

# **Effect of High-Power Nanosecond Electromagnetic Pulses and Dielectric Barrier Discharge in Air on the Structural, Physicochemical and Flotation Properties of Eudialyte**

Igor Zh. Bunin<sup>(⊠)</sup>, Valentine A. Chanturiya, and Mariya V. Ryazantseva

N.V. Mel'nikov Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Science, Moscow, Russia

bunin\_i@mail.ru

**Abstract.** Eudialyte is a rock and ore-forming mineral of lujaurites and uvites with its content in these rocks up to 20–30%, and an eudialyte group minerals are currently viewed as major rock-forming minerals in the super-large rare-metal deposits in the world. In Russia, eudialyte ores of the Kola Peninsula are the promising source for rare and rare-earth metal production. The application of advanced high-power electric discharge technologies in the processing of rebellious minerals and ores allows achieving effective disintegration and separation of fine disseminated mineral complexes and creating optimal conditions to provide the high contrast of the microstructural, physicochemical and technological (flotation) properties of mineral components and subsequent separation during flotation due to the appearance of hydrophobic and hydrophilic nanoformations on their surface. In this paper, we used analytical scanning electron microscopy (SEM-EDX) and Fourier-transform infrared spectroscopy (FTIR), microhardness testing, flow potential determination, laboratory flotation testing and other techniques to study the influence of high-power nanosecond electromagnetic pulses (HPEMP) and dielectric barrier discharges (DBD) in air at the atmospheric pressure on the structural surface state, microhardness, physicochemical, and technological properties of eudialyte. The dominant mechanisms of surface softening, and directional change in the surface morphology, structural-chemical, physicochemical and flotation properties of eudialyte under non-thermal exposure to high-voltage nanosecond pulses and low temperature plasma of DBD are studied. Our results show it is possible in principle to use electromagnetic pulsed energy effects to improve the effectiveness of disintegration and to alter technological (flotation) properties of eudialyte-group rock-forming minerals.

**Keywords:** Eudialyte · High-power nanosecond electromagnetic pulses · Dielectric barrier discharge · Surface · Microscopy · Microhardness · Electrokinetic potential · Contact angle · Flotation

# **1 Introduction**

At the present time, both in Russia and globally, eudialyte ores with significant concentrations of hafnium, zirconium, niobium, and rare-earth elements (REEs) are considered a perspective natural source of rare metals (RMs) and REEs [\[1\]](#page-9-0). For example, eudialyte ores of the Lovozero deposit (Kola Peninsula, Russia) are characterized by an high enough content of hafnium  $0.2-0.3\%$  of HfO<sub>2</sub>, zirconium  $11-13\%$  of ZrO<sub>2</sub>, niobium and titanium  $0.6-1.0\%$  of Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>, tantalum 0.06–0.10% of Ta<sub>2</sub>O<sub>5</sub>, strontium  $0.2-1.5\%$  of SrO as well as REE (Sm, Gd, Tb, Er, Y) [\[1,](#page-9-0) [2\]](#page-9-1). Eudialyte is a rock and ore-forming mineral of lujaurites and uvites with its content in these rocks up to 20–30%, and an eudialyte group minerals are currently viewed as major rock-forming minerals in the super-large rare-metal deposits in the world. The ideal chemical formula of eudialyte (the Khibiny reference sample) is  $Na<sub>15</sub>Ca<sub>6</sub>Fe<sub>3</sub>Zr<sub>3</sub>Si(Si<sub>25</sub>O<sub>73</sub>)$ (O, OH, H<sub>2</sub>O)<sub>3</sub>(Cl, OH)<sub>2</sub>  $[1–3]$  $[1–3]$ . The framework part of the eudialyte structure is centrosymmetric, has a strong negative charge (~–24) and consists of alternating layers (*TZTM*…) along the *c*-axis, where the *T*-layers are mutually isolated silicon-oxygen rings  $[Si_9O_{27}]$  and  $[Si_3O_9]$ , where the *Z*-layers are discrete Zr- and/or Ti-octahedra and the *M*-layers are discrete six-membered rings of  $Ca_6O_{24}$  composed of calcium octahedra [\[2\]](#page-9-1). The structural motives (rings) of eudialyte are connected by additional atoms (cations) of Fe, Na, Zr, Mn, and Ti (Ta) with coordinate numbers of 4–6; the framework cavities contain additional cations with valences from  $+1$  to  $+6$ , additional anions, anion groups, and water molecules [\[2\]](#page-9-1).

