarsukite ($\text{Na}_2\text{TiOSi}_4\text{O}_{10}$) manifested on the TGA curve as two exothermal effects at 628.9°C and 756.3°C . The endoeffect at 907.7°C corresponds to converting of free silicic acid to the quartz phase.

Table 1. The effect of heat treatment on the phase composition of titanosilicates.

Sample №	Temperature, °C	Sample characteristics, phase composition (XPA)
1	120	$\text{Na}_9\text{Ti}_5\text{Si}_{13}\text{O}_{38}(\text{OH})(\text{H}_2\text{O})_{15}$ -ETS-10 and zorite impurity
2	250	Semi-crystalline $\text{Na}_9\text{Ti}_5\text{Si}_{13}\text{O}_{38}(\text{OH})(\text{H}_2\text{O})_{15}$
3	500	XRD amorphous phase
4	650	$\text{Na}_2\text{TiOSi}_4\text{O}_{10}$ – narsarsukite+XRD amorphous phase
5	750	$\text{Na}_2\text{TiOSi}_4\text{O}_{10}$ -narsarsukite
6	900	Vitreous mass

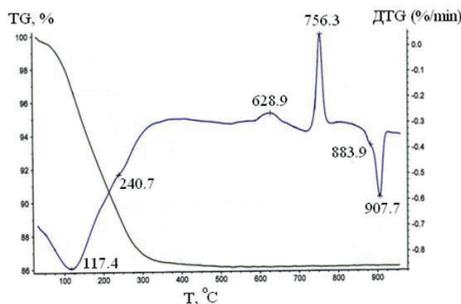


Fig. 3. TGA data on the synthesized titanosilicate.

In heated framework ETS - 10, restructuring occurs as a result of dehydration of crystalline titanosilicate. The emerging overcharged amorphous particles form seeds for a new, frameless phase consisting of tightly packed particles with a laminated structure (Fig. 4).

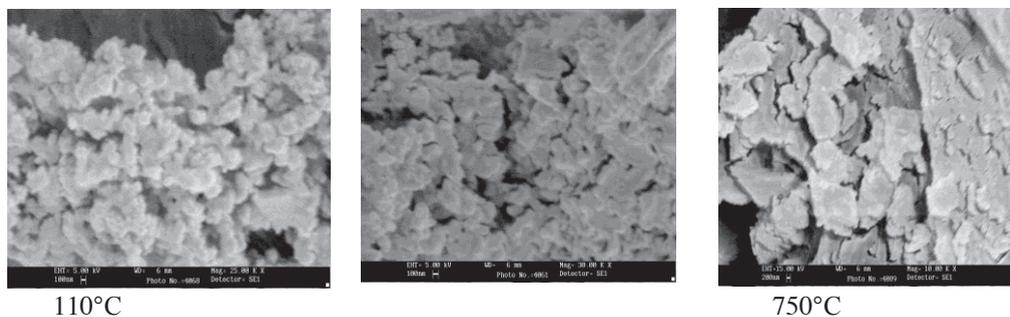


Fig. 4. SEM image of titanosilicate heated at different temperatures.

Temperature increase promotes compacting of the material's crystal structure, which is demonstrated by the BET analysis of its surface properties (Table 2). All the samples feature low porosity, with pore sizes varying between 15 and 53 nm.

Table 2. Effect of thermal treatment on the surface properties of titanosilicates.

Sample №, T, °C	S _A , m ² /g	Total pore volume, cm ³ /g	Average pore diameter, nm
1 - 110°C	12.20	0.033	15.6
2 - 250°C	11.07	0.021	15.1
3 - 500°C	9.65	0.02	15.6
4 - 650°C	1.42	0.003	44.1
5 - 750°C	0.40	0.001	52.8

Sorption properties of thermally treated titanosilicates are listed in Table 3. The ion-exchange capacity (IEC) was determined in batch experiment. The initial metal concentration in solution was 0.2 g/l; the sorbent weight was 0.2 g; S:L=1:200, and the contact time was 48h.

Table 3. Effect of thermal treatment on sorption properties of titanosilicates.

Sample №	IEC, mg/g		
	Cu	Cs	Sr
1	39.7	40.6	16.2
2	36.5	14.9	16.2
3	18.9	5.6	15.0
4	4.0	5.6	9.2
5	2.0	4.6	5.3

In Sample 1, the uptake of copper and cesium cations (at 110 °C) has proved to be almost 100% of the metals' contents in initial solution. At higher temperatures, the sorption capacity decreases due to alteration of the samples' surface properties and deactivation of sorption-active centers.

Determination of the titanosilicate photochemical activity of (PCA) was performed after air-drying and after calcination. The PCA was determined in the visible light range (at λ 540) using a ferroin solution by a known method (Zhigotskii et al., 2008; Sedneva et al., 2007). The efficiency of indicator decay as a PCA E measure, %, was calculated using the following equation:

$$E = [(C_0 - C)/C_0] \cdot 100\%$$

where C_0 and C (g/l) are the initial and final contents of *o*-phenatroline in solution, respectively.

With temperature increase, the PCA index diminished, reaching zero at 650 °C (Fig. 5). This is caused by structural compaction and isolation of photocatalytically active centres.

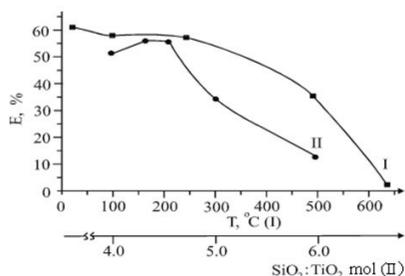


Fig. 5. Relationship between the PCA of ETS-10 and thermal treatment temperature (I) and the TiO₂:SiO₂ molar ratio in synthesis (II).

At silica-to-titanium dioxide ratios other than 4.2-4.6 (mole) the titanasilicate loses the capacity for photocatalysis. This is because at ratios lower than 4 the titanasilicate acquires more of the ETS-4 impurity, whereas exceeding of the 4.5 value promotes increasing of the quartz content, neither of which possess photocatalytic properties.

Our findings suggest that ETS-10 can be obtained from an ASOT solution at a component molar ratio of TiO₂:SiO₂:Na₂O:KF=1:4.5:4:0.25 at pH=10.8. The product has a high sorption and photocatalytic activity. Precipitates with higher silica contents or a pH of over 11 contain zorite and quartz impurities. When thermally treated, the titanasilicate dehydrates and its structure decays to an XRD-amorphous state (450-500 °C). This is followed by the formation of a new crystalline phase (narsarsukite) consisting of densely packed laminated particles. Further heating (to 900 °C) results in vitrification of the material.

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