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Nanoparticles in titanite ore

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ABSTRACT Nanoparticles in titanite $CaTiSiO_5$ were found using transmission electron microscopy. Chemical and XPS analyzes of the nanoparticles were performed. The study showed the content of the elements Si, Ti and Ca to be about 19, 14 and 12 % in the ore, respectively, belonging to the titanite phase. Based on TEM images, it was established that titanite exhibits a disordered lamellar structure with a diameter of 3 to 5 nm and an interplanar distance of about 6.3 Å.

KEYWORDS titanite, nanoparticles, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS)

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1. Introduction

As for the reserves of titanium raw materials, Russia currently is at the second place in the world. Despite this, its extraction and processing is practically not carried out. Among the most promising and products in demand on the market, we should note weather-resistant and decorative pigments, composite fillers, non-toxic titanium tanning agents, highly effective sorbents for purifying liquid and solid waste from radionuclides and toxic substances [1–3]. The content of the mineral sphene (calcium titanosilicate ($CaTiSiO_5$)) in the ore mass varies widely. Using traditional technology, sphene concentrate is obtained from the foam product of apatite-nepheline ore flotation. This is a fairly complex process in terms of technological flows, so the extraction of sphene does not exceed 10 %. Meanwhile, there are areas, so-called "sphenite lens nests", in which the concentration of sphene reaches 80 %. An increased content of sphene negatively affects the process of flotation separation of apatite due to the similarity of the properties of calcium-containing minerals. On the other hand, such accumulations of sphene can be quite easily separated from the total mass of ore, and the extraction of sphene can reach 60 – 70 % of the original ore [4]. Up to 1930, it was not known how to process titanite (sphene) in industry. This question arose after the discovery of its industrial reserves in the Khibiny Mountains. Various methods have been proposed for the decomposition of sphene: treatment with bleach; fusion with table salt and exposure of the solution to superheated steam, production of carbides followed by chlorination, decomposition with hydrochloric acid, etc., however, these methods have not found their application in industry due to their complexity [5]. Despite the well developed study of processing sphene concentrate into titanium pigments, which began in 1968, and their subsequent successful testing on a pilot scale, implementation work has been suspended since 2016 due to the optimization of the main production at JSC Apatit, which led to the actual closure of the workshop for the production and processing of sphene concentrate, and therefore the minerals are sent to tailings dumps [6]. A significant part of nepheline, titanomagnetite (16 – 18 % TiO_2), sphene (37 % TiO_2), aegirine annually in the amount of 15 – 20 million tons replenish the dumps of processing factories. More than 500 million tons of waste have already been generated [7]. In this regard, the aim of this work is to study the structure and chemical composition of titanite to develop methods for its subsequent use as highly effective sorbents for purifying liquid media from toxic substances.

2. Samples and experiment

The study object is titanite – calcium titanosilicate ($CaTiSiO_5$). The place of origin of the mineral is the Koashva deposit (Koashva quarry, Murmansk region, personal mineral collection of V. N. Yakovenchuk) [5]. At the first stage, titanite (sphene) wedge-shaped crystals with its matrix (includes apatite $Ca_5[PO_4]_3(Cl/F/OH)$, nepheline $KNa_3[AlSiO_4]_4$ and rock-forming pyroxene group) was crushed using a laboratory jaw crusher, after which a study of the structure, chemical and phase composition, was carried out (Fig. 1).

FIG. 1. Picture of the sphene (original and after grinding)

The quantitative chemical composition was determined by inductively coupled plasma atomic emission spectrometry on a SpectroBlue device (Spectro Analytical Instruments) for all elements except S. The quantitative content of S was determined by the infrared absorption method on a CS-230 automatic analyzer.

The study of the samples surface chemical composition was carried out using a photoelectron spectrometer from SPECS Surface Nano Analysis GmbH (Germany). The spectrometer is equipped with a PHOIBOS-150-MCD-9 hemispherical analyzer, an XR-50 characteristic X-ray source with a double Al/Mg anode. Non-monochromatic Al Kα radiation ($h\nu = 1486.6$ eV) was used to record the spectra. To consider the effect of charging the samples, we used the spectrum of Ti2$p_{3/2}$ ($E_b = 459.0$ eV), corresponding to the TiO_2 carrier. The relative concentrations of elements in the analysis zone are determined based on the integrated intensities of the XPS peaks, considering the photoionization cross section of the corresponding terms. For a detailed analysis, the spectra were decomposed into individual components. Accordingly, after subtracting the background using the Shirley method, the experimental curve was decomposed into several lines corresponding to the photoemission of electrons from atoms in different chemical environments. Data processing was carried out using the CasaXPS software package. The shape of the peaks is approximated by a symmetric function obtained by multiplying the Gaussian and Lorentzian functions.

The structure of the mineral was studied using high-resolution TEM on a JEM-2010 electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV and a resolution of 140 pm. Images were recorded using a CCD Soft Imaging System camera (Germany).