The application of the gravitational-magnetic separation method ensures the high concentration of eudialyte ores and recovery of eudialyte into concentrate up to 75–80%. The eudialyte group minerals are highly soluble in mineral inorganic acids, however, in the process of acid leaching, the recovery of zirconium does not exceed 75%. The main losses of Hf, Zr, Nb, Ta and REE are associated with the transition of silicon to the solution in the form of silicic acids and formation of silica gels, in which Si and Zr polymerize forming hydrated silica-based polymers [\[1\]](#page-9-0). To reduce the loss of RM and REE elements, it is recommended to use mechanical activation, physicochemical and energy effects on rebellious ores as preparatory operations before the leaching of concentrates and eudialyte flotation. Ultrasonic treatment of mineral suspension during acid leaching of eudialyte concentrate provided the maximum concentration of zirconium and  $\sum$ REE in productive mineral solution 87 and 76%, respectively [\[4\]](#page-9-3). As a result of pretreatment of eudialyte concentrate with high-power electromagnetic pulses, an increase in the recovery of valuable components during acid leaching was 9.4% for ZrO<sub>2</sub> and 6.4% for  $\sum$ REE [\[5\]](#page-9-4).

The application of advanced high-power electric discharge technologies [\[6](#page-9-5)[–13\]](#page-10-0) in the processing of rebellious minerals and ores allows achieving effective disintegration and separation of fine dissiminated mineral complexes and creating optimal conditions to provide the high contrast of the microstructural, physicochemical and technological (flotation) properties of mineral components and subsequent separation during flotation due to the appearance of hydrophobic and hydrophilic nanoformations on their surface.

# **1.1 Research Purpose**

The effectiveness and mechanism were examined behind the effects of nonthermal impact of high-power nanosecond electromagnetic pulses and dielectric barrier discharges in air under standard conditions on the morphology and chemical composition of the surface, microhardness, electrical, physicochemical properties, adsorbability and floatability of eudialyte from the Lovozero deposit.

# **1.2 Research Scope**

In this paper, we studied the following aspects of the research problem:

- (i) a comparative analysis of the mechanisms of nonthermal action of repetitive high-power nanosecond electromagnetic pulses (HPEMP) [\[6\]](#page-9-5) and low-temperature plasma of dielectric barrier discharge (DBD) [\[14\]](#page-10-1) in air at atmospheric pressure on the structural, physicochemical, and flotation properties of eudialyte;
- (ii) direct changes in the chemical composition and surface softening (decrease in microhardness; formation of surface defects) of eudialyte in the result of exposure to HPEMP and DBD for achieving a controlled change in electrical properties, hydrophilic-hydrophobic surface balance, and flotation activity of mineral;
- (iii) effective modes and conditions of pulsed power mineral samples treatment through a nonthermal action of nanosecond HPEMP and non-thermal plasmas of DBD to improve the flotation activity of eudialyte in order to increase the efficiency of flotation concentration of complex eudialyte ores.

# **2 Experimental**

# **2.1 Materials and Research Technique**

The investigations were carried out on eudialyte samples from the Lovozero deposit (Kola Peninsula, Russia), with particle-size classes from 630 to 63  $\mu$ m (97.7%) in size. For adsorption and flotation experiments, we used the eudialyte mineral particles from 100 to 63  $\mu$ m in size. The size of the plane-parallel polished sections was  $10 \times 10 \times 4.5$  mm. The chemical formula of the investigated eudialyte is:  $\text{Na}_{15}\text{Ca}_{6}\text{(Fe}^{2+}, \text{Mn}^{2+})_{3}\text{Zr}_{3}\text{[Si}_{25}\text{O}_{73}]$  $(0, OH, H<sub>2</sub>O<sub>3</sub>(OH, Cl)<sub>2</sub>$  [\[5\]](#page-9-4). The chemical composition of eudialyte concentrate  $(\%)$ is: Si (22.7); ZrO<sub>2</sub> (8.34); TiO<sub>2</sub> (3.99); Fe (3.24); Ca (3.33); Al (3.0);  $\sum$ REE (2.5); Mn  $(1.42)$ ; SrO  $(1.95)$ ; Nb<sub>2</sub>O<sub>5</sub>  $(0.94)$ ; Mg  $(0.20)$ ; BaO  $(0.15)$ . The eudialyte concentrate included the following minerals: eudialyte, nepheline, loparite, lamprophyllite, aegirine and albite [\[4,](#page-9-3) [5,](#page-9-4) [12\]](#page-10-2).

