



Influence of High-Power Electromagnetic Pulses on the Structural-Chemical and Physicochemical Properties of Rare-Earth Minerals

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Abstract

The investigation of the structural-chemical state and sorption properties modification of columbite and eudialite surface under the impact of high-power nanosecond pulses (HPEMP) was performed using XPS and FTIR. It was defined that preliminarily treatment of rare-metal minerals with high-power nanosecond pulses is promising tool for the directional changes in their physicochemical and structural-chemical properties as it was confirmed by the increasing of mineral's sorption activity.

Keywords: columbite, eudialite, high – power electromagnetic pulses, XPS, FTIR

Introduction

The flotation of rare earth minerals is important for the economic recovery of rare earth minerals from their ores. Flotation is a key step in the industrial production of RE materials, understanding the process of RE flotation will facilitate improvement in the flotation recovery and more efficient production of RE s for their numerous application. Systematic studies on RE flotation are urgently required, the research presented in this study id directed toward the better understanding the RE minerals flotation regularities.

Materials and methods

The mineral samples of columbite and eudialite used in this study (size fractions - 100 + 63 μm) contained about 98% of the studied mineral according to XRD results.

The treatment of minerals 'samples by high-power nanosecond video pulses [1] was carried out in air atmosphere under standard conditions and the following electro physical parameters of the impulse treatment: $\tau \sim 1 - 5 \text{ ns}$ – pulse front, $\tau \sim 50 \text{ ns}$ – pulse duration, $U \sim 25 \text{ kV}$ – pulse amplitude, $E \sim 107 \text{ V/m}$, pulse repetition rate is 100 Hz, pulse energy $\sim 0.1 \text{ J}$, processing time (t) of mineral samples were varied from 10 s to 150 s. Before electromagnetic pulse treatment, the concentrate samples were wetted with distilled water with ration of solid to liquid respect to S: L = 5: 1 according to recommendations [2].

X-ray photoelectron spectra were obtained on a Versa Probe II spectrometer (ULVAC-PHI; Material Science and Metallurgy Collective Center) at NITU MISiS using monochromatic Al K α radiation with an energy of 1486.6 eV; power X - ray source $\sim 50 \text{ watts}$. The XPS spectra were recorded in the constant transmit energy mode of the analyzer, which was 160 eV for the recording of survey spectra, and 29.35 eV for recording the spectrum of Si 2 p. The survey spectrum was recorded with a step of 1.0 eV, the high resolution spectrum of the 2 p line of silicon – with a step of 0.1 eV.

To prevent the effect of charging minerals, powder samples were pressed into an indium plate, then the samples were

placed in the spectrometer chamber and examined at room temperature under vacuum with a residual pressure of less than $6.7 \times 10^{-8} \text{ Pa}$, the diameter of the analysis area was 200 μm .

To eliminate the effect of charging the samples the registration of spectra was performed using double neutralization. The obtained spectra were calibrated by the binding energy of the low-energy component in the spectrum of 1 s electrons of carbon atoms (C 1s line) of hydrocarbons adsorbed on the sample surface; The binding energy of this component was assumed to be 285.0 eV. To obtain qualitative and quantitative information on the composition of the surface of minerals, the spectra of individual lines of elements were fitted according to standard procedures using the Casa XPS program.

The technique of the adsorption experiment was as follows: a 0.5 g mineral was placed in the cell of a laboratory flotation machine and agitated in distilled water for 3 minutes (S: L = 1: 20), then the pH was adjusted to the required value (NaOl - pH 9.0 (NaOH); Flotisor sm 15 – pH 3.5 (H₂SO₄); CH₃ (CH₂)₆ C (O) N (H) OH – 6.0 (HCl) and the reagent was added (300 mg / l), the contact time with the collector – 3 minutes, after that the solid phase was separated by filtration, washed with a tenfold volume of distilled water and dried in air.

IR spectra were obtained in the wavelength range from 4000 cm^{-1} to 400 cm^{-1} (spectral resolution 4 cm^{-1}) using an Fourier transform spectrometer (IR – Affinity, Shimadzu) and the diffuse reflectance attachment (Diffuse IR, Pike Technologies). For each sample, at least five spectra were obtained; the number of scans was 50 for each spectra.

Results and discussion

XPS

Table 1 presents the experimental results of the columbite (manganocolumbite) surface chemical composition 'changes as a result of pulsed energy impact; the chemical composition was determined by the survey XPS spectra. The compo-

Tab. 1. Influence of high-power electromagnetic pulses on the chemical composition of the columbite surface according to XPS results, at. %
 Tab. 1. Wpływ impulsów elektromagnetycznych dużej mocy na skład chemiczny powierzchni kolumbitu zgodnie z wynikami XPS, przy. %

