

Synthesis of minerals

Gurbanova O.A.¹, Evdokimov A.I.¹, Antipin A.M.², Volkov A.S.¹, Khasanova S.³, Dimitrova O.V.¹ Hydrothermal synthesis and crystal structure of a new orthophosphate of lithium, aluminum, copper and iron. UDC 548.736

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Abstract. A new orthophosphate of lithium, aluminum, copper and iron was obtained by hydrothermal synthesis in the multicomponent system of $\text{Li}_3(\text{PO}_4)\text{-AlCl}_3\text{-CuCl}_2\text{-FeCl}_2\text{-NiCl}_2$. The structure was determined by x-ray diffraction method, with $a=4.881(1)$, $b=7.819(1)$, $c=8.390(2)\text{\AA}$, $\alpha=69.267(5)^\circ$, $\beta=89.962(8)^\circ$, $\gamma=75.448(3)^\circ$, space group $\text{P}\bar{1}$, $Z=1$ and $V=288,5(5)\text{\AA}^3$. A comparative crystal chemical analysis with isotopic compounds with the general formula of $\text{Li}_5\text{Cu}_2\text{M}(\text{PO}_4)_4$, where $\text{M} = \text{Fe}, \text{Al}$ was conducted.

Keywords: hydrothermal synthesis, orthophosphates.

The compounds containing magnetic ions in the high-spin state (Cu^{2+} , Ni^{2+} , etc.) are of interest as materials with potential magnetic properties. At the same time, the continuing interest in the synthesis of the phosphates containing alkali and transition metals is determined by the presence of compounds whose structural features contribute to the appearance of ion-conducting properties, such as LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) (Padhi AK, 1997, Ait Salah A., 2005, and $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ ($\text{M} = \text{Fe}, \text{Ti}, \text{V}, \text{Al} / \text{Ge}$) (Whittingham MS 2004, Kobayashi E., 2010. Nanjundaswamy KS, 1996). The simultaneous presence of these elements can lead to the appearance of materials with multifunctional properties.

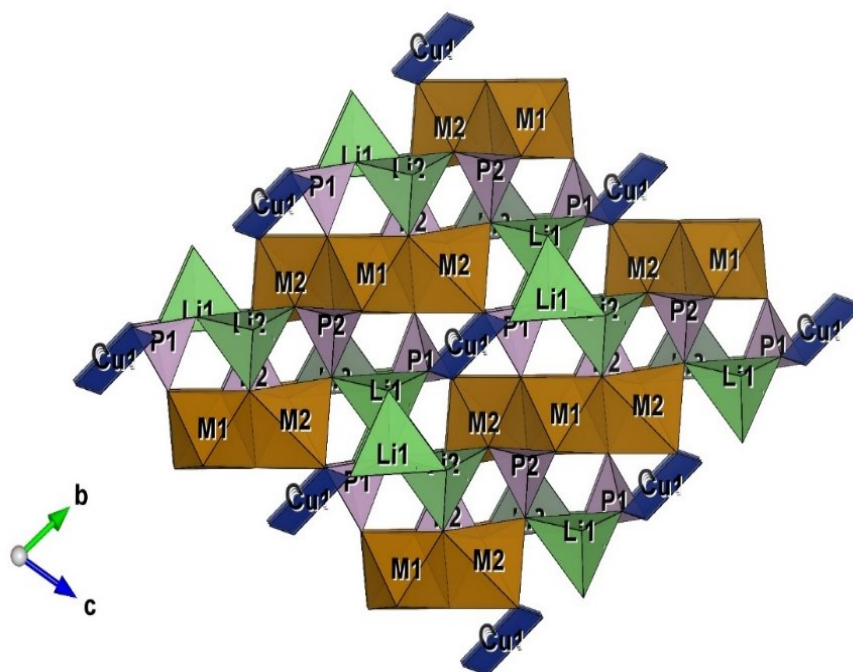


Fig. 1 Crystal structure of $\text{Li}_{3,95}\text{CuFe}_{1,31}\text{Al}_{0,65}\text{Ni}_{0,09}(\text{PO}_4)_4$