The conditions of exposing the eudialyte samples to the effect of nanosecond HPEMP and irradiation from the low-temperature nonequilibrium plasma (LTP) of DBD in air under standard conditions were described in  $[15-17]$  $[15-17]$ , along with the electrophysical parameters of the high-voltage pulse generators. The duration of sample treatment varied in the range of  $t_{\text{treat}} = 10-150$  s. With the HPEMP effect, the duration of high-voltage nanosecond pulses was  $4-10$  ns. Pulse amplitude was  $U \sim 25-30$  kV; strength of the electric field in the 5 mm interelectrode gap,  $E \sim 10^7$  V  $\times$  m<sup>-1</sup>; rate of nanosecond pulse

repetition was  $f = 100$  Hz. Electrode voltage in the cell of the barrier discharge generator (DBD) was 20 kV; pulse duration was  $8 \mu s$ ; duration of a pulse leading edge was  $\sim$ 300 ns; rate of pulse repetition was 15 kHz; length of interelectrode gap was  $\sim$ 5 mm [\[16\]](#page-10-5).

The structural state modification of eudialyte surface (morphology, defects and chemical composition) in the result of electromagnetic pulse effects was analyzed on the planeparallel polished sections of the mineral by means of analytical electron microscopy (SEM-EDX). The mineral's microhardness was determined according to Vickers (*HV*, MPa) using the procedure in [\[18\]](#page-10-6) and a PMT-3M microhardness tester. The load on the indenter was 200 g, and the period of loading was 10–15 s.

The streaming (flow) potential ( $\zeta$  -potential, mV) of mineral particles (size  $\leq 50 \,\mu$ m) was determined using a Microtrac ZETA-Check Zeta Potential Analyzer. The contact angle of wetting  $(\Theta^{\circ})$  of polished sections of the mineral surfaces with water before and after energy treatment was measured with sessile drops of distilled water ("resting" on the surface)  $\sim$  2–3 mm in diameter, following the procedure in [\[16\]](#page-10-5). Analysis was done using a digital optical microscope and the ImageJ program with special DropSnake and LB-ADSA plug-ins [\[19\]](#page-10-7).

The method for determining the adsorption of caprylhydroxamic acid (IM 50), sodium oleate and the Clariant Flotinor SM-15 reagent on the surface of eudialyte particles before and after irradiation to HPEMP and DBD included the stages of agitation of mineral samples with reagent solutions, separation of the solid phase by filtration, followed by washing, drying of filtrate particles and analysis of mineral particle surface by Fourier-transform infrared spectroscopy (FTIR, spectrophotometer Shimadzu UV-1700) [ $20$ ]. The flotation tests of the weighed mineral samples (3.0 g) were performed in the chamber of a flotation machine with a volume of 20 mL: the samples were agitated in an aqueous medium for 1 min; during this time, the pH of the medium was adjusted to a value of 6.0 for caprylhydroxamic acid, 9.0 for sodium oleate, and 3.5 for the Flotinor SM-15 reagent. Then, we supplied a collector, the contact time of the mineral with the reagent was 3 min; foam product selection was 1.5 min.

#### **3 Results and Discussions**

#### **3.1 Effect of HPEMP and DBD on the Morphology and Defects of Eudialyte Surface**

According to SEM data, the original (native) eudialyte grains had a conchoidal fracture, forming a concave profile of smooth surface areas separated by sharp uneven edges (Fig. [1a](#page-4-0)). The non-thermal effect of HPEMP caused damage to the surface of a significant part of the mineral grains with the formation of new forms of surface relief. Depending on the processing time  $(t<sub>treat</sub>)$ , the surface relief of mineral particles became parallelfractured at  $t_{\text{treat}} = 30$  s (Fig. [1b](#page-4-0)) and polygonal-fractured at  $t_{\text{treat}} = 60$  and 90 s (Fig. [1c](#page-4-0)). We revealed the coarsening of the surface relief, as evidenced by an increase in the arithmetic mean roughness  $R_a$ : the maximum increase in a R (from 0.33 to 1.8–2  $\mu$ m) recorded at  $t_{\text{treat}} = 150$  s.