N pulses, 10 ³	Nb	Ta	O	Fe	Si	Al	F	Zn	Pb	Th	C
0	1.7	0.2	54.2	5.5	6.9	3.4	1.3	0.7	1.2	0.3	24.6
1	1.2	0.2	53.4	5.2	7.3	3.3	1.3	0.5	1.0	0.2	26.6
5	1.7	0.3	52.4	4.3	6.6	3.5	1.1	0.7	1.0	0.3	28.3
10	2.0	0.1	51.9	4.9	5.4	3.1	1.5	0.5	1.1	0.2	29.4
15	2.2	0.1	48.8	8.3	5.5	2.6	2.4	0.7	1.4	0.2	25.7
30	2.4	0.7	53.0	6.1	5.5	2.8	1.9	0.6	1.2	0.4	23.8

Tab. 2. Influence of the treatment by high-power electromagnetic pulses on the columbite surface state according to XPS, at. %
 Tab. 2. Wpływ obróbki impulsami elektromagnetycznymi o dużej mocy na stan powierzchni kolumbitu określone XPS, przy. %

N pulses, 10 ³	O 1s	
	$E_{CB} = 530.0 \text{ eV}$ Nb ₂ O ₅ , Fe ₂ O ₃	$E_{CB} = 532.0 \text{ eV}$ SiO ₂ , Al ₂ O ₃ , OH, H ₂ O _{adsorbed} , O-C _{org}
0	15	85
1	15	85
5	20	80
10	20	80
15	23	77
30	24	76

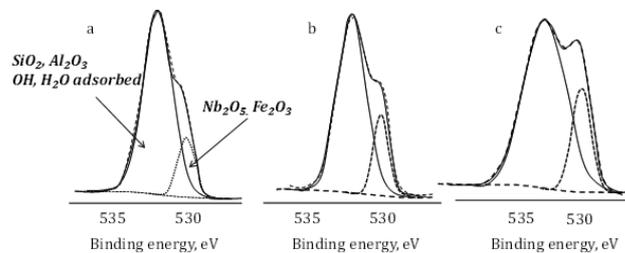


Fig. 1. O 1s line of columbite samples before (a) and after (b), (c) the treatment by high – power electromagnetic pulses during 150 s (b) and 300 s (c)
 Rys. 1. Linia O 1s próbek kolumbitu przed (a) i po (b), (c) obróbki impulsami elektromagnetycznymi o dużej mocy przez 150 s (b) i 300 s (c)

sition of the mineral surface before and after the treatment was characterized by the presence of Nb, O and Fe atoms in an amount sufficient to analyze their chemical and valent state by XPS.

Registration and subsequent analysis of the Nb 3d, Fe 2p lines showed that the spectral characteristics did not change as result of the treatment, namely, the Nb 3d 5/2 doublet (BE = 206.9–207.0 eV) corresponded to the state of niobium pentoxide Nb₂O₅ [3]; The position of the Fe 2p3/2 peak (BE = 711.4–711.8 eV) indicated that the chemical state of the iron atoms in the surface layer of the particles of the studied mineral was close to maghemite (γ – Fe₂O₃) or lepidocrocite (γ – FeO (OH)) [4].

The O 1s line (figure 1) was fitted with two components: the first with a binding energy BE ~ 530.0 eV corresponded to structural oxygen in the structure of Nb₂O₅ and γ – Fe₂O₃ (γ – FeOOH); the second contribution with BE ~ 532.0 eV was attributed to silicon and aluminum oxides and, presumably, hydroxogroups adsorbed on the surface of the mineral, oxygen in organic pollutants, and chemisorbed water molecules [5].

The a result of the columbite samples electromagnetic treatment for 10–150 s (range from 103 to 1.5 × 10⁴ pulses) is a consistent increase in the O 1s spectra component with a binding energy of BE ~ 530.0 eV, corresponding to structural oxygen atoms in niobium and iron oxides (Table 2, Fig. 1), and a decrease by 5–9 at.% of the the high-energy com-

ponent with BE ~ 532.0 eV, which characterizes the presence on the mineral surface of SiO₂, Al₂O₃, adsorbed water and functional hydrosogroups (Table 2). Since the surface concentration of Si and Al (at.%) remained constant during the treatment (Table 1), it can be assumed that at long treatment times (1.5–3.0) × 10⁴, 2.5–5.0 min) were accompanied by thermal removal of hydroxo groups and chemisorbed water molecules from the surface of columbite (dihydroxylation – dehydration) due to local temperature increase [6].

DRIFT

IR spectra of columbite samples after contact with the collector in the initial state, as well as after treatment by high-power nanosecond electromagnetic pulses are given in the figure 2. IR spectra of the columbite sample in the initial state (Figure 2 a) demonstrate the presence of the bands indicating the adsorption of the collector. The presence of a peak at 1530 cm⁻¹ and 1600 cm⁻¹ indicates the formation of Fe (III), tantalum and niobium on the surface [7, 8], and a weak shoulder at 1670 cm⁻¹ indicates the presence of a physically adsorbed hydroxamic acid [9]. Based on this, capryl-hydroxamic acid is adsorbed chemically on the surface of columbite predominantly, with the formation of complex compounds with metal atoms; the amount of physically adsorbed hydroxamic acid is small. A comparative analysis of the IR spectra showed a profile change: the shoulder at 1670 cm⁻¹ identified for the initial sample and corresponding to