The new phase was synthesized under the hydrothermal conditions at $T = 270\text{-}280^\circ\text{C}$ and $P = 70$ atm. in standard 5 cm^3 autoclaves lined with fluoroplastic. Mass ratios of the starting components of the system $\text{Li}_3\text{PO}_4 : \text{Al}(\text{OH})_3 : \text{CuCO}_3 : \text{FeCl}_2 : \text{NiCl}_2 = 5 : 3 : 2 : 3 : 1$; LiCl , NaCl were used as a mineralizer. The duration of the experiment was 20 days. The only hydrothermal crystallization product in the experiment turned out to be prismatic blue crystals with the dimensions of $0.1 \times 0.05 \times 0.05$ mm. According to a qualitative x-ray spectral analysis (JeolJSM-6480LV, INCA Energy-350 energy dispersive diffraction spectrometer) Li, Al, Cu, Ni, P, and O atoms were present in this composition. The

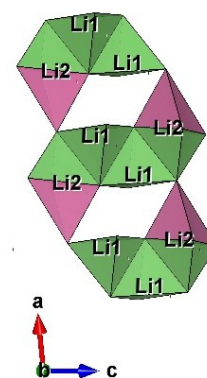


Fig. 2. Fragment of Li tetrahedra (green) and low populated Ni positions (pink) in the crystal structure of $\text{Li}_{3,95}\text{CuFe}_{1,31}\text{Al}_{0,65}\text{Ni}_{0,09}(\text{PO}_4)_4$

preliminary X-ray diffraction study showed the following cell parameters: $a = 4.881(1)\text{\AA}$, $b = 7.819(5)\text{\AA}$, $c = 8.390(2)\text{\AA}$, $\alpha = 69.267(5)^\circ$, $\beta = 89.962(8)^\circ$, $\gamma = 75.448(3)^\circ$ and space group $\text{P}\bar{1}$. Similar parameter values were also found in the compounds of $\text{Li}_5\text{Cu}_2\text{Al}(\text{PO}_4)_4$ (Shvanskaya L.V., Yakubovich O.V., 2014) and $\text{Li}_5\text{Cu}_2\text{Fe}(\text{PO}_4)_4$ (Upreti S., Yakubovich OV, 2011), the resulting compound was their Li, Cu, Al, Fe and Ni analogue. A set of diffraction reflections of this crystal was obtained at room temperature on a Xcalibur S CCD single crystal diffractometer using $\text{MoK}\alpha$ radiation with $\lambda = 0.71073\text{\AA}$ for the complete inverse sphere in angular ranges θ 3.35-50.3. The crystal structure was solved

by direct methods and refined in the anisotropic approximation of thermal fluctuations of atoms using the SHELX97 program (Sheldrick, 1997) to $R[F_2 > 2(F_2)] = 0.041$, $wR(F_2) = 0.08$, $S = 1.33$, the number of independent reflections was 1014.

The resulting formula obtained was $\text{Li}_{3.95}\text{CuFe}_{1.31}\text{Al}_{0.65}\text{Ni}_{0.09}(\text{PO}_4)_4$.

The studied compound is described in comparison with the isostructural compounds $\text{Li}_5\text{Cu}_2\text{Al}(\text{PO}_4)_4$ and $\text{Li}_5\text{Cu}_2\text{Fe}(\text{PO}_4)_4$. In their structures, the triples from pentahedrons (Cu) and octahedra (Al, Fe,) connected by common edges and the phosphorus tetrahedra connected with them by common vertices were distinguished (Fig. 1).