In the result of processing under DBD conditions, for all the modes of energy exposure used, the formation of a different number of imprints of current microchannels of electrical breakdown no larger than  $3-4 \mu m$  in size (Fig. [1d](#page-4-0)) is a characteristic (distinctive) feature of the eudialyte grains micromorphology. For a larger number of grains, we found a few current channels; however, among the studied samples, the individual particles contained a large number of such defects (Fig. [1e](#page-4-0)). In the case of a barrier discharge action, microcracking (microdamages) of the mineral surface, which is characteristic of samples after exposure to HPEMP, is less developed or practically absent. Detailed studies of the surface areas between the microchannels revealed neoformations with a size of 500 nm or less, closely adjacent to each other (Fig. [1f](#page-4-0)). The crystalline microfragments with a size of  $1-2 \mu m$  were removed from the mineral surface, apparently due to the action of ponderomotive forces. At  $3 \times 3 \mu m^2$  in size of the scan under microscopic analysis, the arithmetic mean roughness of the surface profile  $R_a$  was from 2.1 to 5.7 nm before and after exposure to DBD ( $t_{\text{treat}} = 150 \text{ s}$ ), respectively.



<span id="page-4-0"></span>**Fig. 1** Micrographs of eudialyte surface: (**a**) before and (**b–f**) after exposure by (**b**, **c**) high-power nanosecond electromagnetic pulses and (**d–f**) dielectric barrier discharge (*t*treat = 50–100 s); (**a–e**) SEM, (**f**) AFM; the scales are (a) 50, (b) 100, (c) 80, (d) 20, (e) 100, and (f)  $3 \times 3 \mu m^2$ 

The spectral (FTIR) curves of the native (before pulsed electromagnetic energy treatment) eudialyte sample and the mineral samples after the nanosecond HPEMP and DBD irradiation are shown in Fig. [2.](#page-6-0) An analysis of the spectral curve profiles showed the following results. In the region of stretching vibrations of the Si–O bond of the native sample, we identified five absorption bands: 940, 980, 1010, 1070, and 1135 cm<sup>-1</sup>. For the HPEMP treated sample ( $t<sub>treat</sub> = 30$  s), the 940 cm<sup>-1</sup> band was smoothed out, and with a longer treatment time ( $t_{\text{treat}} = 60$ , 80–90 s), this band was transformed into a shoulder of about 900 cm<sup>-1</sup>. Also, a very weak shoulder near 1100 cm<sup>-1</sup> appeared.

According to the experimental data  $[1–3, 21]$  $[1–3, 21]$  $[1–3, 21]$  $[1–3, 21]$ , the presence of a band at 940 cm<sup>-1</sup> in the FTIR spectrum indicates a high content of ten-membered disks  $Si<sub>10</sub>O<sub>27</sub>$ ,  $Si<sub>9</sub>MO<sub>30</sub>$  in the structure of the eudialyte. Therefore, the observed changes in the spectral curves can be associated with the destruction of the silicon–oxygen framework of the mineral. Such damage to the eudialyte structure occurs due to the destruction of the bond inside  $Si<sub>10</sub>O<sub>27</sub>$ , and  $Si<sub>9</sub>MO<sub>30</sub>$  disks. Thus, it should be assumed that when high-voltage pulsed fields (HPEMP or DBD) act on eudialyte particles, the mineral surface undergoes structural changes, which manifest themselves in changes in the IR-spectra of the mineral Fig. [2.](#page-6-0) These changes are the result of the deformation and/or local destruction of the silicon–oxygen framework of eudialyte. The minerals of the eudialyte group are the natural analogues of zeolite-like microporous materials (amphoterosilicates) with a complex structure of mixed frameworks [\[22\]](#page-10-10). Therefore, the migratory (interlayer) and/or electron-relaxation polarization [\[23\]](#page-10-11) of the eudialyte under the action of high-voltage electric fields (HPEMP) is a probable mechanism of microdamages in these crystals. Also, under the conditions of DBD-radiation, the pressure of the gas (low-temperature plasma), formed in the process of local spark (plasma) discharges, affects on the mineral surface.