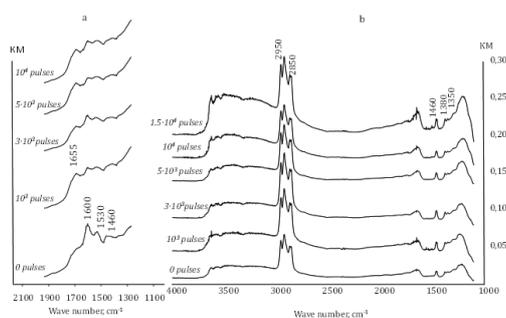


Fig. 2. DRIFT spectra of columbite (a) and eudialite (b) samples after the interaction with Flotisor sm 15 for untreated samples (0 pulses) and samples after the treatment by high-power electromagnetic pulses

Rys. 2. Widma DRIFT próbek kolumbitu (a) i eudialitu (b) po interakcji z Flotisor sm 15 dla próbek nietraktowanych (0 impulsów) i próbek po obróbce impulsami elektromagnetycznymi o dużej mocy

the physical sorption of hydroxamic acid transform into the clear band (Figure 2a) for the samples after the treatment by high-power electromagnetic pulses that indicates an increase in the quantity of physically adsorbed collector.

IR spectra of treated and untreated eudialite samples after the contact with Flotisor sm 15 are shown in Figure 2 b. The presence of the bands indicating the adsorption of the reagent were identified: 1350 cm^{-1} ; 1380 cm^{-1} ; 1460 cm^{-1} ; 2850 cm^{-1} ; 2950 cm^{-1} . At the same time, the position of the spectral peaks for the adsorbed Flotisor sm 15 coincides with the spectrum of the pure substance indicating the physical adsorption of the collector.

The calculation of the spectra ' peak areas demonstrates that the preliminary high-power electromagnetic treatment of eudialyte results in the increasing of the Flotisor sm 15 adsorption. The area of the band at 1380 cm^{-1} increases 4.3–7 times (from 0.03 (untreated sample) to 0.124 relative units (10^3 pulses) and further to 0.22 ($5 \cdot 10^3$ pulses), the area of the peak at 1460 cm^{-1} increases by 3.5–7 times (from 0.05 (0 pulses) to 0.18 (10^3 pulses) and further to 0.35 ($5 \cdot 10^3$ pulses).

As a result of studies, it was identified that the use of pulsed energy (high-power electromagnetic pulses) gives a possibility of the minerals technological properties regulation. It was found that usage of high-power electromagnetic treatment of eudialite before the acid leaching allows to increase the zirconium recovery of 1.7 times and $\Sigma\text{ REE}$ – 1.4 times [10]. It is shown that the usage of high – power electromagnetic treatment ($N\text{ pulses} = 5 \times 10^3 \div 10^4$) allows to improve the columbite floatability by 4–9% [11].

Conclusion

The structural and chemical transformations of the manganocolumbite surface as a result of non-thermal treatment by high-power nanosecond electromagnetic pulses were studied. According to XPS data, at the initial stages at low treatment durations (from 10^3 pulses to 5×10^3 pulses), the surface state of mineral was characterized by the presence of hydroxyl groups and adsorbed water molecules. With the increasing of the treatment duration up to $5 \times 10^3 - 1.5 \times 10^4$, chemisorbed water and hydroxogroups were removed from the surface of columbite.

With usage of DRIF was defined that treatment by high-power electromagnetic pulses allows to control the physicochemical properties of columbite and eudialyte. The growth of the sorption activity for eudialyte towards Flotisor sm 15 was defined. It was identified that the areas of the bands describing the adsorption of the reagent into mineral surface increased on average 4 to 7 times for the samples after the high-power electromagnetic treatment. It is shown that treatment by high-power electromagnetic pulses results to the increasing of the of manganocolumbite sorption activity towards octanohydroxamic acid. The shoulder at 1670 cm^{-1} , identified for the untreated sample and corresponding to the physically adsorbed reagent transform in the clear absorption band in the case of the sample that was treated by high-power electromagnetic pulses.

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Wpływ impulsów elektromagnetycznych dużej mocy na właściwości strukturalne, chemiczne i fizykochemiczne minerałów ziem rzadkich

Badanie modyfikacji stanu strukturalno-chemicznego i właściwości sorpcyjnych powierzchni kolumbitu i eudialitu pod wpływem impulsów nanosekundowych o dużej mocy (HPEMP) przeprowadzono za pomocą XPS i FTIR. Ustalono, że wstępna obróbka minerałów metali rzadkich impulsami nanosekundowymi o dużej mocy jest obiecującym narzędziem do kierunkowych zmian ich właściwości fizykochemicznych i strukturalno-chemicznych, co zostało potwierdzone przez zwiększenie aktywności sorpcyjnej minerału.

Słowa kluczowe: kolumbit, eudialyte, impulsy elektromagnetyczne dużej mocy, XPS, FTIR