As in the above-mentioned structures both lithium positions also contain vacancy defects. In the distorted pentahedrons Li1 and Li2 the four nearest oxygen atoms are located at 1.946 (5) – 2.086 (5) and 1.866 (5) – 2.246 (6) Å, respectively, which correlates with the studied compound. An increased distance from the additional fifth oxygen atom and Li (2.80 Å) in this compound and satisfactory values of the bond balance sum make it possible to take it into account as belonging to the second coordination sphere and not to include Li in the tetrahedral environment. The coordination polyhedron with low occupation by Ni atoms near the position of Li2 atoms is a distorted tetragonal pyramid with cation – oxygen distances in the range of 1.85 (1) – 2.25 (1) Å. (Fig. 2). A similar polyhedron with a very low occupancy by Cu atoms is observed both in the $\text{Li}_5\text{Cu}_2\text{Al}(\text{PO}_4)_4$ compound, with a wide variation in bond lengths of 1.82 (2) – 2.53 (2) Å and in the $\text{Li}_5\text{Cu}_2\text{Fe}(\text{PO}_4)_4$ structure with Fe atoms in the position (1.891–2.334 Å). In the $\text{Li}_5\text{Cu}_2\text{Al}(\text{PO}_4)_4$ structure the authors discuss the theoretical possibility of two-dimensional cationic conductivity by lithium ions due to presence vacancies in the Li1, Li2 positions and the mixed Cu/Li structural position. The studied structure also has a small deficiency of Li in the Li1 and Li2 positions, however, filling the mixed M2 Fe/Al structural position excludes the possibility of conductivity. The number of Li atoms in the structure studied is smaller than that of Cu, Fe and Cu, Al analogues due to the presence of both Fe and Cu in the structure, which, in addition, leads to a significant deficiency in M2 position occupied by $0.2\text{Fe} + 0.325\text{Al}$.

Phosphorus atoms occupy two independent crystallographic positions of a general type with average P – O bond lengths in the tetrahedra of 1.536 (2) and 1.538 (2) Å, which coincides with similar values in the structures of Fe and Al analogues 1.536 (2) and 1.539(2) Å.

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- Kovalskaya T.N.¹, Ermolaeva V.N.¹, Varlamov D.A.¹, Kalinin G.M.¹, Kovalskiy G.A.^{1,2}, Chaychuk K.D.¹ Synthesis of eudialyte from alkaline pegmatites. Preliminary data.**
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- Abstract:** The paper describes the results of the first experiments on the synthesis of zirconosilicate - eudialyte, which is a typical rock-forming mineral of ultra-alkaline complexes (Lovozerky, Khibinsky) and related pegmatites. The experiments were carried out at temperature 600 °C and pressure 2 kbar. Natural eudialyte from pegmatite from the Northern quarry of the Umbozero mine (Lovozero massif) was used as a seed (1% from start materials mass). As a result of experiments small crystals of eudialyte were observed.
- Keywords:** eudialite, synthesis, hydrothermal conditions, alkaline pegmatites.
- Eudialyte, whose perfect formula is $\text{Na}_{15}\text{Ca}_6\text{Fe}_{2+3}\text{Zr}_3(\text{Si}_{26}\text{O}_{73})(\text{O},\text{OH},\text{H}_2\text{O})_3(\text{Cl},\text{OH})_2$, is one of the most important zirconosilicates (Rastsvetaeva et al., 2020) widespread in ultra-alkaline massifs (Lovozerky, Khibinsky) (Yakovenchuk et al., 1999). However, its synthesis remains an urgent problem in experimental mineralogy while the process of decomposition of eudialyte under various conditions and the release of metal cations from it has been thoroughly studied (Smirnova et al., 2015).
- Experiments on its synthesis were carried out in order to determinate the physical and chemical conditions for the formation of eudialyte. Experiments on the synthesis of eudialyte were conducted in platinum ampoules with a diameter of 4-5 mm on high-pressure gas installations at a temperature of 600 °C and pressure of 2 kbar, which corresponds to the physical and chemical conditions for the formation of high-temperature pegmatites of the Lovozerky and Khibinsky massifs (Ageeva et al., 2002; Pekov, 2004). Stoichiometric gels of simplified eudialytic compositions were used as starting materials. To create a gel with gel method

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next reagents were used: Na_2CO_3 , CaO , Fe_2O_3 , ZrOCl_2 and amorphous SiO_2 . Natural eudialyte of the Lovozero massif (pegmatite of the Northern quarry of the Umbozero mine) was used as a seed in amount

of 1-3% of the weight of the quantities weighted for experiment.