Migration polarization manifests itself in the solid dielectrics with an inhomogeneous structure, microimpurities in the form of conductive and semiconducting microinclusions, and the layers with different conductivity [\[23\]](#page-10-11). This type of polarization occurs due to the movement of weakly bound ions over a considerable distance, which causes the formation of space charges at the boundary of the structural components of the mineral-dielectric and, probably, the mineral substance destruction occurs.

#### **3.2 Effect of High-Power Nanosecond Electromagnetic Pulses and Dielectric Barrier Discharge on Microhardness, Physicochemical and Flotation Properties of Eudialyte**

Microstructural changes in the surface layer of eudialyte caused by non-thermal action of nanosecond HPEMP and (or) low temperature plasma of DBD produced the softening (reduced strength) effect on the mineral surface and a significant decrease in the mineral microhardness (Mohs hardness of eudialyte, 5–5.5). Effect of HPEMP caused high softening of the mineral surface; a monotonic decrease in the microhardness of eudialyte was noted, as the time of electric pulse treatment increased, the microhardness decreased from 740 MPa in the initial state to 560 MPa at  $t_{\text{treat}} = 150$  s, that is the maximum relative change in microhardness ( $\Delta HV_{\text{max}}$ ) was ~24%. Under short-time pulse influences ( $t_{\text{treat}}$ )  $= 10-30$  s), the mineral microhardness decreased considerably ( $HV = 650$  MPa;  $\Delta HV$  $\sim$  12%), which indicates the effectiveness of short-duration energy effects involving strength reducing in dielectric properties of natural minerals [\[18\]](#page-10-6).

Due to the action of the strong electric field, products of low-temperature plasma and other effective factors resulting from a DBD in air, the eudialyte surface softened and mineral microhardness decreased monotonically with an increase in treatment time from  $HV = 790$  to 420 MPa at  $t_{\text{treat}} = 0$  and 150 s, respectively;  $\Delta HV_{\text{max}} \sim 47\%$ . In the case of a short-term mineral treatment ( $t_{\text{treat}} = 10 \text{ s}$ )  $HV = 630 \text{ MPa}$ , that is  $\Delta HV \sim$ 20%. Thus, short-term  $(t_{\text{treat}} = 10-30 \text{ s})$  electromagnetic pulse influences are effective for local disintegration of the mineral surface.

As the duration of electromagnetic pulsed treatment (HPEMP and DBD) increased, together with the change in microhardness, such structural-sensitive properties of the

<span id="page-6-0"></span>

**Fig. 2** FTIR spectra of eudialyte before (1) and after (2–4) pulsed electromagnetic energy treatment by (**a**) HPEMP, (**b**) DBD (*t*treat = 30 (2), 60 (3), and Fig. 2 FTIR spectra of eudialyte before (1) and after (2–4) pulsed electromagnetic energy treatment by (a) HPEMP, (b) DBD (t<sub>ireat</sub> = 30 (2), 60 (3), and 90 (4) s) mineral surface as electrokinetic potential, and contact angle of wetting changed significantly. In the liquid phase of the mineral suspension, the cations Na, Fe, Mn, which passed into the liquid phase during dissolution in deionized water, were ions that determined the potential near the surface of eudialyte particles (with a negative frame charge [\[2\]](#page-9-1)). The hydroxyl groups of the liquid phase (hydroxide anions) were counterions (in the electric double layer), which determines the negative sign of the electrokinetic potential of eudialyte in a neutral medium. In the result of HPEMP treatment, we observed a decrease in the negative values of the electrokinetic potential of eudialyte particles from –96.5 mV in the native state to –81.5 mV at  $t_{\text{treat}} = 50$ –100 s. As the treatment time increased to  $t_{\text{treat}} = 150$  s, an increase in the negative values of the electrokinetic potential to −85 mV occurred.