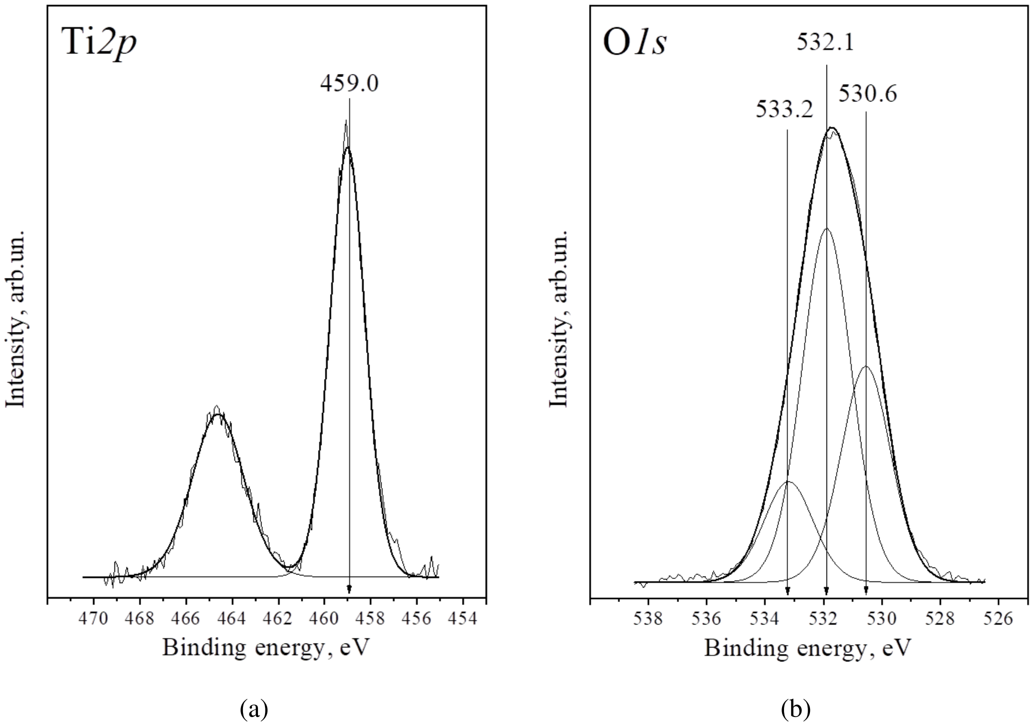
3. Results and discussion

Atomic emission spectroscopy with inductively coupled plasma made it possible to determine the quantitative content of chemical elements in the sample (Table 1). The content is more than 10 Wt % of such elements as Si, Ti and Ca, which probably belongs to the Titanite phase; the content is less than 5 Wt % – Al, K_2O, Na_2O, which belongs to the Nepheline and Microcline minerals, and less than 1 Wt % of elements such as Fe, P, Sr, Ba, Zr, Ce, Nb, Mg, Li and S.

TABLE 1. Quantitative chemical analysis

Element	**Si**	**Ti**	**Ca**	**Al**	**K_2O**	**Na_2O**	**Fe**	**P**
Wt, %	18.8	13.6	12.1	4.8	4.3	3.1	0.9	0.8
Element	**Sr**	**Ba**	**Zr**	**Ce**	**Nb**	**Mg**	**Li**	**S**
Wt, %	0.6	0.1	0.1	0.1	0.1	0.1	0.02	0.04

The Ti2*p* spectra of the studied samples are shown in Fig. 2. It is known that the Ti2*p* spectrum due to the spin-orbit interaction is a doublet Ti2$p_{3/2}$ – Ti2$p_{1/2}$ with a spin-orbit splitting value of 5.7 eV. In the spectrum of the Ti2*p* samples, one doublet is observed with a Ti2$p_{3/2}$ binding energy of 459.0 eV, which corresponds to titanium in the Ti^{4+} state. No traces of titanium are observed in any other chemical states. In the literature for TiO_2, the Ti2$p_{3/2}$ binding energy values are given in the range of 458.7 – 459.2 eV [8–13]. Fig. 2 also shows the O*1s* spectra of the studied samples. The spectra are described by several peaks corresponding to oxygen in different environments, so the O*1s* peak in the region of 530.3 – 530.6 eV is undoubtedly referred to oxygen in the TiO_2 structure [8–12], the peak in the region of 532.0 – 532.3 eV can be attributed to surface OH^- groups [8–12], the peak in the region of 533.2 – 533.3 – to the adsorbed water and oxygen in the structure of silicon oxide [8–12, 14]. Fig. 3 shows the Si*2p* spectra of the studied samples. The Si*2p* peak in the region of 100.8 eV can be attributed to silicon carbide, the peaks in the region of 101.6 and 102.8 eV are attributed to silicon oxide in different chemical environments [14, 15]. Relative atomic concentrations of elements in the near-surface layer of the studied samples are presented in Table 2.