Table 1. Compositions (wt. %) of synthetic eudialytes

component	experiment 23		experiment 24		experiment 25	
	seed	new eudialyte	seed	new eudialyte	seed	new eudialyte
SiO_2	53,56	49.91	55.13	50.12	53.81	51.02
ZrO_2	18.59	15.12	19.1	16.03	18.43	17.89
TiO_2	0.07	0	0.1	0	0.1	0
Al_2O_3	0.24	0.09	0.17	0.1	0.19	0.15
Fe_2O_3	0.28	1.61	0.21	1.32	0.25	1.16
MnO	0	0	0	0	0	0
MgO	0	0	0	0	0.1	0
CaO	15,41	17,41	15,29	16,95	15,01	16.23
Na_2O	7,84	11,50	7,55	10,36	7,73	10.67
K_2O	0	0	0,07	0	0	0
SrO	0,79	0,99	0,81	0,13	0,75	0.45
Nb_2O_5	0,82	0,17	0,78	0,15	0,80	0.11
La_2O_3	0,25	0,15	0,20	0	0,23	0
Ce_2O_3	0,25	0	0,15	0	0,20	0
Cl	1.8	2.45	2.1	1.96	2.16	0
F	0	0	0	0	0	2.15
Total	99,2	98.70	99,6	97,12	97,6	99.83

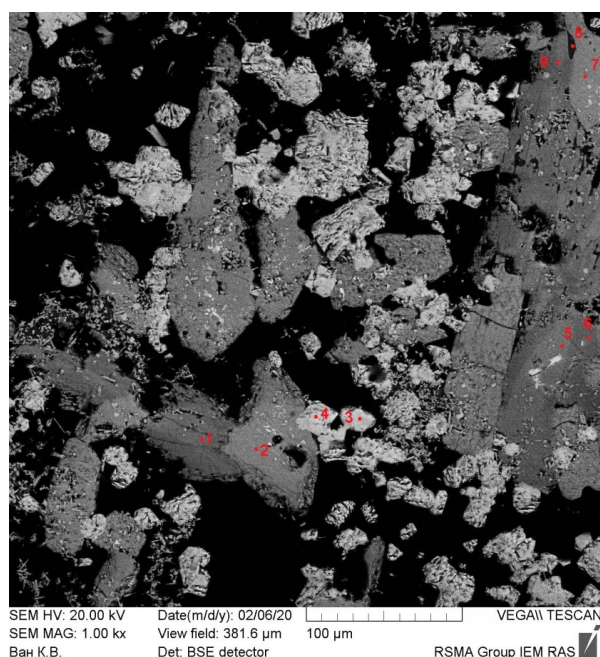


Fig. 1. Products of the experiment on the synthesis of eudialyte with 1M NaCl solution. Points 1, 2 - seed grains of eudialyte, 3, 4 - newly formed eudialyte, points 5, 6 - aegirine.

1M NaCl and NaF solutions were used as fluid, quantitative weighted for experiment/fluid ratio was 10/1 by the weight. The duration of the experiment was 10 days. The composition of eudialyte used as a seed was $(\text{Na}_{14.03}\text{K}_{0.24})_{14.27}\text{Ca}_{3.34}(\text{Fe}_{2.30}\text{Mn}_{0.60})_{2.90}(\text{Zr}_{3.23}\text{Ti}_{0.24})_{3.47}(\text{Si}_{0.81}\text{Nb}_{0.19})(\text{Si}_{25}\text{O}_{73})\text{Cl}_{1.08}\text{S}_{0.12}$.

The experimental products were beige-green fine-crystalline aggregates. In a more detailed microscopic study using a scanning electron microscope Tescan Vega II XMU (Tescan, Czech Republic) equipped with X-ray microanalysis INCA Energy 450 with energy dispersion (INCA Xsight) and crystal diffraction (INCA Wave 700) X-ray spectrometers (Oxford instruments, England) and the INCA Energy+ software platform, in experiments where 1M NaCl was used as a fluid, was found a typical associations of alkaline pegmatites – aegirine + eudialyte (fig.1). The compositions of the obtained minerals are shown in Table 1.

The presented data show that the newly formed eudialyte is somewhat different in composition from the seed, but during crystallization it is enriched with niobium from the seed. Apparently, in an alkaline environment, niobium turns into a mobile form, since in the experiment the stoichiometric gel did not contain niobium in its composition. The anionic group of the synthesized eudialyte fully corresponds to the composition of the liquid in the experiment: in experiments with NaCl solution, chlorine is part of eudialyte, and fluorine – in the experiment with NaF solution.

In the future, it is planned to conduct experimental studies with more complex eudialyte systems in composition – the gradual introduction of niobium, strontium and other impurity components into the initial mixtures.

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