The impact of a DBD caused a nonmonotonic change in the electrokinetic potential of eudialyte particles with increasing treatment time  $(t_{\text{treat}} = 10{\text -}150 \text{ s})$ . A short-term  $(t<sub>treat</sub> = 10 s)$  irradiation of DBD contributed to an increase in the negative values of the electrokinetic potential to –110 mV. In the range of changes in the mineral treatment time  $t_{\text{treat}} = 30 - 150$  s, we observed a monotonous decreasing in the potential to  $-87$  mV  $(t_{\text{treat}} = 30 - 50 \text{ s})$  and  $-82 \text{ mV}$  at  $t_{\text{treat}} = 150 \text{ s}$ . Based on the electrochemical mechanism of fixing the flotation reagent-collector on eudialyte surface, this established pattern of the electrokinetic potential change allows us to make a prediction about the possibility of increasing the sorption of the anionic reagent (sodium oleate) (after short HPEMP or DBD mineral pretreatment at  $t_{\text{treat}} = 30 - 50$  s), and increasing the extraction of eudialyte during flotation.

With increased time of electromagnetic pulsed actions (both HPEMP and DBD), the water contact angle of the eudialyte surface wetting changed nonmonotonically: at  $t_{\text{treat}} = 10-30$  s, the contact angle increased from 57° ( $t_{\text{treat}} = 0$  s) to 63° ( $t_{\text{treat}} = 10$  s, HPEMP) and to 73–77.5° ( $t_{\text{treat}} = 10$ –30 s, DBD). It is possible that the established effect of increasing the hydrophobicity of the eudialyte surface in the result of relatively short-term energy impacts ( $t_{\text{treat}} \sim 30 - 50$  s) causes an enhancement (increase) of the sorption and flotation mineral properties. In the range of change  $t_{\text{treat}} = 50{\text -}150$  s, the contact angle decreased to 55–57°.

Previously [\[20\]](#page-10-8), using Fourier-transform infrared spectroscopy (FTIR) method, we found that eudialyte treatment by HPEMP within  $t_{\text{treat}} = 10$  and 50 s causes an increase in the sorption of the Flotinor SM-15 reagent on the surface of mineral particles. At the same time, the sorption properties of eudialyte did not change with respect to sodium oleate and caprylhydroxamic acid. In the result of the impact of the DBD during  $t_{\text{treat}} =$ 10 s and  $t_{\text{treat}} = 300-480$  s, the sorption of the Flotinor reagent on the surface of mineral particles increased by 1.5 and 2.2 times, respectively. DBD treatment in the range of  $t_{\text{treat}} = 30{\text -}150$  s caused a decrease in the reagent adsorption by 1.8–2.4 times.

To study the sorption activity of eudialyte particles modified under HPEMP conditions, in [\[17\]](#page-10-4) we conducted the experiments to study the adsorption mechanism of collecting agent (sodium oleate, NaOl) and combination of NaOl and sodium sulfate  $(Na_2SO_3)$ regulating agent. The results of the adsorption and spectroscopic (FTIR) experiments were testified to an increase in the sorption activity of eudialyte with respect to NaOl and with a combination of NaOl and  $Na<sub>2</sub>SO<sub>3</sub>$  reagents in the result of HPEMP pretreatment of mineral particles in the range of irradiation time  $t_{\text{treat}} = 10{\text -}100 \text{ s}.$ 

Based on the results obtained on the change in the electrokinetic potential of eudialyte (potential shift towards positive values), an increase in the contact angle and an increase in the sorption of reagents, we studied the effect of HPEMP and DBD pretreatment ( $t_{\text{treat}} =$ 10–150 s) on the flotation properties of the eudialyte concentrate. We studied the change in the flotation properties of the eudialyte concentrate in the presence of environmental regulators (Na<sub>2</sub>SO<sub>3</sub> and  $\text{Al}_2(\text{SO}_4)_{3}$ ) in combination with NaOl and gangue depressants (Na<sub>2</sub>P<sub>6</sub>O<sub>18</sub>, flow rate 50 g/t and C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>—25 g/t in combination with Flotinor).

In the result of a short-term  $t_{\text{treat}} = 10-30$  s HPEMP concentrate pretreatment, an additional increase in the total eudialyte into concentrate recovery by 10–15% occurred. The recovery was  $\varepsilon = 57\%$  ( $t_{\text{treat}} = 10$  s) and 63% ( $t_{\text{treat}} = 30$  s) due to a change in the structural and chemical state of the mineral particles surface, an increase in the hydrophobicity and sorption activity of eudialyte. The  $Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>$  reagent is a stronger activator of the eudialyte flotation process, the combination of this reagent with sodium oleate had a significant effect on the flotation properties of the eudialyte concentrate: the eudialyte into concentrate extraction during flotation was 80%, and after HPEMP concentrate pretreatment ( $t_{\text{treat}} = 50$  s) recovery was 84%.