(a) (b)

FIG. 2. Ti*2p* and O*1s* spectra of the studied samples. The spectra are normalized to the integrated intensity of the peaks corresponding to the C*1s* spectra

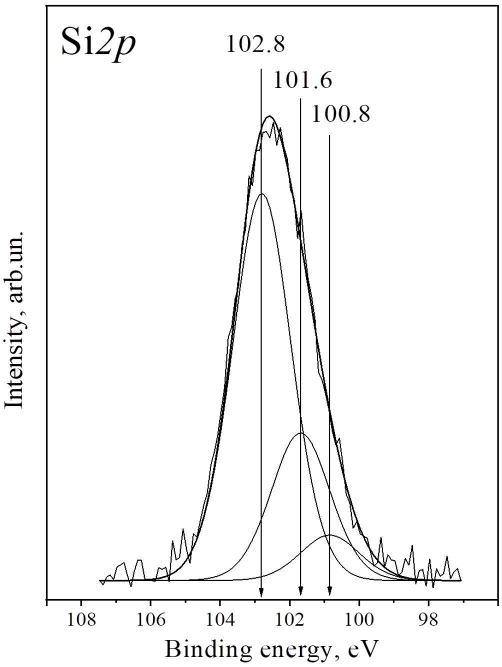
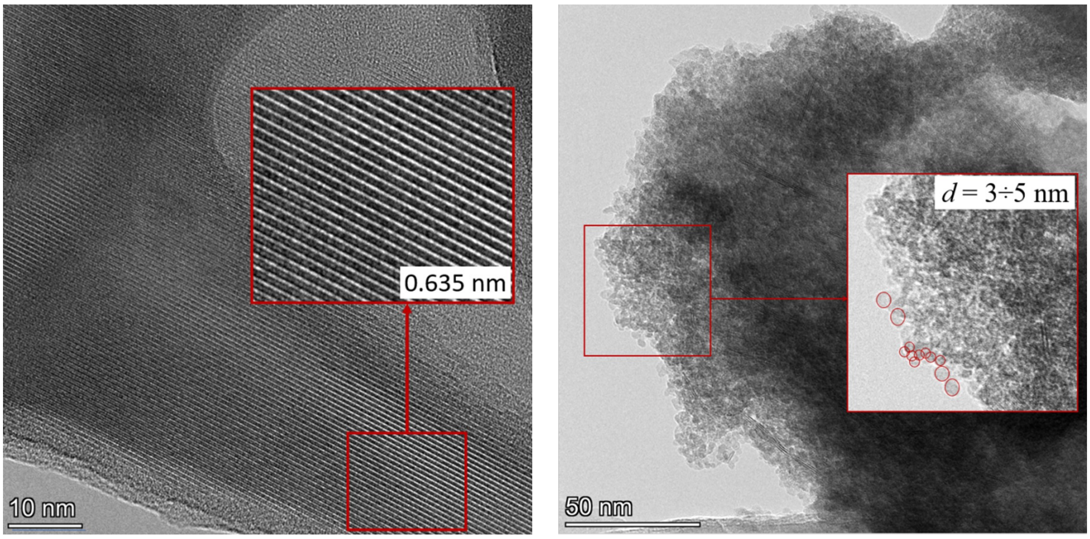


FIG. 3. Si*2p* spectra of the studied samples. The spectra are normalized to the integrated intensity of the peaks corresponding to the C*1s* spectra

TABLE 2. Relative atomic concentrations of elements in the near-surface layer of the studied samples (atomic ratios are normalized to [C])

[O]	[Ti]	[Ca]	[Si]	[K]	[Na]	[Al]	[P]
1.55	0.08	0.14	0.40	0.06	0.10	0.11	0.06

TEM-images (Fig. 4) show the morphology of titanite as a disordered lamellar structure with a diameter size ranging from 3 to 5 nm. Similar picture were obtained for another titanite from Cardiff [16]. A more detailed examination on the left image on Fig. 4 shows an ordered structure with an interplanar distance between atoms of about 6.3 Å, corresponding to titanite (PDF 04-010-2760).



(a) (b)

FIG. 4. TEM image of Titanite from the Koashva quarry, Murmansk region

4. Conclusions

In this work, the titanite from the Koashva quarry was studied. Content detected is more than 10 Wt % of such elements as Si, Ti and Ca, which belongs to the Titanite phase; the content is less than 5 Wt % – Al, K_2O, Na_2O, which belongs to the Nepheline and Microcline minerals, and less than 1 Wt % of elements such as Fe, P, Sr, Ba, Zr, Ce, Nb, Mg, Li and S. According to XPS spectra of the Ti$2p$ samples, one doublet is observed with a Ti$2p_{3/2}$ binding energy of 459.0 eV, which corresponds to titanium in the Ti^{4+} state. Spectra of the O$1s$ are described by several peaks corresponding to oxygen in different environments: in the region of 530.3 – 530.6 eV it is referred to oxygen in the TiO_2 structure, in 532.0 – 532.3 eV it is attributed to surface OH- groups and in 533.2 – 533.3 it belongs to adsorbed water and oxygen in the structure of silicon oxide. Spectra of the Si$2p$ with peak in the region of 100.8 eV is attributed to silicon carbide, peaks 101.6 and 102.8 eV are attributed to silicon oxide in different chemical environments. This confirms the idea of the phase composition of the studied mineral, which is a promising material for further research targeted on using it as an effective photosorbent for purifying liquid media from toxic substances.

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