The impact of the dielectric barrier discharge caused a significant and nonmonotonic change in the flotation properties of the eudialyte concentrate. Preliminary short-term  $(t_{\text{treat}} = 10 - 40 \text{ s})$  treatment of samples with DBD caused a decrease in the recovery of eudialyte into concentrate and into the flotation froth by  $\sim$ 15–50% (consumption of reagents of 25 g/t for  $C_2H_2O_4$ , 50 g/t for Na<sub>2</sub>P<sub>6</sub>O<sub>18</sub>, 400 and 600 g/t for Flotinor SM-15), and the greatest depression of minerals was observed at  $t_{\text{treat}} = 10$  s. As the duration of DBD irradiation increased ( $t_{\text{treat}} \ge 50$  s), we observed a smaller decrease in the flotation activity of concentrate minerals. Compared to the initial recovery value  $(\varepsilon)$ , the difference in values was  $\Delta \varepsilon = 5 \text{--} 12\%$ .

Thus, the established parameters of energy effects and reagent regimes of flotation can be used to improve the efficiency (in case of HPEMP impact) and selectivity (DBD) of the flotation process during the processing of eudialyte ores.

# **4 Conclusions**

In the result of the studies carried out using analytical electron microscopy (SEM-EDX), Fourier-transform infrared spectroscopy (FTIR), method of microhardness testing, electrokinetic potential determination, laboratory flotation testing and other techniques, there were identified mechanisms of the non-thermal action of high-power nanosecond electromagnetic pulses and low-temperature plasma of dielectric barrier discharge on the morphology and defects of surface, and structural surface state, as well as on the structurally sensitive (microhardness, electrokinetic potential, contact angle, sorption) properties of eudialyte and flotation properties of eudialyte concentrate.

For the first time ever, we described the effect of a change in the structural and chemical properties of eudialyte surface as a result of high intensity electric fields of HPEMP and DBD action initiating mineral surface fracturing due to the softening and breaking of bonds in the structural fragments of the mineral framework (apparently,  $Si<sub>10</sub>O<sub>27</sub>$ , and  $Si<sub>9</sub>MO<sub>30</sub>$  disks).

According to the SEM data, the formation of new surface reliefs in the range  $t_{\text{treat}}$ = 30–60 s from parallel to polygonal fractured shapes under HPEMP irradiation was

observed. Effect of HPEMP caused high softening of the mineral surface; as the time of electric pulse treatment increased, the microhardness decreased from 740 MPa in the initial state to 560 MPa at  $t_{\text{treat}} = 150$  s; the  $\Delta HV_{\text{max}}$  was ~24%. After the treatment under DBD, the micromorphology of eudialyte surface is distinctively characterized by the presence of imprints of electrical current breakdown microchannels of up to 3–  $4 \mu$ m. Due to the action of the strong electric field, products of low-temperature plasma and other effective factors resulting from a DBD in air, the microhardness of eudialyte surface was decreased from  $HV = 790$  to 420 MPa at  $t_{\text{treat}} = 0$  and 150 s, respectively;  $\Delta HV_{\rm max} \sim 47\%.$ 

We developed the following effective parameters of electromagnetic pulse treatment: HPEMP is a duration of high-power nanosecond pulses of 4–10 ns; pulse amplitude is *U*  $\sim$  20–30 kV; rate of nanosecond pulse repetition is  $f = 100$  Hz, and DBD is a electrode voltage in the cell of  $\sim$ 20 kV; pulse duration is 8–10  $\mu$ s; duration of pulse leading edge is  $\sim$  300 ns; rate of pulse repetition is 15 kHz.

Based on the results obtained on the change in the electrokinetic potential of eudialyte (potential shift towards positive values), an increase in the contact angle and an increase in the sorption of reagents, we studied the effect of HPEMP and DBD pretreatment on the flotation properties of the eudialyte concentrate. The intensifying effect of highpower electromagnetic pulses on the process of eudialyte concentrate flotation has been experimentally established, and the advantages of using the short-term  $(t_{\text{treat}} = 10-30,$ 50 s) energy impacts for enhanced efficiency of complex eudialyte-bearing ore flotation are justified.

**Acknowledgements.** This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation, project No. 13.1902.21.0018 (agreement No. 075-15-2020- 802). We are grateful to PhD (geological and mineralogical sciences) E.V. Koporulina, and to the PhD (technical sciences) N.E. Anashkina for their help in the experimental studies.

# **References**

- <span id="page-9-0"></span>1. Rastsvetaeva RK, Chukanov NV, Aksenov SM (2012) Eudialyte-group minerals: crystal chemistry. Nizhny Novgorod State University Press, Nizhny Novgorod, Properties and Origin (In Russian)
- <span id="page-9-1"></span>2. Rastsvetaeva RK (2007) Crystallogr Rep 52(1):47
- <span id="page-9-2"></span>3. Rastsvetaeva RK, Chukanov NV, Pekov IV et al (2020) Minerals 10(587):1
- <span id="page-9-3"></span>4. Chanturiya VA, Minenko VG, Samusev AL et al (2017) J Min Sci 53(5):890
- <span id="page-9-4"></span>5. Chanturiya VA, Bunin IZ, Ryazantseva MV et al (2018) J Min Sci 54(4):645
- <span id="page-9-5"></span>6. Chanturiya VA et al (1999) Trans Russ Akad Sci 366(5):680
- 7. Chanturiya VA, Bunin IZ, Ryazantseva MV, Filippov LO (2011) Miner Process Extr Metall Rev 32(2):105
- 8. Kurets VI, Solov'ev MA, Zhuchkov AI, Barskaya AV (2012) Electric discharge technologies for processing and destruction of materials. Tomsk Polytechnical University Press, Tomsk (In Russian)
- 9. Punanov IF, Zhidkov IS, Cholakh SO (2018) High-voltage nanosecond breakdown of condensed media. Ural State University Press, Yekaterinburg (In Russian)
- 10. Chanturiya VA (2017) Gornyi Zhurnal (11):7 (In Russian)
- 11. Bunin IZ, Ryazantseva MV, Samusev AL, Khabarova IA (2017) Gornyi Zhurnal (11):77 (In Russian)
- <span id="page-10-2"></span>12. Chanturiya VA, Minenko VG, Samusev AL et al (2020) Miner Process Extr Metall Rev 41:1
- <span id="page-10-0"></span>13. Huang W, Chena Y (2021) Powder Technol 393(11):116
- <span id="page-10-1"></span>14. Avtaeva SV (2011) Barrier discharge. Lambert Academic Publishing, Saarbrücken, Research and Application
- <span id="page-10-3"></span>15. Chanturiya VA, Bunin IZ, Ryazantseva MV et al (2019) J Min Sci 54(4):645
- <span id="page-10-5"></span>16. Bunin IZ, Chanturiya VA, Ryazantseva MV et al (2020) Bull Russ Acad Sci Phys 84(9):1161
- <span id="page-10-4"></span>17. Chanturiya VA, Bunin IZ, Ryazantseva MV et al (2021) J Min Sci 57(1):96
- <span id="page-10-6"></span>18. Bunin IZ, Chanturiya VA, Anashkina NE et al (2015) J Min Sci 51(4):799
- <span id="page-10-7"></span>19. Stalder AF, Melchior T, Muller M et al (2010) Colloids Surf A: PhysChem Eng Asp 364(1– 3):72
- <span id="page-10-8"></span>20. Chanturiya VA, Bunin IZ, Ryazantseva MV et al (2019) Bull Russ Acad Sci Phys 83(6):789
- <span id="page-10-9"></span>21. Rastsvetaeva RK, Chukanov NV, Pekov IV, Varlamov DA (2020) Vestnik Geonauk (1):3 (In Russian)
- <span id="page-10-10"></span>22. Chukanov NV, Pekov IV, Rastsvetaeva RK (2004) Usp Khim 73(3):227 (In Russian)
- <span id="page-10-11"></span>23. Poplavko YM, Pereverzeva LP, Raevsky IP (2009) Physics of active dielectrics. Southern Federal University Press, Rostov-on-Don (in Russian)